CrossMark
click for updates

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

ChemComm

Chemical Communications
www.rsc.org/chemcomm

ROYAL SOCIETY OF CHEMISTRY

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Journal Name

ARTICLE TYPE

A novel strategy to synthesize well-defined PS brushes on silica particles by combination of lithium-iodine exchange (LIE) and surface-initiated living anionic polymerization (SI-LAP)

Jiakang Min,[a,b] Yichao Lin,[a,b] Jun Zheng*[a] and Tao Tang*[a]

Core-shell hybrid particles, possessing a hard core of silica particles (SiPs) and a soft shell of brushlike polystyrene (PS), are successfully prepared by combination of lithium-iodine exchange (LIE) and surface-initiated living anionic polymerization (SI-LAP). Molecular weights, graft density and brush thicknesses of PS brushes were controllable.

Increasing attentions have been paid to polymer nanocomposites since they were first investigated in the 1990s.[1-3] Many inherent properties of materials are improved and some new functions are manufactured simultaneously by just adding a very low volume fraction of nanoparticles into polymer matrices.[4-6] However, the good wishes are strongly breached by the severe tendency of particles to aggregate in polymeric matrices. So keeping particles highly and uniformly dispersed in polymer composites is the crucial factor to solve this problem. To the best of our knowledge, completely miscible composites can be fabricated by coating particles with a layer of a matrix-miscible polymer such as a polymer brush.[7, 8] Polymer brush is a stretched soft macromolecular structure which is linked through one end with a solid surface. Further study has shown that these core-shell hybrid particles can provide new insights into polymer science and technology because of their unique structural features[9]. However, the graft density, chain length and molecular weight of polymer shell must be tunable, since good interfacial interaction between polymer shell and matrix is essential.[10a]

Generally, the polymer brush can be synthesized by covalent attachment to inorganic surfaces with reactive end groups. Two synthetic methods are available, that is, "grafting from"[10b] and "grafting to". The "grafting from" approach starts grafting from surfaces by surface-initiated polymerization (SIP), in which the polymerization initiator needs to be covalently fixed onto the solid surface and then initiates polymerization with the monomers under suitable conditions[10c]. So far, the surface-initiated living radical polymerization (SI-LRP) is one of the most common and powerful pathways because of its convenience and versatility, in terms to SIP methodology of building polymer brushes.[11,12] Kohji Ohno and the co-workers successively used atom transfer radical polymerization (ATRP) for preparing silica particles (SiPs) with a shell layer of a well-defined PMMA brush in 2005,[13] and reversible addition-fragmentation chain transfer (RAFT) for preparing PS brush on SiPs in 2011.[14] Unfortunately, limitation

occur during the radical recombination process, which lead to crosslinking on the surface of the particles at higher temperatures due to uncontrolled radical reactions.[15]

Besides SI-LRP, there are also others polymerization methods including cationic polymerization,[16] ring–opening metathesis polymerization (ROMP),[17] ring–opening polymerization (ROP),[18] and surface-initiated photopolymerization (SIPP)[19] and so on. The surface-initiated living anionic polymerization (SI-LAP) is the best among the polymerization mechanisms mentioned above in controlling the molecular weights, polydispersities and graft density, which are important structural parameters for polymer brushes. Zhou et al. have used the 1,1-diphenylethylene (DPE) derivative as an initiator precursor and subsequent "grafting from" polymerization of styrene after the ethylene moiety on the DPE was activated by the addition of *n*-BuLi.[20-22] Unfortunately, this method shows a poor ability in controlling polydispersity values of polymer brush (ranging from 1.1 to 2.02[20-23]). It seemed that densely and tunable polymer brushes could not be fabricated by SI-LAP. Alternatively, Hubner et al. selected "grafting to" for functionalization of silica particles using anionic polymerization.[24] This method was based on the reaction of end-functionalized polymers with reactive sites on a substrate surface, which shows an increase of brush graft density. However, because of inherent shortcomings for "grafting to" method, the ability for controlling brush graft density (such as keeping the same graft density with different brush lengths) is poor due to steric hindrance, and it is necessary to separate free polymer from the products in order to obtain the pure functionalized particles.

In this work, we demonstrated a novel strategy to synthesize well-defined PS brushes (as an example) on SiPs through the combination of lithium-iodine exchange (LIE) and surface-initiated living anionic polymerization (SI-LAP). Since the LIE was discovered in the late 1930s by Wittig[25] and Gilman,[26, 27] the remarkably rapid, reversible metathesis reaction had been widely employed for replacement of iodine atoms in the substrates with lithium to prepare relatively stable organometallics. Herein using this technique, core-shell hybrid particles with inner solid SiPs core surrounded by PS brushes were synthesized successfully. The molecular weights with tunable graft density and brush thickness of a series of well-defined PS brushes were under control. The whole strategy is illustrated in Figure 1a. In the first step, SiPs with the diameter of 200 nm (Figure 2d) were modified

with 3-iodopropyltrimethoxysilane (ITS) to obtain SiO₂@ITS-12h for 12 h or SiO₂@ITS-24h for 24 h at 110 °C in toluene. This process allowed replacing the original surface Si-OH groups by Si-I groups partly or completely (depending on the amount of ITS, with the assumption of 5-6 Si-OH groups per nm² of silica surface[24]). In the second step, the resultant SiO₂@ITS was reacted with enough (2.1-2.2 molar equivalent, relative to Si-I groups) commercial *tert*-butyllithium (*tert*-BuLi, 1.6M) for 6 h at -78 °C in a mixed solvent of *n*-hexane and diethyl ether.[28, 29] Subsequently, the mixture was rised to room temperature and kept for 2 h to remove the residual *tert*-BuLi which was consumed by rapid proton abstraction from diethyl ether.[30] At last, PS brushes were immobilized on the surface of silica particles via anionic polymerization of styrene monomer.
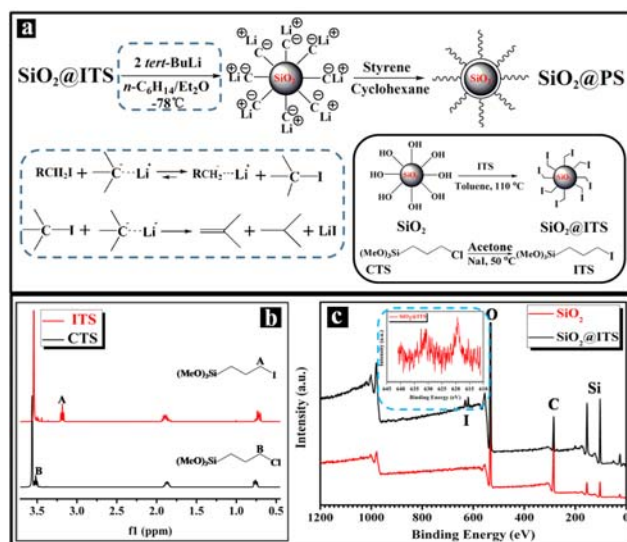

Figure 1. (a) Synthetic routes to SiO₂@ITS and SiO₂@PS hybrid particles; (b) ¹H NMR spectra of ITS and CTS; (c) XPS patterns of SiO₂@ITSs and raw SiPs.

The ITS was prepared by incorporating dry sodium iodide (NaI) into commercially-available 3-chloropropyltrimethoxysilane (CTS, 94%, ¹H NMR (CDCl₃). Figure 1b shows ¹H NMR spectra of ITS and CTS. The notable change between δ 3.24-3.12 (-CH₂I) and δ 3.54-3.48 (-CH₂Cl) indicated that chlorine was successfully replaced by iodine. XPS measurements revealed that the surface of SiO₂@ITSs mainly consisted of C and O, with the covalent linkage of a small quantity of iodine (Figure 1c). Further study indicated that the XPS signals of iodine are electrons from 3d5 and 3d3 electronic orbits, whose binding energies were 618 eV and 633 eV, respectively (inset in Figure 1c). The amount of ITS on the surface of SiPs was determined by TGA analysis. The weight retentions at 800 °C were 91.5 wt% for raw SiPs, 90.2 wt% for SiO₂@ITS-12h (Figure S1) and 89.4 wt% for SiO₂@ITS-24h (Figure 2a). There was 1.3 wt%, 2.1 wt% mass difference between raw SiPs and SiO₂@ITS-12h, raw SiPs and SiO₂@ITS-24h. The weight loss of raw SiPs might be caused by associated water loss and continued condensation. According to eq (1) in the supporting information, it could be roughly estimated that the graft densities of iodine on the particle surface of SiO₂@ITS-12h and SiO₂@ITS-24h were 1.89 and 3.09 molecules/nm², respectively.

PS brushes on SiPs (SiO₂@PSs) were synthesized through the combination of lithium-iodine exchange (LIE) and surface-initiated living anionic polymerization (SI-LAP). In the LIE process, the alkyl iodide was replaced by alkyllithium through SiO₂@ITS reacting with *tert*-BuLi at -78 °C. Then the anionic polymerization of styrene was initiated by alkylanion. The grafted amount of PS brush in the resultant products (nominated as SiO₂@ITS-xh@PS-yh, here "x" is the reaction time between SiPs and ITS, and "y" is the polymerization time of styrene) under various conditions was determined by TGA (see Table 1). Then all the SiO₂@PSs hybrid particles (8×1 g) were put into an aqueous hydrofluoric acid (HF) solution with 5 vol% HF (a mixed solution of hydrofluoric acid (HF, 10 ml) with ultrapure water (70 ml)) to perform the cleavage of grafted PS brushes. The weight-average molecular weights (M_w) and polydispersity indices (PDI) of the grafted PS brushes (SiO₂@ITS-24h@PSs) were checked by SEC-MALLS (Figure 2b and Table 1). It could be seen that the molecular weight of PS brush layers scaled linearly with polymerization time (Figure S2 in the SI). On the basis of the amount of PS brush layers determined by TGA and M_n derived from SEC-MALLS, the graft density of PS could be estimated according to eq (1). Figure 2c shows the dependence of graft density of PS brushes (SiO₂@ITS-24h@PSs) on anionic polymerization time. The graft density was nearly constant despite the polymerization time. And its value approximately equal to 0.79 chains/nm² (SiO₂@ITS-24h@PSs) and 0.47 chains/nm² (SiO₂@ITS-12h@PSs, see Table 1), respectively. The detailed information on PS brushes on SiPs is summarized in Table 1.

The morphology of the obtained SiO₂@ITS-24h@PS-32h hybrid particles was observed by HRTEM (Figure 2e). Supposing that the density of the PS layers was about 1.04 g/cm³, the brush thickness of SiO₂@ITS-24h@PS-32h was calculated to be 23 nm based on the TGA data, which was in good agreement with HRTEM results. It could be seen that the length of the PS brushes increased with the M_w of PS in the cases with the same graft density. In order to investigate the dispersion state of SiO₂@PSs hybrid particles in PS matrix, the raw SiPs and SiO₂@ITS-24h@PS-32h hybrid particles were mixed with PS matrix by solution blending, where the content of SiPs was 5 wt% in the two cases. As expected, the SiO₂@PSs hybrid particles were highly and uniformly dispersed in PS matrix (Figure 2f), but the raw SiPs had severe tendency to aggregate in PS matrix (Figure S3).

From the graft density it was inferred that the efficiency of LIE was around 25% in this work, which was lower than the previously reported results (~90%).[28] In order to disclose the reason of this phenomenon, an XPS measurement was used to confirm the content of iodine on the surface of the sample after the LIE process. According to Figure 3a, the dramatical decrease in the intensity of iodine peak in XPS profiles after LIE indicated that most of alkyl iodine was replaced by alkyllithium. Further study showed that there was the formation of a nonnegligible quantity of hydrocarbon derived from reduction of the alkyl iodides. As shown in Figure 3b, this side reaction was the result of rapid reaction of the product RCH₂Li with the cogenerated *tert*-BuI to give RCH₃, isobutylene, and LiI that was inactive for anionic polymerization.[28, 31] In our work, the deactivation effect

of the side reaction might be enlarged since the LIE was implemented on the interphase not homogeneous phase within 6 h. Thus, we thought that the final efficiency was the balance result of the extent of LIE and the side reaction mentioned above.
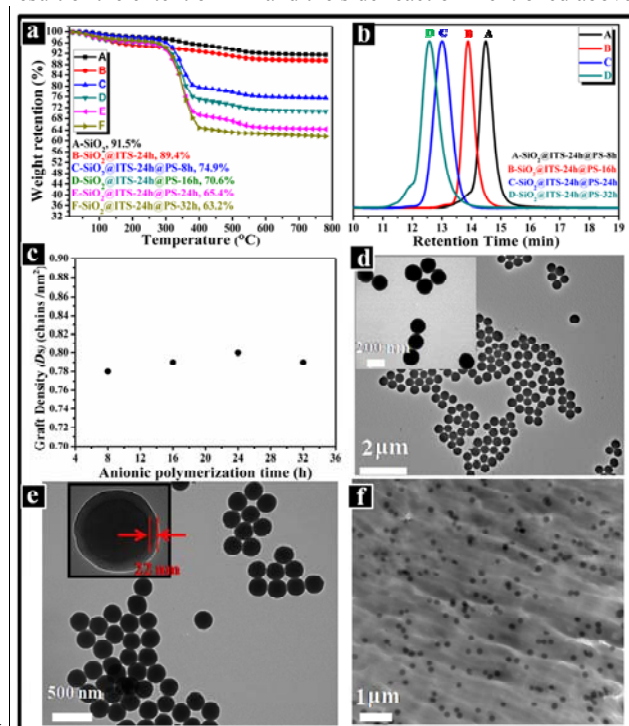

Figure 2. (a) TGA curves of A-SiO₂, B-SiO₂@ITS-24h, (C, D, E, F)-SiO₂@ITS-24h@PSs hybrid particles; (b) SEC-MALLS curves of grafted PS brushes from SiO₂@ITS-24h; (c) Graft density of grafted PS brushes from SiO₂@ITS-24h as a function of anionic polymerization time; (d) TEM images of raw SiPs; (e) HRTEM images of hybrid particles of SiO₂@ITS-24h@PS-32h; (f) TEM images of PS/SiO₂@ITS-24h@PS-32h composite containing 5 wt% net SiPs.

Table 1. Data on Grafted PS Brushes on SiPs by Surface-Initiated Living Anionic Polymerization.

Sample	GA [a] (%)	M_w [b] (kg/mol)	PDI [b]	Graft Density (D_s) [c] (chains/nm²)	Brush Length L [d] (nm)
SiO₂@ITS-12h@PS-8h	8.4	83	1.03	0.48	4
SiO₂@ITS-12h@PS-16h	10.4	106	1.02	0.47	6
SiO₂@ITS-12h@PS-24h	13.4	142	1.02	0.47	8
SiO₂@ITS-12h@PS-32h	16.0	184	1.05	0.46	10
SiO₂@ITS-24h@PS-8h	16.6	110	1.02	0.78	10
SiO₂@ITS-24h@PS-16h	20.9	145	1.02	0.79	14
SiO₂@ITS-24h@PS-24h	26.1	197	1.04	0.80	18
SiO₂@ITS-24h@PS-32h	28.3	227	1.05	0.79	22

[a] Grafted amount of PS (wt%), determined by TGA (Figure S1 and Figure 2a). [b] Determined by SEC-MALLS (Figure S4 and Figure 2b). [c] Determined by eq (1). [d] Determined by HRTEM (Figure S5 and Figure 2e).
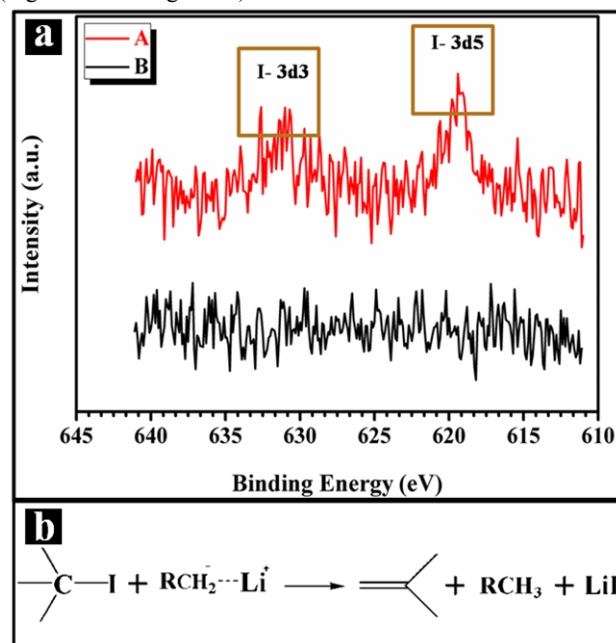

Figure 3. (a) XPS patterns of iodine element on SiO₂@ITS: (A) before, and (B) after LIE; (b) side reaction accompanied with LIE.

Conclusions

It was demonstrated that surface-decorated SiPs with alkyl iodides can transformed into anionic polymerization initiation sites via lithium-iodine exchange (LIE). Core-shell hybrid particles were synthesized through surface-initiated living anionic polymerization (SI-LAP). The length of well-defined PS brushes was tunable by control of polymerization time. This method provides a novel strategy to synthesize core-shell hybrid particles and polymer nanocomposites.

Notes and references

[a] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China. Fax: +86 (0) 431 85262827; Tel: +86 (0) 431 85262004; E-mail: ttang@ciac.ac.cn, zhengjun@ciac.ac.cn

[b] University of Chinese Academy of Sciences, Beijing 100039, China.

1 A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Karauchi, O. Kamigaito, *J. Mater. Res.,* 1993, **8**, 1179.

2 R. A. Vaia, H. Ishii, R. A. Giannelis, *Chem. Mater.,* 1993, **5**, 1694.

3 T. P. Lan, T. J. Pinnavaia, *Chem. Mater.,* 1994, **6**, 2216.

4 T. Taniike, M. Toyonaga, M. Terano, *Polymer,* 2014, **55**, 1012.

5   T. Zhou, W. Ruan, M. Rong, M. Zhang, Y. Mai, *Adv. Mater.,* 2007, **19**, 2667.

6   D. Schneider, M. Schmitt, C. Hui, R. Sainidou, P. Rembert, K. Matyjaszewski, M. Bockstaller, G. Fytas, *ACS Macro. Lett.,* 2014, **3**, 1059.

7   S. Fischer, A. Salcher, A. Kornowski, H. Weller, S. Förster, *Angew. Chem. Int. Ed.,* 2011, **50**, 7811.

8   S. T. Milner, *Science,* 1991, **251**, 905.

9   Y. Uyama, K. Kato, Y. Ikada, *Adv. Polym. Sci.,* 1998, **137**, 1.

10   (a) S. K. Kumar, N. Jouault, B. Benicewicz, T. Neely, *Macromolecules*, 2013, **46**, 3199; (b) S. K. Pillalamarri, F. D. Blumab, M. F. Bertino, *Chem. Commun.*, 2005, 4584; (c) L. Chen, Y. Lei, A. G. Shilabin, J. D. Delaney, G. R. Baran, S. M. Sieburth, *Chem. Commun.*, 2012, **48**, 9604.

11   F. Zhou, W. T. S. Huck, *Phys. Chem. Chem. Phys*., 2006, **8**, 3815.

12   S. Edmondson, V. L. Osborne, W. T. S. Huck, *Chem. Soc. Rev.*, 2004, **33**, 14.

13   K. Ohno, T. Morinaga, K. Koh, Y. Tsujii, T. Fukuda, *Macromolecules,* 2005, **38**, 2137.

14   K. Ohno, Y. Ma, Y. Huang, C. Mori, Y. Yahata, Y. Tsujii, T. Maschmeyer, J. Moraes, S. Perrier, *Macromolecules,* 2011, **44**, 8944.

15   D. A. Savin, J. Pyun, G. D. Patterson, T. Kowalewski, K. J. Matyjaszewski, *Polym. Sci., Part B: Polym. Phys.,* 2002, **40**, 2667.

16   R. Jordan, A. Ulman, *J. Am. Chem. Soc.,* 1998, **120**, 243.

17   G. Morandi, S. Pascual, V. Montembault, S. Legoupy, N. Delorme, L. Fontaine, *Macromolecules,* 2009, **42**, 6927.

18   (a) M. Weck, J. J. Jackiw, R. R. Rossi, P. S. Weiss, R. H. Grubbs, *J. Am. Chem. Soc.,* 1999, **121**, 4088; (b) S. H. Wibowo, A. Sulistio, E. H. H. Wong, A. Blencowe, G. G. Qiao, *Chem. Commun.,* 2014, **50**, 4971.

19   F. Chen, X. Jiang, R. Liu, J. Yin, *ACS Appl. Mater. Interfaces*., 2010, **2**, 1031.

20   Q. Zhou, X. Fan, C. Xia, J. Mays, R. Advincula, *Chem. Mater*., 2001, **13**, 2465.

21   Q. Zhou, S. Wang, X. Fan, R. Advincula, *Langmuir,* 2002, **18**, 3324.

22   R. Advincula, Q. Zhou, M. Park, S. Wang, J. Mays, G. Sakellariou, S. Pispas, N. Hadjichristidis, *Langmuir,* 2002, **18**, 8672.

23   O. Kir, W. H. Binder, *Euro. Polym. J.*, 2013, **49**, 3078.

24   E. Hübner, J. Allgaier, M. Meyer, J. Stellbrink, W. Pyckhout-Hintzen, D. Richter, *Macromolecules,* 2010, **43**, 856.

25   G. Wittig, U. Pockels, H. Dröge, *Chem. Ber.,* 1938, **77**, 1903.

26   H. Gilman, A.L. Jacoby, *J. Org. Chem.,* 1938, **3,** 108.

27   H. Gilman, W. Langham, A.L. Jacoby, *J. Am. Chem. Soc.,* 1939, **61**, 106.

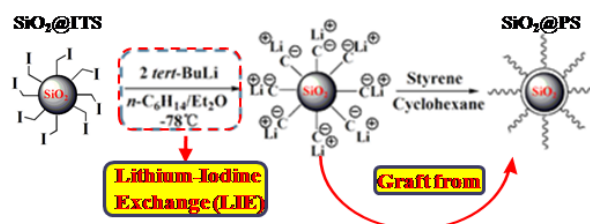28   W. F. Bailey, E. R. Punzalan, *J. Org. Chem.,* 1990, **55**, 5404.

29   W. F. Bailey, J. D. Brubaker, K. P. Jordan, *J. Org. Chem.,* 2003, **681**, 210.

30   T. F. Bates, M. T. Clarke, R. D. Thomas, *J. Am. Chem. Soc.,* 1988, **110**, 5109.

31   W. F. Bailey, T. T. Nurmi, J. J. Patricia, W. Wang, *J. Am. Chem. Soc.,* 1987, **109**, 2442.

TOC:

SiO$_2$ particles coated by well-defined brushlike polystyrene are successfully prepared by combination of lithium-iodine exchange and surface-initiated living anionic polymerization.