PAPER

Check for updates

Surface functionalization of silica using catalytic hydroesterification modified polybutadienes†

Min Young Kim,‡[abc] Chang-Hee Lee‡[abc] and Chul-Ho Jun ID *[abc]

A new method for covalent immobilization of catalytic hydroesterification modified polybutadiene on a silica surface is described. Compared to conventional immobilization procedures, the new protocol enables control of the functional group composition on the modified silica surface.

Molecular level engineering of organic functional groups on inorganic solid surfaces has a variety of applications ranging from chemical sensors to cell adhesion.[1] Conventional immobilization protocols using alkoxy, allyl and meth-allylsilane groups to promote covalent bonding can be utilized to introduce various monomeric functional groups on surface (Fig. 1a).[2] However, it is difficult to produce well-defined multi-functionalized materials by using these approaches.[3]

Previously, we described an interesting method for modification of polybutadiene, which uses $Ru_3(CO)_{12}$ and 2-pyridinemethanol as catalysts, an alcohol and sodium formate.[4] The process generates the corresponding ester modified polybutadiene. By employing selected ratios of two or more alcohols in this protocol, modified polybutadienes bearing various ratios of a mixture of ester on their surfaces can be obtained.

In the study described below, we extended this strategy by developing a new method for covalent immobilization of organic functional group containing catalytic hydro-esterification modified polybutadiene on a silica surface (Fig. 1b). In addition, we have shown that polymer-based hybrid materials containing various proportions of the azo-benzene group can be prepared using this procedure and utilized to determine the extent of loading of functional groups onto silica by using UV/vis absorption spectroscopy. Finally, we found that fluorophores, incorporated into a polymer-based hybrid material containing a pyrene fluorophores, generated using the new approach, can be applied for recyclable nitrobenzene sensing.

Because it is readily available in various molecular weight distributions, phenyl group terminated polybutadiene **1** was used as the polymer platform for assessing the new approach for covalent bond immobilization of organic functional group containing catalytic hydroesterification modified poly-butadiene on a silica surface.[5] Reaction of **1** with sodium formate (**2**), and 9 : 4 : 4 ratio of 2-phenylethyl alcohol (**3a**), 2,2′-(1,4-phenylene)diethanol (**3b**), and 6-chlorohexanol (**3c**) and 2-pyridinemethanol (**5**) in the presence of $Ru_3(CO)_{12}$ (**4**) at 150 °C for 12 h was found to produce the modified poly-butadiene **6a**. Modified polybutadiene **6a** was purified by precipitation from methanol and the extent of incorporation was determined by using ^{1}H NMR spectroscopy. Based on the protons of terminal phenyl group, we determined that 38% of the vinyl groups in **1** were converted to a 9 : 4 : 4 ratio of the corresponding 2-phenylethyl, 4-(2-hydroxyethyl)phenethyl, and 6-chlorohexyl ester moieties (eqn (1)).
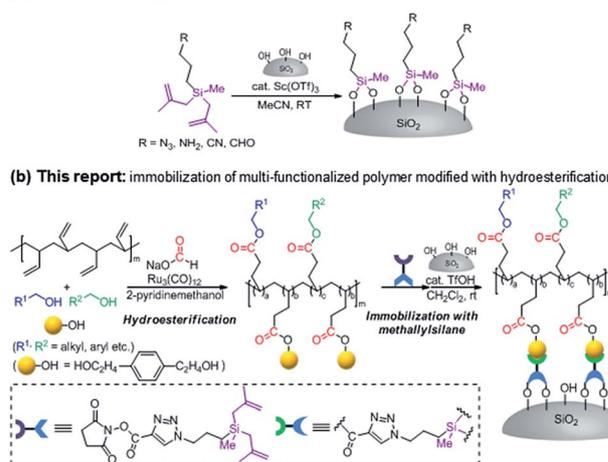

Fig. 1 (a) Conventional immobilization method using methallylsilane derivatives. (b) Conceptual basis of the new method for constructing a catalytic hydroesterification modified multi-functionalized polymer.

[a]*Department of Chemistry, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 03722, Republic of Korea. E-mail: junch@yonsei.ac.kr*
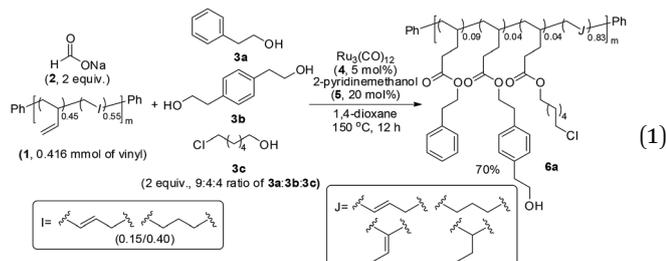
[b]*Center for NanoMedicine, Institute for Basic Science (IBS), Seoul, Republic of Korea*

[c]*Yonsei-IBS Institute, Yonsei University, Seoul 03722, Republic of Korea*

‡ These authors equally contributed to this work.

$$(1)$$

The alcohol and chlorine moieties proportionally embedded into 6a group by using the one-pot hydroesterification protocol can be utilized to incorporate diazo groups for quantitative UV/vis absorption spectroscopic analysis (Fig. 2a). Specifically, reaction of 6a with sodium azide affords the azide group containing polybutadiene 7, which reacts with the 4-(dimethylamino)azobenzene-4′-sulfonamide (DABS) linked acetylene 8 by using a click reaction[6] to form the DABS embedded polybutadiene 9 (64%). Reaction of 9 with NHS-ester-functionalized methallylsilane 10 in the presence of 4-dimethylaminopyridine (11) in dichloromethane at 100 °C for 12 h was found to form the dimethallylsilane group containing polymer 12. Finally, immobilization reaction of derivatized polymer 12 onto silica
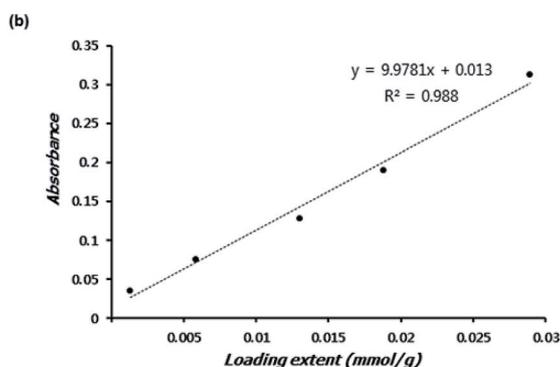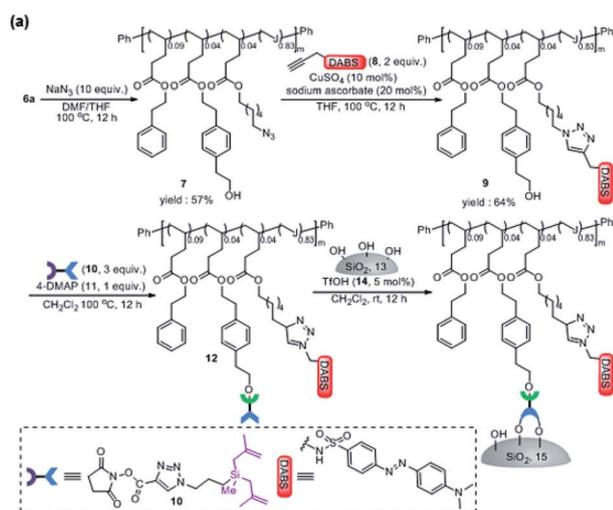

Fig. 2 (a) Preparation of UV/vis absorbing DABS bearing polybutadiene immobilized silica 15. (b) Correlation between the UV/vis absorbance of 15 at 497 nm and the loading extent.

nanoparticles 13, carried out in the presence of 5 mol% of trifluoromethanesulfonic acid (TfOH, 14), produces the multiply functionalized, diazobenzene chromophore-containing polymer-based hybrid material 15.

To determine the correlation between the loading efficiency and UV/vis absorption intensity of the diazo chromophore in 15, the amounts of the DABS group incorporated polymer 12 used in the immobilization reaction with silica 13 were varied (Fig. 2b).[7] For this purpose, 1, 3, 5, 8 and 10 mg of 12 were independently reacted with 50 mg silica nanoparticle in the presence of TfOH (5 mol%) at room temperature for 12 h to give 15. Comparisons were made of the modified silicas produced in the manner to assess the extents of loading by using elemental analysis and UV/vis absorbances at 497 nm associated with the DABS chromophore. The results show that 15 with a loading extent of 0.001 mmol g^{-1} has an absorbance of 0.035 while 15 loaded to the extent of 0.029 mmol g^{-1} has an absorbance at 497 nm of 0.314. An analysis of all of the modified silicas showed that a linear correlation exists between the intensity of UV/vis absorbance at 497 nm and the loading extent.[8]

An investigation was conducted to determine if this protocol enables precise control of the ratio of the functional groups in the generated modified polybutadiene (Table 1). Polybutadiene 1 was reacted with sodium formate (2) and a 1 : 7 : 2 ratio of pyrenylmethanol (3d), 2-phenylethyl alcohol (3a) and 2,2′-(1,4-phenylene)diethanol (3b) in the presence of Ru$_3$(CO)$_{12}$ (4) and 2-pyridinemethanol (5) at 150 °C for 12 h. By the ^{1}H NMR spectral analysis, we determined that polymer 6b contains a 1 : 7 : 2 ratio of corresponding pyrenylmethyl, 2-phenylethyl, and 4-(2-hydroxyethyl)phenethyl esters. Identical reactions carried out using 3d : 3a : 3b in ratios between 3 : 5 : 2 and 8 : 0 : 2 were found to form polymers 6c–f containing proportionally increasing ratios of the pyrenylmethyl ester group (entry 1–5).[9] Similarly, polymers 6g and 6h produced in reactions using 3 : 6 and 0 : 9 ratios of 3a to 3b with a fixed ratio of 3d, were observed to contain increasing ratios of the diol derived ester groups (entry 6–7).

The fluorescence properties of the polymer 6b–f containing different ratios of pyrenylmethyl ester determined (Fig. 3). Fluorescence spectrum of the low ratio pyrenyl group-embedded polymer 6b contains a maximum emission bands at 395 nm, which corresponds to monomeric fluorescence of pyrene. In this case, the 2-phenylethyl ester group in 6b serves as a spacer between the pyrenyl ester groups. In contrast, the intensities of the emission band at 395 nm in the fluorescence spectrum of the modified polybutadienes 6c–f decrease as the ratio of the pyrenylmethyl ester group increases. In addition, a maximum emission appears simultaneously in the spectra at 480 nm, which corresponds to fluorescence from the pyrene intramolecular excimer. This phenomenon is also seen in the excimer to monomer emission intensity ratios (I_E/I_M).[10] In the case of 6b, I_E/I_M is 0.313 and as the extent of pyrene ester incorporation increases to 10 mol% in 6f this ratio increases to 2.227. These results are consistent with the assignment of the emission band at 480 nm to an intramolecular pyrene excimer, the amount of which increases as the pyrenylmethyl ester

Table 1 Preparation of multi-functionalized polybutadiene using varying mole percentage ratios of pyrenylmethyl, 2-phenylethyl, and 4-(2-hydroxyethyl)phenethyl ester groups[a]
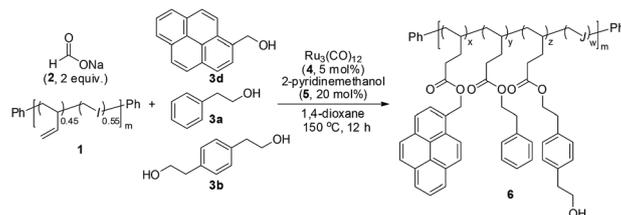
| Entry	Alcohol (2 equiv.) ratio of **3d** : **3a** : **3b**	Ratio (%) $x/y/z/w$	Incorporation rate[b] of esters in **6** (%)	$x : y : z$	Yield[c] (%)
1	1 : 7 : 2	1/11/3/85	34	1 : 7 : 2	72 (**6b**)
2	3 : 5 : 2	4/7/4/85	35	3 : 5 : 2	86 (**6c**)
3	5 : 3 : 2	7/4/3/86	33	5 : 3 : 2	79 (**6d**)
4	7 : 1 : 2	7/1/2/90	23	7 : 1 : 2	99 (**6e**)
5	8 : 0 : 2	11/0/4/85	33	6 : 0 : 2	84 (**6f**)
6	1 : 3 : 6	1/4/9/86	32	1 : 3 : 6	71 (**6g**)
7	1 : 0 : 9	1/0/9/90	23	1 : 0 : 9	73 (**6h**)

[a] All reactions were carried out with **1** (0.416 mmol of vinyl group), **2** (0.832 mmol), **3d**, **3a**, **3b**, **4** (5 mol%), and **5** (20 mol%) in 1 mL of 1,4-dioxane at 150 °C. [b] Incorporation rate of the ester group was calculated as: $100 \times (x + y + z)/(45, \text{vinyl\%})$. [c] Isolated yields.

groups more populated the polymer. The result of this analysis clearly shows that the extent of pyrenyl group impregnated on polymer can be readily controlled in the new hydroesterification protocol.

To explore the immobilization method further, the dimethallylsilane group-embedded polymer **16** was prepared by ester bond forming reaction of the residual alcohol groups in the 4-(2-hydroxyethyl)phenethyl ester moiety of polymer **6b** with NHS-ester-functionalized methallylsilane **10** (Fig. 4a).[11] Then immobilization reaction of polymer **16** with silica nanoparticles **13** in the presence of 5 mol% of **14** was carried out to produce the polymer-based hybrid material **17**.

It is known that electron-deficient nitroaromatic compounds are efficient electron transfer quenchers of the fluorescence of aromatic compounds like pyrene.[12] Consequently, the nitroaromatic compound sensing ability of the pyrene containing, polymer-based hybrid material **17** was investigated (Fig. 4b). Inspection of its fluorescence spectra shows that the polymer based hybrid material **17** strongly fluoresces with a maximum at 395 nm. The ratio of the pyrene excimer to monomer fluorescence intensities (I_E/I_M) of **17** was observed to be 0.333, a value that is similar to the I_E/I_M (0.313) of the non-immobilized polymer **6b**. Upon addition of nitrobenzene (NB) to a solution of **17** in CH_2Cl_2, the intensity of fluorescence at 395 nm decreases, and disappears completely when the concentration of NB reaches 1.248 mM. It should be noted that the pyrene group incorporated silica nanoparticle **17** can be separated from the assay solution, washed and reused for NB detection 5 times without diminishment of its NB sensing ability (Fig. 4c).

In the study described above, we developed a new method for immobilization of catalytic hydroesterification modified multi-functionalized polybutadiene on a silica surface. The protocol enables generation of organic–inorganic hybrid silica surface nanomaterial containing controlled ratios of multiple functional groups. Moreover, this protocol was used to produce polymer-based hybrid materials, bearing proportionally regulated ratios of DABS group, which were utilized to assess the loading efficiencies of functional groups onto silica employing UV/vis absorption spectroscopy. Finally, a pyrene-incorporated polymer-based silica hybrid materials, generated by using the new approach, were demonstrated to be applicable to recyclable nitrobenzene sensing.
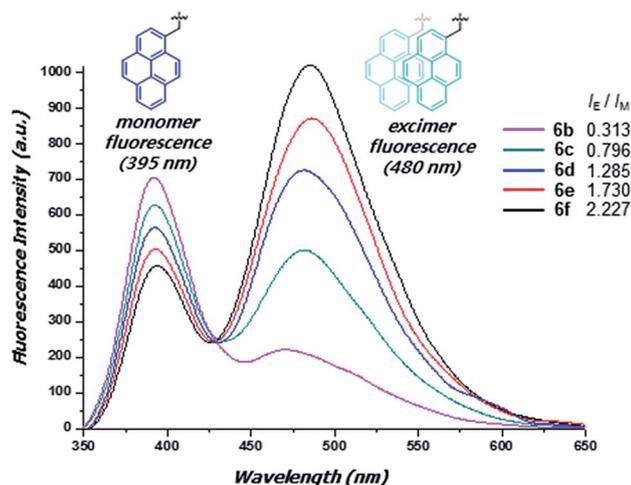
Fig. 3 Fluorescence spectra of **6b**–**f** excited at 330 nm in CH_2Cl_2.
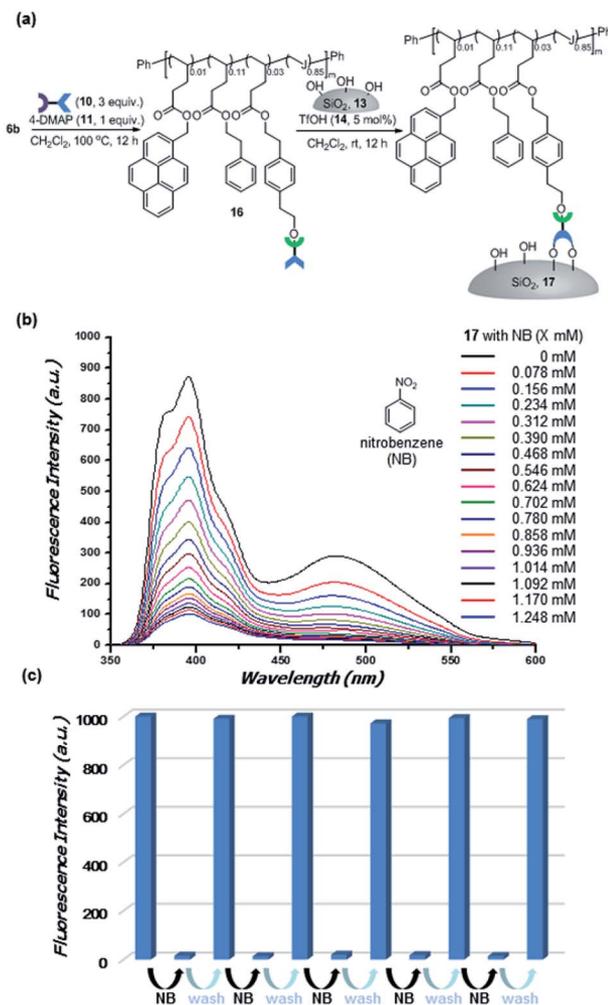
Fig. 4 (a) Immobilization reaction with multi-functionalized polymer modified by catalytic hydroesterification on silica. (b) Fluorescence spectra of solutions of **17** (I_E/I_M = 0.333) in CH$_2$Cl$_2$ in the presence of different concentrations of nitrobenzene (NB) (excitation at 330 nm). (c) Fluorescence intensities of solutions of **17** in CH$_2$Cl$_2$ at 395 nm following addition of nitrobenzene (0.078 mM) and washing with CH$_2$Cl$_2$.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

1 (a) S. Flink, F. C. J. M. van Veggel and D. N. Reinhoudt, *Adv. Mater.*, 2000, **12**, 1315; (b) Z. Farka, T. Juřík, D. Kovář, L. Trnková and P. Skládal, *Chem. Rev.*, 2017, **117**, 9973; (c) Y. Chen, H. Chen and J. Shi, *Adv. Mater.*, 2013, **25**, 3144; (d) E. Aznar, M. Oroval, L. Pascual, J. R. Murguía, R. Martínez-Máñez and F. Sancenón, *Chem. Rev.*, 2016, **116**, 561; (e) U. Hanefeld, L. Gardossi and E. Magner, *Chem. Soc. Rev.*, 2009, **38**, 453; (f) R. Georgiadis, K. P. Peterlinz and A. W. Peterson, *J. Am. Chem. Soc.*, 2000, **122**, 3166; (g) M. Krishnamoorthy, S. Hakobyan, M. Ramstedt and J. E. Gautrot, *Chem. Rev.*, 2014, **114**, 10976; (h) H. Jiang and F.-J. Xu, *Chem. Soc. Rev.*, 2013, **42**, 3394.

2 (a) K. B. Yoon, *Acc. Chem. Res.*, 2007, **40**, 29; (b) F. Hoffmann, M. Cornelius, J. Morell and M. Fröba, *Angew. Chem., Int. Ed.*, 2006, **45**, 3216; (c) S. K. Vashist, E. Lam, S. Hrapovic, K. B. Male and J. H. T. Luong, *Chem. Rev.*, 2014, **114**, 11083; (d) C. M. Crudden, M. Sateesh and R. Lewis, *J. Am. Chem. Soc.*, 2005, **127**, 10045; (e) T. Shimada, K. Aoki, Y. Shinoda, T. Nakamura, N. Tokunaga, S. Inagaki and T. Hayashi, *J. Am. Chem. Soc.*, 2003, **125**, 4688; (f) Y. Maegawa, N. Mizoshita, T. Tani, T. Shimada and S. Inagaki, *J. Mater. Chem.*, 2011, **21**, 14020; (g) Y.-R. Yeon, Y. J. Park, J.-S. Lee, J.-W. Park, S.-G. Kang and C.-H. Jun, *Angew. Chem., Int. Ed.*, 2008, **47**, 109; (h) Y. R. Han, J.-W. Park, H. Kim, H. Ji, S. H. Lim and C.-H. Jun, *Chem. Commun.*, 2015, **51**, 17084; (i) J.-W. Park and C.-H. Jun, *J. Am. Chem. Soc.*, 2010, **132**, 7268.

3 Y. Tong, E. Tyrode, M. Osawa, N. Yoshida, T. Watanabe, A. Nakajima and S. Ye, *Langmuir*, 2011, **27**, 5420.

4 (a) D.-S. Kim, W.-J. Park, C.-H. Lee and C.-H. Jun, *J. Org. Chem.*, 2014, **79**, 12191; (b) W.-J. Park, C.-H. Lee, D.-S. Kim and C.-H. Jun, *Chem. Commun.*, 2015, **51**, 14667.

5 J.-W. Park, D.-S. Kim, M.-S. Kim, J.-H. Choi and C.-H. Jun, *Polym. Chem.*, 2015, **6**, 555.

6 (a) H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004; (b) Q. Wang, T. R. Chan, R. Hilgraf, V. V. Fokin, K. B. Sharpless and M. G. Finn, *J. Am. Chem. Soc.*, 2003, **125**, 3192; (c) F. Himo, T. Lovell, R. Hilgraf, V. V. Rostovtsev, L. Noodleman, K. B. Sharpless and V. V. Fokin, *J. Am. Chem. Soc.*, 2005, **127**, 210; (d) P. Wu, M. Malkoch, J. N. Hunt, R. Vestberg, E. Kaltgrad, M. G. Finn, V. V. Fokin, K. B. Sharpless and C. J. Hawker, *Chem. Commun.*, 2005, 5775.

7 R.-Y. Choi, C.-H. Lee and C.-H. Jun, *Org. Lett.*, 2018, **20**, 2972.

8 When the loading extent in **15** is 0.052 and 0.089 mmol g^{-1}, the UV/vis absorbance at 497 nm is 0.381 and 0.273, implying that no linear correlation exists above 0.052 mmol g^{-1}.

9 The amount of cross-linked product caused by double hydroxyl groups of **3b** is measured as 8% based on ^{1}H NMR analysis of **6f**.

10 (a) J. R. MacCallum, *Eur. Polym. J.*, 1981, **17**, 797; (b) M. d. G. Miguel, H. D. Burrows and B. Lindman, *Prog. Colloid Polym. Sci.*, 2002, **120**, 13.

11 (a) Y.-K. Sim, H. Jung, S. H. Kim, J.-W. Park, W.-J. Park and C.-H. Jun, *Chem. Sci.*, 2018, **9**, 7981; (b) Y.-K. Sim, J.-W. Park, B.-H. Kim and C.-H. Jun, *Chem. Commun.*, 2013, **49**, 11170.

12 (a) S. Pramanik, C. Zheng, X. Zhang, T. J. Emge and J. Li, *J. Am. Chem. Soc.*, 2011, **133**, 4153; (b) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105; (c) G. Das, B. P. Biswal, S. Kandambeth, V. Venkatesh, G. Kaur, M. Addicoat, T. Heine, S. Verma and R. Banerjee, *Chem. Sci.*, 2015, **6**, 3931; (d) Y. R. Han, S.-H. Shim, D.-S. Kim and C.-H. Jun, *Org. Lett.*, 2018, **20**, 264; (e) S.-B. Kim, C.-H. Lee and C.-H. Jun, *Chem. Commun.*, 2018, **54**, 9961.