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Grafting of Poly(ethylene glycol)s onto Nanometer Silica Surface by a One-Step Procedure

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Poly(ethylene glycol)s (PEGs) have been grafted onto nanometer silica surface in toluene at 80°C using toluene diisocyanate (TDI) as a coupling agent. This was done using a one-step procedure involving a first reaction of TDI with silica and a subsequent reaction of isocyanate-bound silica with PEG. The PEG grafted silicas have been characterized by FTIR spectroscopy, ^{13}C CPMAS NMR spectroscopy, thermogravimetric analysis TGA), and elemental analyses. The maximum PEG grafting is 16%, and the maximum overall grafting is 36%, as determined by TGA. The effects of the amount of PEG, temperature, catalyst, and molecular weight of PEG have been studied.

Keywords silica, poly(ethylene glycol), surface modification, grafting, diisocyanate

Introduction

The common impeding problems encountered in the field of polymer/inorganic nanocomposites are agglomeration of inorganic nanoparticles and their incompatibility with organic matrices due to the inorganic nature. Surface modification by grafting organic polymers onto nanometer inorganic surfaces is an effective way to deal with the above problems.[1,2] Grafting of polymers onto a silica surface has been extensively studied.[3–12] The procedures include "grafting from", "grafting onto" and "grafting through" approaches. With a "grafting from" approach,[3–5] compounds bearing initiating groups such as azo group are introduced onto a silica surface first, and then such modified silicas are served as initiators. Consequently, polymerization starts from the silica surface. As to the "grafting onto" approach,[6–8] prepolymers containing reactive groups such as amino and carboxyl groups are attached onto a silica surface. In the "grafting through" approach,[9–12] silica is premodified with a special silane coupling agent bearing a double bond to introduce polymerizable groups onto the silica surface, and then reacts as a comonomer of vinyl monomers.

PEGs are non-toxic linear polymers and have been widely used in diverse applications because of their excellent biological and conductive performance. They have

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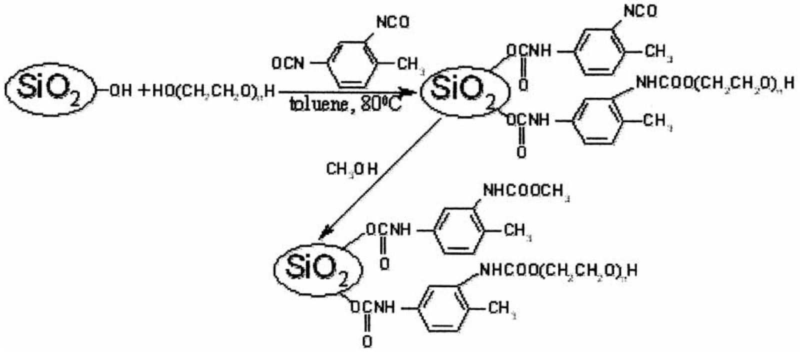
been grafted, via the "grafting onto" approach, onto solid surfaces such as glass,[13–15] quartz,[16] and silicon wafers[17] for protein immobilization and capillary electrophoresis, etc. Most of the procedures involve functionalized PEGs carrying alkoxysilane, epoxy or amino end groups. As to silica powder, Fujiki et al.[7] have reported the reaction of amino functionalized PEGs with ultrafine silica premodified with 3-glycidoxypropyl trimethoxysilane.

The present work deals with grafting of hydroxy terminated PEGs onto nanometer silica surface, via the "grafting onto" approach, using TDI as the coupling agent by a one-step procedure. The idea of using a diisocyanate as a coupling agent to graft polyethers onto inorganic surfaces has been reported for glass fiber,[18] nano-apatite,[19] and carbon black[20] via a two-step procedure, as usually done with polymeric substrates.[21,22] In the first step, the inorganic surfaces are treated with an excess amount of diisocyanate so that only one isocyanate group per molecule reacts with hydroxy group of inorganic substrates. In the second step, the remaining isocyanate group reacts with PEGs via formation of urethane bonds. Yosomiya et al.[18] have reported that the apparent activation energy of the reaction between silanol group of glass fiber and diisocyanate is approximate to that between ordinary alcohol and isocyanate, indicating that glass fiber has comparable reactivity to ordinary alcohol towards diisocyanate. Considering that the silanol groups of silica powder are somewhat similar to those of glass fiber, and that PEGs are less reactive than ordinary alcohols due to their long chains, we envisaged a one-step procedure, in which all the components were mixed together, for carrying out the grafting reaction (Sch. 1), and expected that TDI would react firstly with silica using one isocyanate group and subsequently with PEG using the remaining isocyanate group, as in an usual two-step procedure. One-step procedures have obvious advantages over two-step procedures, especially for air sensitive systems like this case. Here we report the detailed study of this one-step procedure.

Experimental

Materials and Reagents

Nanometer silica (type MN1S) was from the Zhoushan-Mingri Company (China) with a mean particle size of 15 nm and a specific surface area of 160 m^2/g. It was dried



Scheme 1. Illustration of the grafting of PEG onto silica surface via TDI coupling.

in vacuo at 110°C for 6 h before use. PEGs were obtained from T.T.R.C. (China) and dried by azeotropic distillation with toluene. TDI (80/20 mixture of 2,4- and 2,6-isomers) was used as received. Toluene was dried over 4 Å molecular sieves and distilled. Pyridine and triethylamine (TEA) were refluxed over KOH and distilled.

Reaction of TDI with Silica

A mixture of silica (1 g) and TDI (amount varied as specified in Fig. 1) in toluene (50 ml) was heated to and held at 80°C for 4 h under nitrogen, then cooled to room temperature. Methanol (20 ml) was then added. It was brought to and held at 80°C for 1 h to block the isocyanate groups existing at the free ends of grafted molecules and to destroy unreacted diisocyanate. After cooling to room temperature, it was suction filtered and washed with methanol, then extracted with methanol in a Soxhlet apparatus for 24 h to remove any ungrafted diisocyanate derivatives. The products were dried *in vacuo* at 110°C for 6 h.

Grafting of PEGs onto Silica Surface

In a typical procedure, a mixture of silica (1 g), PEG2000 (1.4 g, 0.7 mmol) and TDI (0.244 g, 1.4 mmol) in toluene (50 ml) was heated to and held at 80°C for 7 h under nitrogen. Methanol (20 ml) was added to quench unreacted isocyanate groups. It was then suction filtered and washed with toluene and methanol, then extracted in a Soxhlet apparatus with toluene for 24 h and subsequently with methanol for 24 h to remove any ungrafted PEG and its derivatives.

The percentages of the overall grafting and net grafting of PEGs were calculated by the following equations:

$$\text{Overall grafting (\%)} = \frac{\text{Overall organic composition (g)}}{\text{Bare silica (g)}} \times 100$$

$$\text{PEG grafting (\%)} = \frac{\text{Grafted PEG (g)}}{\text{Bare silica (g)}} \times 100$$

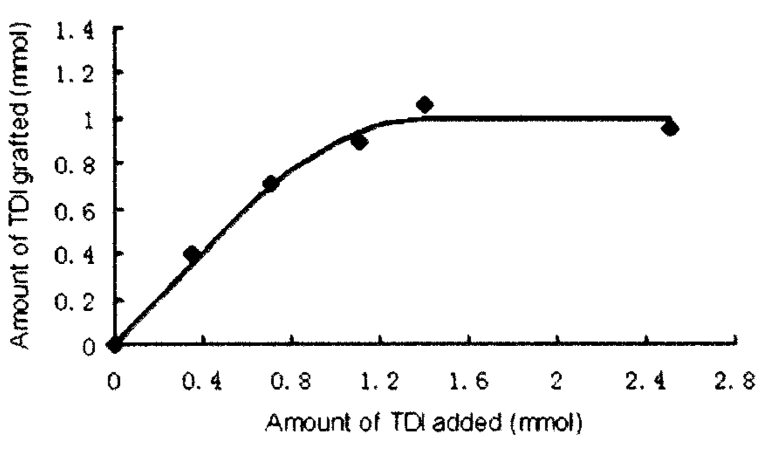


Figure 1. The amounts of TDI grafted onto silica vs. those added to the reaction system.

The amounts of overall organic composition and grafted PEG were calculated from TGA weight loss data obtained between 150°C and 700°C, and between 300°C and 700°C, respectively.

The ratio of the number of silica surface bound isocyanate groups, which were reacted with PEG to that available before grafting of PEG was described as NCO efficiency and calculated by the following equation:

$$\text{NCO efficiency (\%)} = \frac{\text{Grafted PEG (mmol/g)}}{\text{Grafted TDI (mmol/g)}} \times 100$$

Characterization

FTIR spectra in KBr pellets were recorded on a Nicolet 560 FTIR spectrophotometer. ^{13}C CPMAS NMR spectra were recorded on an INSTRUM av300 spectrometer operating at 75.5 MHz for ^{13}C. Thermogravimetric analysis (TGA) was carried out on a TA 2050 instrument with a heating rate of 20°C/min in flowing N_2. Elemental analyses were performed on an Elementar Vario EL analyzer.

Results and Discussion

Reaction of TDI with Silica

As diisocyanate is usually used in large excess when served as a coupling agent to graft prepolymers[19] or small molecules bearing initiating groups for graft polymerization,[3,23] the reaction between silica and TDI was studied in order to find a suitable amount of TDI. Figure 1 shows the amounts of TDI grafted onto silica surface vs. those added to the reaction systems. The amount of TDI grafted onto the silica surface increases initially with increased amount of TDI added to the system, then levels off to ca. 1.0 mmol per gram of bare silica after 1.4 mmol of added TDI per gram of bare silica. This indicates that more than 1.4 mmol of TDI per gram of bare silica is not necessary.

Grafting of PEGs onto Silica Surface

Figure 2 gives FTIR spectra of silica, TDI-modified silica and PEG grafted silica. Compared to bare silica, TDI-modified silica shows characteristic peaks of urethane, amide II and aromatics at 1651, 1539, 1602, and 1506 cm^{-1}, indicating that the reaction of TDI with silica takes place through formation of a urethane bond. Apart from those peaks mentioned above, PEG grafted silica shows additional peaks at 2950, 2920, and 2880 cm^{-1} which belong to the CH_2 stretch vibration, implying successful grafting of PEG onto silica via TDI coupling.

The grafting of PEG is also supported by ^{13}C CPMAS NMR spectrum of grafted silica, which is shown in Fig. 3B. The peak at 155 ppm is due to urethane structure, those in 140–100 ppm region represent aromatic carbons of TDI moiety. The methoxy group of the urethane structure and methyl group of TDI moiety appear at 51 and 17 ppm, respectively. All the above mentioned peaks can be found in the spectrum of TDI-grafted silica (Fig. 3A), which confirm the grafting of TDI. An additional peak at 70 ppm corresponds to ether carbons of PEG chain, revealing grafting of PEG through TDI coupling.

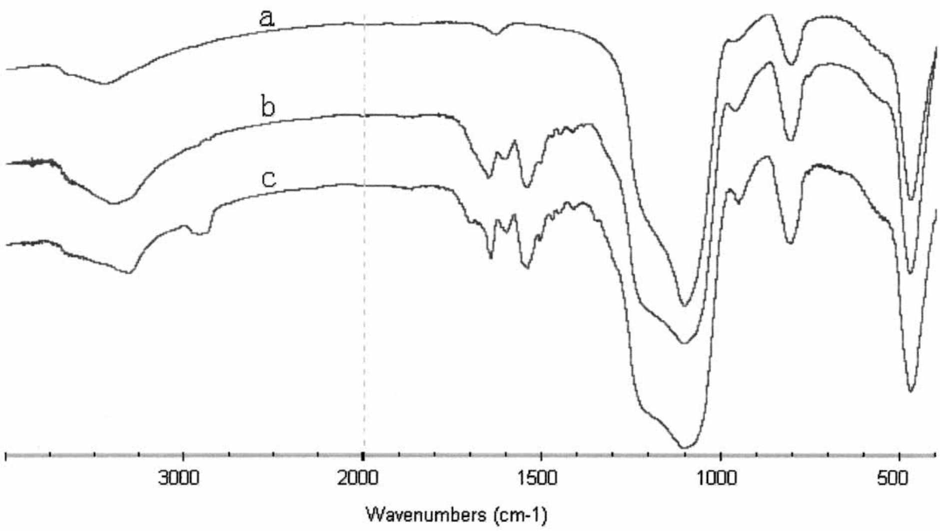


Figure 2. FTIR spectra of (a) silica, (b) TDI-modified silica and, (c) PEG grafted silica.

It has been reported that PEG can be either covalently grafted onto silica via -Si-O-C ester linkage or firmly adsorbed through hydrogen bonding between the PEG etheric oxygen and the surface hydroxyl of silica.[24–26] In a control experiment, we treated silica (1 g) with PEG 2000 (7 g) in toluene (50 ml) in the absence of TDI under the same conditions as for the grafting reactions. After filtration and Soxhlet extraction, the amount of unextractable PEG was 2.5% as determined by TGA. In another control experiment, we treated TDI-modified silica, which was end-capped with methanol, with PEG 2000 in toluene under the same conditions, no unextractable PEG was found by TGA due to presumably lack of surface hydroxy groups, most of which had reacted with TDI. As will be discussed later, in our one-step procedure, TDI is bound to silica before grafting of PEG, most of silanol groups have been consumed when grafting of PEG occurs, hence the amount of PEG directly grafted onto silica via -Si-O-C is presumably, if there is any, much less than 2.5% (the maximum value in the absence of TDI). It can be concluded that PEG is grafted onto silica through covalent bonding via TDI coupling.

Quantification of Grafting by TGA

Figure 4 shows TGA diagrams of original silica, TDI-modified silica and PEG grafted silica. The weight loss of TDI-modified silica is mainly between 150°C and 300°C with only a small amount between 300°C and 700°C (3.6% relative to bare silica). The PEG grafted silica shows two distinct weight loss regions: one between 150°C and 300°C corresponding to the major weight loss of TDI moiety, and the other between 300°C and 700°C contributed mainly by PEG which is known to decompose at this temperature region. The percentage of PEG grafting was calculated from the weight loss between 300°C and 700°C after subtracting the contribution of TDI moiety to this region.

The compositions of PEG grafted silicas were also determined by elemental analyses of carbon and nitrogen. As shown in Table 1, the values are very close to those estimated from overall and PEG graftings obtained from TGA data, proving that TGA is an

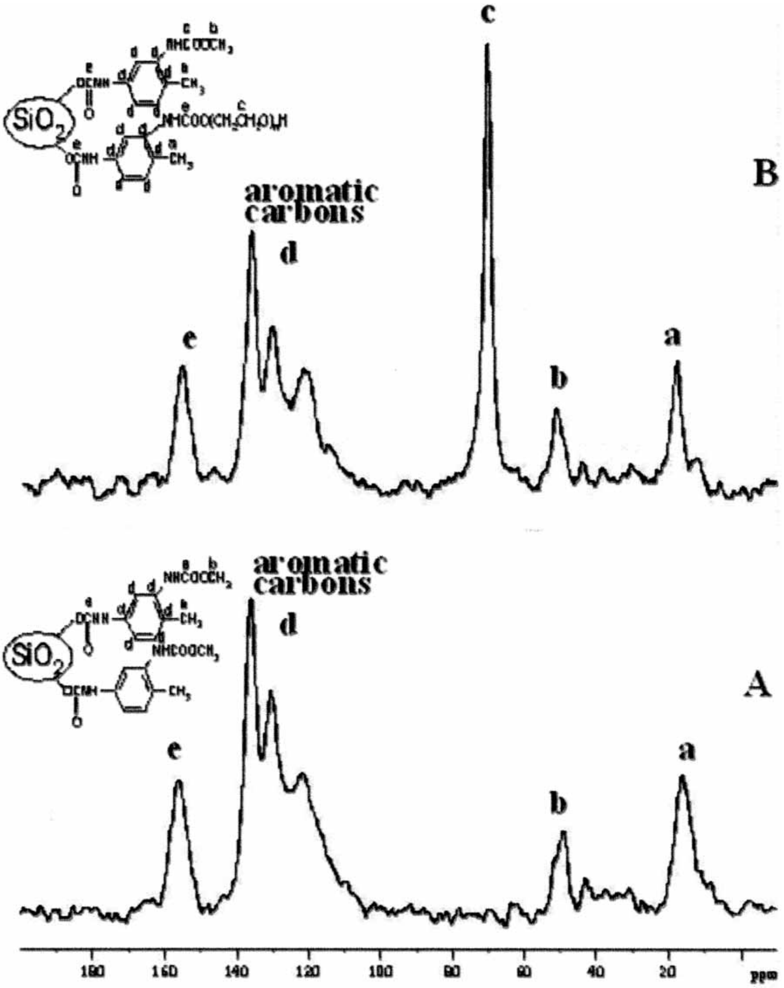


Figure 3. ^{13}C CPMAS NMR spectra of (A) TDI-grafted silica and (B) PEG-grafted silica.

appropriate mean to determine overall grafting as well as PEG grafting. Also, elemental analyses provide supplementary evidence for grafting of PEG onto silica surface.

Effect of the Amount of PEG on Grafting

A series of reactions with 0.5-5 equivalents of PEG 2000 to TDI was carried out while all other conditions were kept unchanged. The amount of TDI was fixed to 1.4 mmol per gram of silica, which can ensure maximum reaction of silanol groups of silica with TDI in the absence of PEG, as indicated by Fig. 1. As discussed earlier, the maximum number of silanol groups which are active towards TDI is around 1.0 mmol/g, thus even with 0.5 equivalent of PEG2000 (to TDI, Table 1), the number of hydroxy groups from PEG2000 is still more than those on 1 g of silica. The grafted TDI is 1.03 mmol/g, indicating that almost all of reactive silanol groups have reacted with TDI, and that the presence of 0.5 equivalent of PEG2000 does not affect the reaction of silica. Although

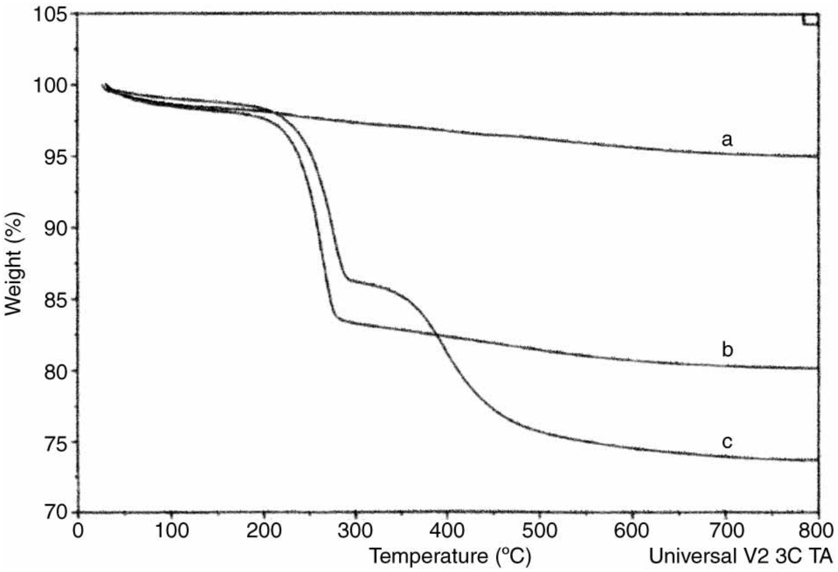


Figure 4. TGA diagrams of (a) original silica, (b) TDI-modified silica and, (c) PEG grafted silica (sample Entry 2).

PEG2000 does compete with silica, there is still half amount of TDI reacted with silica when the amount of PEG2000 is much more than that of silica (Entry 4), proving that the reactivity of silica is much higher than that of PEG2000. This suggests that the grafting process proceeds in sequential reactions as in a traditional two-step procedure, i.e., TDI reacts with silica using one of its isocyanate group and subsequently the surface bound isocyanate groups of TDI-modified silica react with PEG. As shown in Table 1, for Entry 1 grafted TDI and grafted PEG are 1.03 and 0.07 mmol/g silica respectively, and NCO efficiency is 7%. This indicates that the amount of TDI reacted only with silica (i.e. not with PEG) is 0.96 mmol/g silica, and that reacted with both PEG and silica is 0.07 mmol/g silica. As the amount of TDI added to the system (1.4 mmol/g silica) is higher than the maximum value which can react with silica (1.0 mmol/g silica), the

Table 1
Effect of the amount of PEG on grafting[a]

Entry	PEG (eq)	Grafting overall/PEG (%)	Grafted TDI/PEG (mmol/g)	NCO efficiency (%)	N (%) Est[b]/Mea[c]	C (%) Est[b]/Mea[c]
1	0.5	35.5/14.1	1.03/0.071	7	2.1/2.4	14.2/14.7
2	1	33.7/13.1	0.99/0.066	7	2.1/2.2	13.6/13.7
3	2.5	31.2/13.8	0.84/0.069	8	1.8/1.8	12.8/12.8
4	5	29.4/14.4	0.72/0.072	10	1.6/1.5	12.1/12.0

[a] Reaction conditions: silica, 1 g; TDI 1.4 mmol; PEG2000, 0.5-5 equivalents to TDI; 80°C, 7 h.
[b] Estimated from overall and PEG graftings.
[c] Measured by elemental analyses.

excess amount of TDI (0.4 mmol/g silica) is consumed by reaction with PEG chains. The reaction of either grafted PEG chains (OH groups) or NHs in the urethane link with isocyanate groups on silica surface is rare, although possible, since the reactivities of such OH and NH groups are considerably reduced once they are bonded to silica surface. In fact, gelation was not observed during the course of reaction.

For the purpose of comparison, a traditional two-step procedure was also carried out using similar conditions as for Entry 4 with 5 equivalents of PEG. The PEG grafting is 11.2%, and the number of grafted TDI is 1.1 mmol/g. These results are comparable to those in Entry 1 with much less PEG.

It is also noted from Table 1 that both the PEG grafting and the NCO efficiency do not vary much with the change of the amount of PEG2000. The PEG grafting is constant to about 14%, and the NCO efficiency is 7–10%. Therefore, the amount of PEG has some effect on the grafting of the coupling agent (TDI) and has little effect on PEG grafting.

Effects of Temperature, Catalyst, and Molecular Weight of PEG on Grafting

As shown in Table 2, the temperature ranging from 50°C to reflux has little effect on PEG grafting, but increases slightly the grafting of TDI. With the mild catalysts TEA and pyridine, the PEG gaftings are only slightly lowered, however, the graftings of TDI are notably decreased, suggesting that these catalysts increase the competition between PEG and silica in reaction with TDI. Therefore, the use of catalysts can not increase PEG grafting in this one-step procedure. The percentage of PEG grafting does not vary much with the size of PEG (9-16%), however, the number of grafted PEG molecules decreases sharply with the increase of molecular weight from 0.24 mmol/g (for PEG400) to 0.03 mmol/g (for PEG6,000). The number of grafted TDI molecules does not change much (0.8–1.0 mmol/g) with the size of PEG, and the NCO efficiency decreases sharply with the increase of molecular weight of PEG from 27% (for PEG 400) to 3% (for PEG 6,000). This implies that the reactivity of PEG decreases with increasing molecular weight due to the bigger chain size and the increased viscosity of the reaction system.

Table 2

Effects of temperature, catalyst, and molecular weight of PEG on grafting

Entry	Temperature (°C)	Catalyst	PEG Size/eq	Grafting overall/PEG (%)	Grafted TDI/PEG (mmol/g)	NCO efficiency (%)
8	50	no	2,000/1	31.0/13.3	0.85/0.07	8
2	80	no	2,000/1	33.7/13.1	0.99/0.07	7
9	reflux	no	2,000/1	34.6/14.4	0.98/0.07	7
10	80	TEA	2,000/1	20.4/9.9	0.51/0.05	10
11	80	Pyridine	2,000/1	24.8/12.4	0.60/0.06	10
12	80	no	400/0.5	27.6/9.4	0.88/0.24	27
13	80	no	1,000/0.5	30.1/12.4	0.86/0.12	14
1	80	no	2,000/0.5	35.5/14.1	1.03/0.07	7
14	80	no	6,000/0.5	33.7/15.9	0.86/0.03	3

Conclusion

PEGs with molecular weights of 400 to 6,000 have been successfully grafted onto nanometer silica surface using TDI as a coupling agent at 80°C in toluene by a one-step procedure. Based on the big difference of reactivity between silica and PEG towards TDI, the grafting process proceeds in sequential reactions involving a first reaction of TDI with silica to give a surface bearing isocyanate groups and a subsequent reaction of such functionalized silica with PEG.

This work gives a simple method to synthesize modified silicas having reactive organic surfaces. Since such modified silicas could increase interfacial interaction in some polymer based composites (where the polymer matrix can react with hydroxy groups of the filler or have compatibility with PEG), they could potentially be useful as functional fillers for modification of some polymers.

Acknowledgments

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