

Towards Controlled Graft Polymerization of Poly[styrene-co-(maleic anhydride)] on Functionalized Silica Mediated by Oxoamminium Bromide Salt. Facile Synthetic Pathway Using Nitroxide Chemistry

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1. Abstract

A TEMPO bromide salt is used to functionalize a silica surface with nitroxyl moieties. The functionalization reaction takes place in 48 h under mild conditions. In a second step, grafts of styrene-maleic anhydride copolymer are grown from the functionalized silica surface by heating it in the presence of the monomers. FT-IR and TGA analysis show that the silica was first functionalized with nitroxide moieties, and then that grafts of styrene-maleic anhydride grew from the functionalized silica surface. A reaction mechanism is proposed in order to explain the findings. The results suggest that the oxoamminium salts are good candidates for the functionalization and grafting of surfaces that contain hydroxy groups and for the generation of hybrid materials with improved properties.

2. Introduction

During the past years, increased efforts have been devoted to the elaboration of organic/inorganic composites [1–3]. In particular, the controlled grafting of polymers using nitroxide-mediated polymerization (NMP) onto silica and silica surfaces has been extensively studied by several groups [4–14]. All these efforts involve both ingenious structures and numerous synthesis pathways. Since the 1980's the oxoamminium salts have been extensively used as oxidizing agents [15,16]. In summary, several synthetic pathways have been developed in order to improve the properties of inorganic/organic composites using nitroxide chemistry, but the use of the chemistry of oxoamminium halogen salts for this purpose has not been reported before. In this way, we report a new and facile synthetic route to produce functionalized silica using, for the first time, an oxoamminium bromide salt. Note that, as far as we know, the oxoamminium salts have never been used in the functionalization of surfaces or in a grafting process. The resulting inorganic/organic alkoxyamine attached to a silica surface was used to synthesize grafts of poly[styrene-co-(maleic anhydride)] using a 'grafting from' method.

3. Experimental part

3.1 Synthesis of 1-Oxo-2,2,6,6-tetramethylpiperidinium Bromide (Br-T)

The Br-T was synthesized according with Hunter *et al.*[17], but we added a small amount of additional bromine to improve the reaction yield (95%). ^1H NMR (CDCl_3): δ =2.3–2.7 (m, 6H), 1.7–2.0 (s, methyl, 12H).

3.2 Silica Surface Functionalization (Si-O-TEMPO)

A solution of Br-T in excess (0.0042 mol in 40 mL of CH_2Cl_2) was added dropwise to a suspension of silica (0.55 g in 20mL of CH_2Cl_2) in the presence of Et_3N (0.0049 mol). The suspension was stirred for 48 h at room temperature. After that, the TEMPO-functionalized silica (Si-O-TEMPO) was filtered and exhaustively washed with CH_2Cl_2 and deionized water. Finally, Si-O-TEMPO was dried overnight at room temperature under vacuum and characterized by FT-IR spectroscopy and TGA.

3.3 Graft Polymerization of Poly[styrene-co-(maleic anhydride)] from the Functionalized Silica Surface

Si-O-TEMPO (0.07 g), styrene (0.087 mol), MA (0.0045 mol, or 4.6 wt.-%), and DMF (0.2 mL) were introduced in a glass reactor equipped with a heating jacket, condenser, and magnetic stirrer, under argon atmosphere. After being stirred for a few minutes, the polymerization mixture was heated and kept at 126 °C for 2 h. Free and grafted SMA were recovered based on the strategy of Bartholome *et al.*[13]

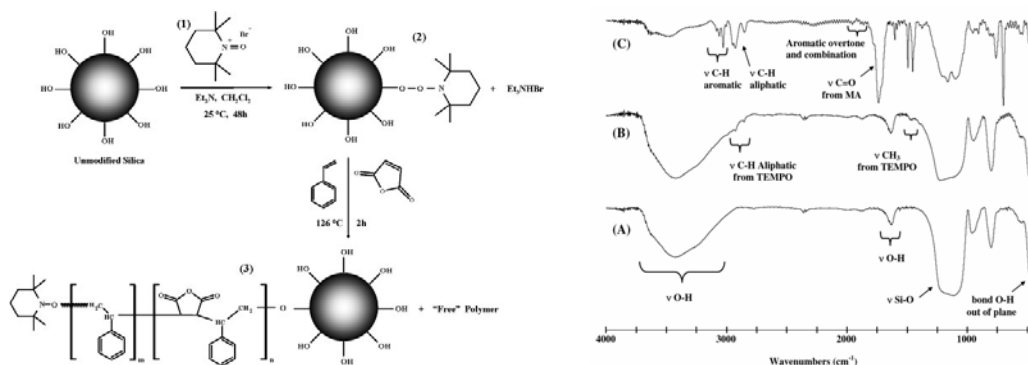
4. Results and discussion

The new synthetic route proposed is shown in Scheme 1. It is believed that the reaction mechanism to obtain (2) involves a nucleophilic substitution mechanism by a free-radical process [18]. The graft of SMA was synthesized from (2) in the presence of St and MA monomers at 126 °C over 2 h. We have recently found [19] that in the initial reaction stages a block of alternate copolymer of St and MA is apparently formed, until the MA is exhausted, and then a second block of pure polystyrene is formed, which indicates the formation of alternating copolymers. From this, we speculate that the grafts formed from silica have a similar poly[(St-alt-MA)-block-St] structure, but this has to be proved further.

4.1 Qualitative evidence of functionalization and grafting onto silica

Unmodified silica, Si-O-TEMPO, and Si-g-SMA-TEMPO were qualitatively analyzed and their structures evidenced by FT-IR spectroscopy as shown in Figure 1. Figure 1A shows characteristic vibrations from unmodified silica, which exhibits strong bands in the 3000–3700 cm^{-1} and 830–1200 cm^{-1} regions, which correspond to the stretching vibrations bonds of intermolecular hydrogen bonded Si–OH and Si–O, respectively. In Figure 1B, which corresponds to Si-O-TEMPO, we can observe small new peaks in the 2925 (ν_{as} , CH_2) and 2851 cm^{-1} (ν_{s} , CH_2) regions, attributed to asymmetrical and symmetrical stretching of the

aliphatic carbons from TEMPO. Also, near 1453 cm^{-1} a new peak attributed to the asymmetrical bending vibration from the methyl groups (ν_{as} , CH_3) of TEMPO can be observed. Finally, Figure 1C, which corresponds to Si-g-SMA-TEMPO, shows new absorption bands in the $3000\text{--}3100\text{ cm}^{-1}$ and $2980\text{--}2850\text{ cm}^{-1}$ regions, which correspond to aromatic stretching vibrations (ν_{s} , C–H) and the methylene stretching vibrations (ν , CH_2) from styrene. Also, a strong vibration at 1736 cm^{-1} was observed and attributed to the characteristic stretching vibration of the carbonyl group from maleic anhydride (ν , C=O).



Scheme 1 (left). Schematic representation of the synthetic route proposed. Figure 1 (right). FT-IR spectra of: A) unmodified silica, B) functionalized silica with TEMPO (Si-O-TEMPO) using oxoammonium salt, and C) graft of poly[styrene-co-(maleic anhydride)] from the silica surface.

4.2 Thermogravimetric Analysis

TGA analysis is shown in Figure 2. Figure 2A reveals a weight loss (5.85 wt.-%) of the unmodified silica. This weight loss is mainly attributed to the loss of physisorbed water. In the first temperature ramp ($5^\circ\text{C}/\text{min}$) the largest loss of water can be observed up to 75°C . When this value was reached a temperature plateau was maintained for 30 min in order to eliminate the largest possible amount of physisorbed water. After that, the temperature was increased in a ramp up to 200°C and at that point a small weight loss (0.53 wt.-%) was observed. This weight loss was attributed to the Si–OH bonds feasible for functionalization. The hydroxy group density of the silica was determined to be around $0.71\text{ }\mu\text{mol}/\text{m}^2$ for –OH groups feasible for functionalization and around $8.5\text{ }\mu\text{mol}/\text{m}^2$ considering all the –OH groups, including those in physisorbed water. Figure 2B shows that after 75°C a positive change in the slope of the curve occurs, that reaches a local maximum value at 136°C attributed to the rupture of the peroxide bond (O–O) between the silica and the nitroxide, although a rupture interval of the O–O bond starting at 100°C and ending at approximately 180°C seems to occur. The weight loss in this interval (2.64 wt.-%) suggests the removal of TEMPO. The derivative in Figure 2C, which corresponds to Si-g-SMA-TEMPO, reveals one local maximum attributed to the degradation of the organic material grafted to the silica. In

order to confirm the polymer degradation, the grafted sample was analyzed up to 500°C, and the result is shown in Figure 2D. The grafting density obtained was 0.293 $\mu\text{mol}/\text{m}^2$.

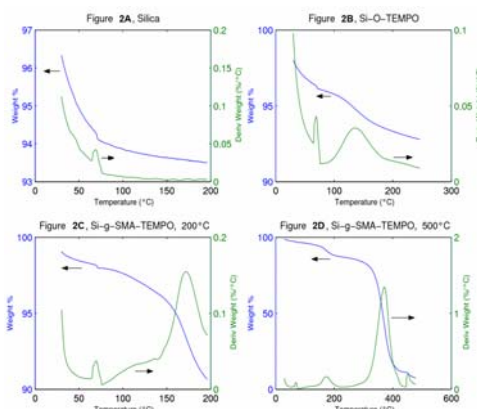


Figure 2. TGA analysis of 2A) unmodified silica, 2B) functionalized silica with TEMPO (Si-O-TEMPO) using oxoammonium salt, 2C) graft of poly[styrene-co-(maleic anhydride)] from silica surface until 200 °C, and 2D) Si-g-SMA-TEMPO until 500 °C.

5. Conclusion

A facile functionalization of silica with nitroxide moieties is presented. The functionalized silica is then grafted with styrene-maleic anhydride copolymer by a second simple synthesis step. Analysis by FT-IR spectroscopy and TGA are consistent with the silica functionalization with nitroxide and then with the growth of SMA grafts from the silica surface. The results suggest that the oxoammonium salts are strong candidates for the functionalization and grafting of surfaces or moieties that contain hydroxyl (–OH) groups using a nucleophilic mechanism by a free radical process. It is believed that this new synthesis pathway opens up several possibilities of potential applications in the generation of molecules and/or hybrid materials with improved properties.

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