

Functionalization of Polymers Hydroxyl-Terminated Using Oxoammonium Bromide Salt. Facile Synthetic Pathway Using Nitroxide Chemistry.

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1. Abstract

A TEMPO bromide salt (Br-TEMPO) is used to functionalize polymers containing hydroxyl terminated groups with nitroxide moieties. The functionalization reaction takes place in 24 h under mild conditions in solution. FT-IR and ¹H-NMR analysis show that these polymers were for first time functionalized with nitroxide moieties using this synthetic pathway. A reaction mechanism is proposed in order to explain the findings, where we postulate the formation in situ of peroxidic bonds. This peroxidic bond was quantified by titration finding moderate functionalization levels (~50%). The results suggest that the oxoammonium salts are good candidates for the functionalization of polymers containing hydroxyl groups.

2. Introduction

Since 1980 the oxoammonium salts have been extensively used as oxidizing agents^[1,2] to produce functionalized polymers with terminal aldehyde or ketone groups. Recently, in our group^[3,4] we demonstrated the functionalization of silica with TEMPO moieties using oxoammonium bromide salts (Br-TEMPO) under mild conditions, where we proposed the formation “*in situ*” of peroxide bonds between TEMPO moieties and the hydroxyl groups. Now, this facile pathway of functionalization has been extended to the functionalization of polymers (not reported before) with hydroxyl terminated groups (polydimethyl siloxane, PDMS and polyethylene glycol, PEG. In particular, in this work our goals were: i) to demonstrate the functionalization of these polymers using oxoammonium bromide salts, ii) to demonstrate and to quantify the formation of the peroxide bond and, iii) to systematically study the best synthesis conditions (amount added of Br-TEMPO) in order to improve the efficiency of functionalization.

3. Experimental

3.1 Materials: 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO), bromine, triethylamine (Et₃N, 99.5%), carbon tetrachloride, tetrahydrofuran (THF) and dichloromethane were

purchased from Aldrich, and methanol from J. T. Baker. All the reagents were used as received.

3.2 Synthesis of oxoammonium bromide salt (Br-TEMPO): In a typical experiment^[3,4] bromine (0.032 mol) was added slowly to a solution of TEMPO (0.032 mol in 100 mL of CCl₄). A brown solid was formed almost instantaneously and was separated from the solution by filtration. A small amount of additional bromine was added to obtain more salt of Br-TEMPO thus improving the reaction yield (95%). The filtrate was exhaustively washed with CCl₄ until the filtered solution showed no more color. The Br-TEMPO was dried over vacuum at 40 °C for 24 h. ¹H-NMR (CDCl₃): δ=2.3–2.7 (m, 6H), 1.7–2.0 (s, methyl, 12H).

3.3 Functionalization of polymers hydroxyl terminated using Br-TEMPO salt: polymers hydroxyl terminated were dissolved using a small amount of dichloromethane into a glass vial under inert atmosphere and magnetic stirring. After that, a solution of Br-TEMPO/dichloromethane was added. The functionalization reaction proceeded during 24h at 40°C. The functionalization reaction conditions are showed in Table 1.

Table 1 Functionalization of polymers hydroxyl terminated using Br-TEMPO salt. Reaction conditions

| Tag | Substrate | Mn | Br-TEMPO (g) | Et ₃ N (g) | CH ₂ Cl ₂ (mL) |
|-----|-----------|-------|--------------|-----------------------|--------------------------------------|
| E1 | PDMS | 15000 | 0.06 | 0.03 | 3.24 |
| E2 | PDMS | 550 | 1.71 | 0.88 | 2.6 |
| E3 | PEG | 600 | 1.54 | 0.80 | 2.6 |
| E4 | PEG | 400 | 2.36 | 1.21 | 2.3 |

Polymers functionalized were washed and filtrated several times with THF to remove triethylamine hydrobromide (Et₃NHBr) formed, which was characterized by ¹H-NMR. Finally, they were dried in a vacuum oven at room temperature overnight and characterized by FT-IR, ¹H-NMR. The efficiency of functionalization was obtained by titration of the peroxidic bond using potassium iodide (KI) and starch as indicator^[5].

4. Results and discussion

The new synthetic route proposed to obtain functionalized polymers with TEMPO moieties using a Br-TEMPO salt are shown in Scheme 1.

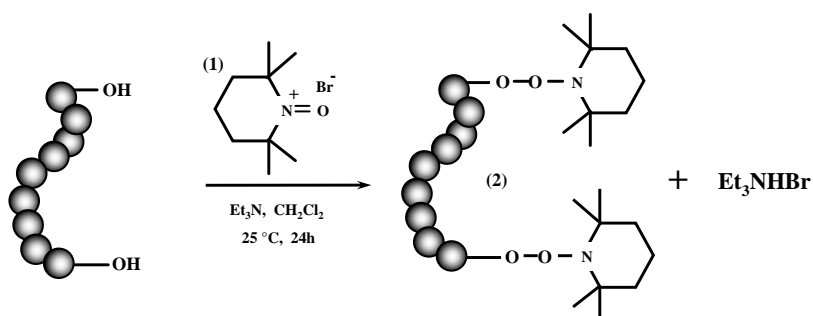


Figure 1. Schematic representation of the functionalization of polymers hydroxyl terminated mediated by oxoammonium bromide salt

It is believed that the reaction mechanism to obtain (2) involves a nucleophilic substitution mechanism by a free-radical process. In this reaction it is proposed that the hydroxyl groups on the polymer are potential sites for attack by a nucleophile such as bromine. The existence of an equilibrium in (1) between the salt and radical species, as a result of a redox system, has been demonstrated.^[2] In this way, it is speculated that (1) provides a bromine radical which, by a free radical mechanism, attacks the -OH bond to generate hydrobromic acid (HBr) and an oxygen-centered radical site in the end of the chain, which is then trapped by the nitroxyl radical to form (2). The HBr formed during this synthesis is trapped by Et_3N to form triethylamine hydrobromide (Et_3NHBr). Figure 2 shows $^1\text{H-NMR}$ spectra corresponding to PEG and PEG-TEMPO

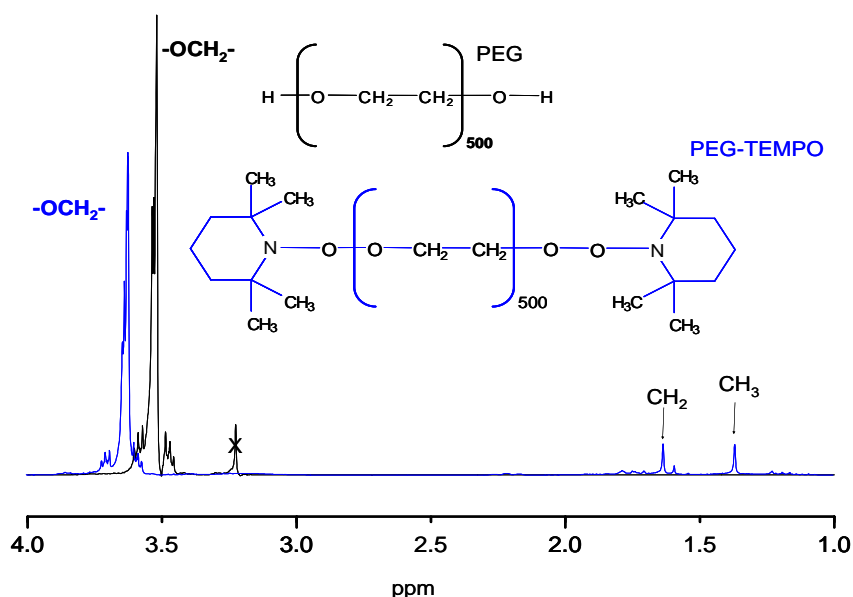


Figure 2. $^1\text{H-NMR}$ spectra corresponding to PEG (virgin polymer, $M_n=500$ Da) and PEG-TEMPO (PEG functionalized with TEMPO using oxoammonium bromide salt)

Figure 2 shows the typical chemical shifts from PEG which exhibits centered

resonances at 3.53 ppm attributable to two protons of $-\text{OCH}_2-$ from PEG structure. New resonances (blue line) at 1.36 ppm and 1.63 ppm were attributed to $-\text{CH}_3$ and $-\text{CH}_2-$ from TEMPO, respectively. Resonances centered at 3.62 ppm were observed and attributed to $-\text{OCH}_2-$ from PEG-TEMPO. Notice that this resonance corresponds to the backbone from PEG and is shifted due to the presence of a new covalent bond between TEMPO and PEG. Similar chemical shifts were observed in the functionalization of PDMS (not shown here). Finally, the efficiencies of functionalization obtained by titration oscillated between 35 to 50%; in the case showed in Figure 2, the efficiency obtained was nearly 50%.

5. Conclusions

In summary, the use of the chemistry of oxoammonium halogen salts in the functionalization of polymers has not been reported before. In this work, for the first time, we functionalized polymers with TEMPO moieties using an oxoammonium bromide salt (Br-TEMPO). The results suggest that: i) the oxoammonium salts are strong candidates for the functionalization of polymers containing hydroxyl ($-\text{OH}$) 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 novel materials (copolymers) following a facile chemistry pathway; ii) The efficiency of functionalization was significantly improved: 1) with temperature (40°C), and 2) using 200 mol.-% of Br-TEMPO, finding modest to high efficiencies of functionalization, and iii) It was indirectly confirmed and quantified the presence to the peroxidic bond by titration, as proposed in our previous work^[3,4].

6. References.

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