Supporting Information

Homogeneous Isocyanate- and Catalyst-free Synthesis of Polyurethanes in Aqueous Media

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1. Spectra of PU-1; PU-2; PU-3; PU-4 and PU-5

PU-1

Figure 1.1 Structure $^1$H NMR spectrum of PU-1.
Figure 1.2 $^1$H NMR spectrum of PU-2.
Figure 1.3. $^1$H NMR spectrum of PU-3.
Figure 1.4. $^1$H NMR spectrum of PU-4.
Figure 1.5. $^1$H NMR spectrum of PU-5.
2. Aqueous Stability of Activated Carbonate Monomer

As previously mentioned, the efficiency of this reaction in aqueous media is highly dependent on the nature and reactivity of the leaving group, which has to be chemoselective towards amines but not water. In order to demonstrate the stability of the poly(ethylene glycol)-derived bis-(pentafluorophenyl)carbonate in aqueous media, $^1$H NMR spectra of the compound were acquired in D$_2$O over a 24-h period. It was observed that the signal due to the methylene protons proximal to pentafluorophenyl carbonates did not decrease in intensity over time, confirming the high stability of bis(pentafluorophenyl) activated carbonates in water.
Figure 1.6. $^1$H NMR spectra of monomer B (PEG activated carbonate) in D$_2$O at different times, showing no change in the characteristic signals.
3. Thermograms

![Thermograms](image)

Figure 1.7. DSC thermograms of the five synthesized polyurethanes, PEG diol and JEFFAMINE.
4. Sustainability

Bis(pentafluorophenyl)carbonate (PFC) was a starting material of choice because it is much less toxic than phosgene and its various equivalents. PFC is also a crystalline solid at room temperature which, being less sensitive to water than phosgene, can be easily shipped, stored, and handled. Furthermore, the pentafluorophenol byproduct is less volatile, less acidic, and less corrosive than hydrochloric acid. These advantages alleviate the cost and complexity of the reactions, and potentially broaden the scope of the starting materials to include acid-sensitive compounds. Additionally, the pentafluorophenol byproduct can also be readily recovered (for recycling back into PFC).

Recovery of Pentafluorophenol

Pentafluorophenol is the main byproduct of our isocyanate- and catalyst-free synthesis of polyurethanes. In order to make this process sustainable, the recovery of the pentafluorophenol had to be addressed. Pentafluorophenol is generated in both steps of the polymerization: first, in the preparation of the activated carbonates where the alcohols are reacted with the PFC, and also in the subsequent polymer-forming step where the activated carbonates are reacted with JEFFAMINE® ED-2003 to generate high molecular weight polyurethanes.

STEP 1: Recovery of pentafluorophenol from the first step of the polymerization was easily achieved, and this is described in the main manuscript.
STEP 2: Following the conclusion of the polymer-forming step, the aqueous reaction mixture is first diluted ten-fold with water. This solution is then transferred into a Vivaspin 20 Concentrator, which is a special ultra-filtration centrifuge tube. In our case, a tube with a molecular weight cut off (MWCO) of 3 kDa was used. Centrifuging the aqueous mixture at 8000 rpm (and at 4 °C) for 30 minutes produced a clear, pentafluorophenol-containing filtrate in the bottom compartment. More water was added to the top mixture, and centrifugation was carried out a second time under identical conditions. Centrifuging the aqueous mixture at 8000 rpm (and at 4 °C) for 30 minutes produced a clear, pentafluorophenol-containing filtrate in the bottom compartment. Figure 1.8 shows the ultra-filtration tube after the extraction.

![Ultra-filtration tube](image)

Figure 1.8 Ultra-filtration tube used in the recycling of pentafluorophenol.
Subsequent freezing and lyophilization of the combined filtrates gave 65% recovery of the pentafluorophenol (purity > 90%). Figure 1.9 shows the $^{19}$F NMR spectrum of the final recovery product.

Figure 1.9. $^{19}$F NMR spectrum of the recovered pentafluorophenol.