APPLICATION NOTE

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Qualitative and quantitative analysis of the polymerization of PS-*b*-P*t*BA block copolymer using picoSpin 80 NMR

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Key words
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Benefit
The Thermo Scientific™ picoSpin™ 80 NMR spectrometer offers near real-time analytical capability for reaction monitoring due to its unique capillary injection design and compact footprint. The picoSpin 80 NMR has also proven to be a low-cost alternative to high-field NMR spectrometers to quantitatively assess polymerization and to determine copolymer structure.

Abstract
The use of the low-field picoSpin 80 NMR spectrometer offers a near real-time analytical capability for reaction monitoring, largely due to its unique capillary injection design and compact footprint. Despite the broad resonance signals typical for polymers, by carefully selecting the regions where signal changes manifest the involved chemical transformation, the integrated peak area provides valuable insight to the reagent conversion as well as the final product structure.

Introduction
Nuclear magnetic resonance (NMR) spectroscopy has proven to be an invaluable analytical tool for reaction monitoring and optimization by elucidating molecular structure, studying reaction kinetics, monitoring reaction progress and gauging product purity[1]. For polymers however, resonance signals from repeating units often coalesce as broad peaks, even with high-field NMR spectrometers. This is largely due to poor molecular rotation and repeating units being situated in marginally different chemical environments. Low-field NMR such as the picoSpin 80 NMR spectrometer lends itself as a low-cost alternative to high-field instruments for polymerization monitoring, resulting in significant cost savings on both instrument procurement and upkeep.

Presented herein is a case study using a picoSpin 80 NMR spectrometer to monitor the polymerization of *t*-butyl acrylate with a polystyrene reagent. The reaction scheme is shown in Figure 1. By carefully identifying and integrating the resonance signals associated with the monomer, the progress of the polymerization was successfully assessed both qualitatively and quantitatively. The number of *t*-butyl acrylate units incorporated into the final copolymer product was also deduced.

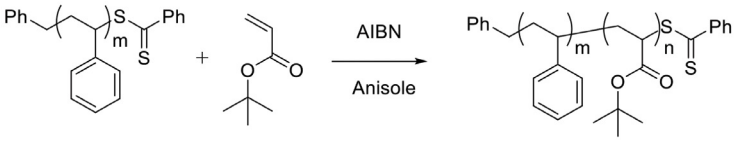


Figure 1: Polymerization of *t*-butyl acrylate with a polystyrene reagent to form PS-*b*-P*t*BA.

Experimental

Monomer *t*-butyl acrylate (*t*BA, 0.150 g, 1.170 mmol), polystyrene reagent (PS, 0.230 g, 0.120 mmol), 2,2'-azobis (2-methylpropionitrile) radical initiator (AIBN, 0.001 g, 0.006 mmol), and anisole (1.156 mL) were added together into a 10 mL flask. The number average molecular weight of PS is 1910.76 g/mol, determined by the end-group analysis using a 500 MHz NMR and confirmed by GPC. The average number of repeating units in PS is 16. This resulted in a molar ratio of 9.75/1 for *t*BA/PS. The mixture was degassed by three freeze-pump-thaw cycles. The mixture was then stirred at 75 °C for 12 h and the polymerization process was observed by ^{1}H NMR spectroscopy.

A picoSpin 80 NMR spectrometer was used to acquire spectra of the polymerization reaction. The instrument is an 82 MHz, pulsed, Fourier transform ^{1}H NMR spectrometer with superior chemical shift resolution and sensitivity. The instrument contains a 2 Tesla temperature controlled permanent magnet and is fitted with a 40 microliter capillary cartridge used for sample injection into the spectrometer.

All samples were manually injected into the capillary cartridge using disposable 1 mL slip-tip polypropylene syringes and 22 gauge blunt-tipped needles. During the reaction, aliquots were taken out and injected directly into the picoSpin capillary cartridge with no sample preparation. Back-to-back sample injection and data acquisition was separated by a solvent/air/solvent/air flush of the capillary cartridge with anisole used as the solvent. Spectra were referenced to the $-CH_3$ signal from anisole (δ3.75 ppm).

All spectra were acquired using the following acquisition parameters: 90° excitation pulse, 750 ms acquisition time and 8 s recycle delay. The spectral data was processed using the Mnova™ NMR analysis program with a standard set of processing parameters including zero filling and phase correction. Apodiation was not used.

Results and discussion

A qualitative look at the polymerization

Figure 1 depicts a narrowly dispersed polystyrene-based reversible addition-fragmentation chain transfer (RAFT) reagent reacting with *t*-butyl acrylate monomer to form a PS-*b*-P*t*BA block copolymer[2-3]. Figure 2 shows the NMR spectrum of the initial reaction mixture containing *t*-butyl acrylate (*t*BA) and polystyrene reagent (PS) in anisole. The signals between δ 1.4–2.8 ppm originate from the 3 protons of the CH_2- and CH- groups of the PS repeating unit. These overlap with the singlet from the 9 *t*-butyl methyl protons of *t*BA (δ 1.7 ppm). The singlet at δ 3.7 ppm is ascribed to the methyl group of anisole. The signals between δ 5.5 – 6.7 ppm correspond to the 3 vinyl protons of *t*BA. Finally, the multiplet in the region δ 6.8 – 7.6 ppm arises from the aromatic rings from both anisole and PS.

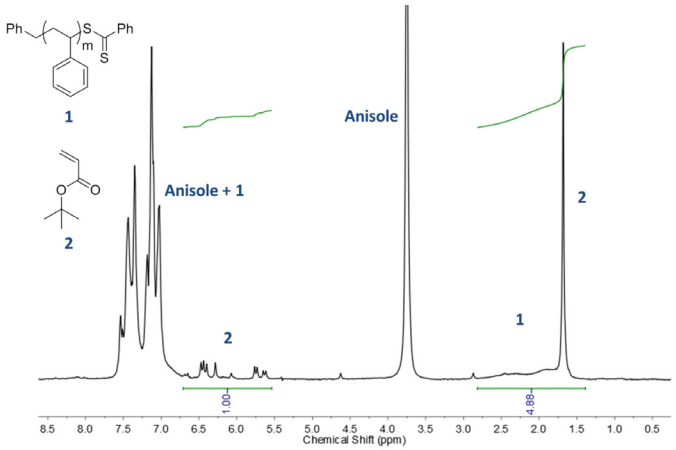


Figure 2: 82 MHz ^{1}H NMR spectrum of the initial reaction mixture containing polystyrene reagent (PS) and *t*-butyl acrylate (*t*BA) in anisole.

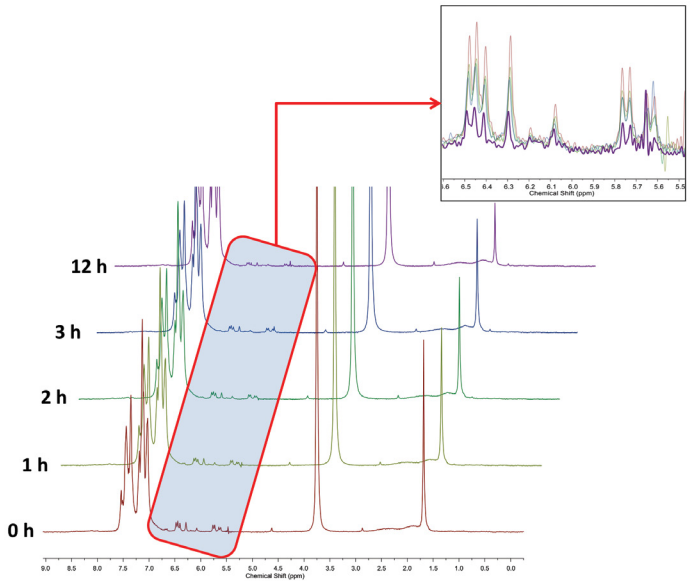


Figure 3: Overlay of the 82 MHz ^{1}H NMR spectral collected at 0, 1, 2, 3, and 12 hour time-points. The insert shows a decrease in intensity of the vinyl protons of *t*BA.

Figure 3 shows the overlaid ^{1}H NMR spectra of the reaction mixture acquired at 5 different time points over the course of the polymerization: 0, 1, 2, 3 and 12 hours, respectively. The main chemical transformation during the polymerization is the opening of the double bonds in the *t*BA monomer, as demonstrated in Figure 4. The insert in Figure 3 clearly demonstrates that the resonance signals from the vinyl protons of *t*BA (δ 5.5–6.7 ppm) decrease as the reaction progresses. A quantitative perspective of the chemical transformation is presented in the subsequent section.

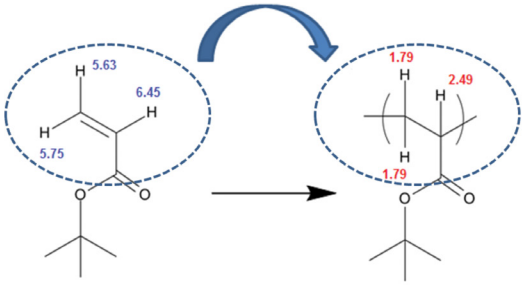


Figure 4: Schematic showing the conversion of vinyl protons to protons in the polymer backbone. The numbers denote the projected chemical shifts of the involved protons by ^{1}H NMR.

It is worth pointing out that the compact footprint of the picoSpin 80 NMR spectrometer allows the instrument to be set up in the laboratory where the chemistry takes place. Furthermore, the unique capillary injection system of the picoSpin minimizes sample workup, offering a near real-time analytical capability critical for reaction monitoring and optimization.

Quantitative Analysis of the Polymerization

Figure 5 shows the ^{1}H NMR spectra of the reaction mixture at *t*=12 hours. As the reaction progressed, the monomer *t*BA was gradually added to the polymer through the opening of the double bonds (Figure 4). Consequently, part of the protons originally contributing to the resonance signals in the region δ 5.5-6.7 ppm were converted to the protons contributing to signals between δ 1.4 – 2.8 ppm. A closer analysis reveals that the ratio $\frac{I_{1.4-2.8\ ppm}}{I_{5.5-6.7\ ppm}}$ increased from 4.88 at *t*=0 to 7.57 at *t*=12 hour.

At *t*=0, there are 9.75 moles of *t*BA for every mole of PS. At *t*=12, the signals between δ 1.4–2.8 ppm include the aliphatic protons from PS, the methyl protons from the *t*-butyl groups in *t*BA, and the protons converted from the vinyl groups in *t*BA. There are 3 aliphatic protons in each PS repeating unit, and there are 16 repeating units in every PS molecule. The total PS protons are therefore 48. The number of methyl protons in *t*BA are 9 × 9.75 = 87.75 and remains unchanged throughout the reaction.

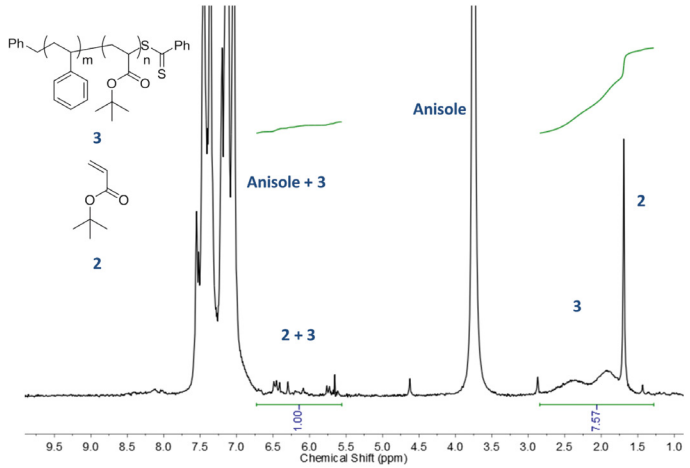
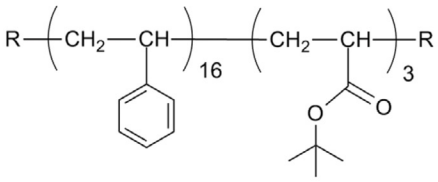


Figure 5: 82 MHz ^{1}H NMR spectrum of the polymerization process after 12 hours at 75 °C.

For the vinyl protons in *t*BA (a total of 3 × 9.75 = 29.25), assuming n% was converted to polymer, 29.25n protons is shifted to the region δ 1.4–2.8 ppm and 29.25 (1-n) protons remain in the region δ 5.5-6.7 ppm.

Based on the calculations below, it was determined that 34% of *t*BA was converted into the block copolymer, corresponding to an average of 34% of 9.75 = 3 *t*BA units in every copolymer molecule.

$$\text{t=12 hour:}\quad \frac{48+29.25n+87.75}{29.25(1-n)}=\frac{7.57}{1.00} \longrightarrow n=0.34$$



Conclusion

The use of the low-field picoSpin 80 NMR spectrometer offers a near real-time analytical capability for reaction monitoring, largely due to its compact footprint and unique capillary injection design. Despite the broad resonance signals typical for polymers, by carefully selecting the regions where signals can quantitatively manifest the involved chemical transformation, the integrated peak area provides valuable insight to the reagent conversion as well as the final product structure. In the case of the polymerization of PS-*b*-P*t*BA, the vinyl and aliphatic regions were selected for integration. By comparing the signal ratio before and after the reaction, it was determined that 34% of the *t*BA monomer was converted to the copolymer. On average, the final product contains 3 *t*BA units. The described workflow and its underlying principles should be of interest for chemists routinely performing polymer synthesis.

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