Determination of Methylene Bridge Crosslinking in Chloromethylated PS-DVB Resins

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ABSTRACT: We present the development of a method for the determination of methylene bridge crosslinking in 13C-labeled chloromethylated polystyrene-divinylbenzene resins. Our system uses a new room temperature reduction of the chloromethyl groups that circumvents the possible challenges associated with additional crosslinking. We demonstrate how the reduction of the chloromethyl groups allowed for the determination of methylene bridging, derived from the methylenebis(ethenylbenzene) crosslinker, based on the integration of the methylene signal in the 13C NMR spectra. Utilizing this method, the total crosslinking within the chloromethylated resin generated at 35 °C was determined to be upward of 10 wt %, which increased from 6 wt % in the unfunctionalized resin. © 2016 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. 2016, 00, 000–000

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INTRODUCTION Crosslinked polymers have been utilized extensively in the production of anion exchange, chelating, and hypercrosslinked resins.1–3 The synthesis of these materials often proceeds through the chloromethylation and subsequent functionalization of polystyrene–divinylbenzene (PS-DVB) copolymers, a process that has been utilized industrially since the early 1950s.1 It has been previously shown that the morphology of chloromethylated PS-DVB resins are strongly dependent on their method of preparation.4–7 During the chloromethylation of PS-DVB additional crosslinking can be incorporated into the resin, presumably from the attack of adjacent aryl groups onto the newly formed chloromethyl functionality, forming undesired methylene bridges.8,9 The incorporation of this crosslinking is problematic as it decreases the swelling capacity of the resins, decreases the available functionality for further derivatization, and is believed to lead to resin breakage over time through osmotic shock.

To date, there has been no direct observation of the methylene bridge functionality. Early characterization methods reported have relied on the swelling differences between pre- and postchloromethylated resins to determine the degree of functionalization.10–13 More recently, numerous NMR studies have been undertaken in the gel phase.14–16 For example, Ford and coworkers developed an NMR method for the analysis of crosslinking due to methylene bridging17 and DVB18,19 content based on the linewidth of the methine in the polymer backbone.

An alternative but powerful approach relies on solid-state NMR. This technique has allowed for the analysis of PS-DVB resins with higher DVB content while avoiding increased linewidths due to dipolar broadening, which is observed in gel-phase NMR experiments.20 Sherrington and coworkers analyzed anion-exchange resins derived from chloromethylated PS-DVB with single-pulse excitation-magic angle spinning (SPE-MAS) NMR and determined that upward of 50–60% of aromatic rings were involved in methylene bridging based on the aromatic integration.21 Analysis of the aromatic region was subsequently used to analyze the methylene bridge content in hypercrosslinked resins.22,23

Although solid-state NMR provides a good analysis of chloromethylated resins with extensive methylene bridge crosslinking through the integration of their anion-exchange derivatives, to our knowledge no methods exist to determine...
the extent of crosslinking that results from the initial chloromethylation of PS-DVB through the resulting methylene signal. Presumably, this has remained elusive because NMR analysis requires post-functionalization of the chloromethylated resin to clarify this region within the $^{13}$C spectra. These transformations may induce additional crosslinking that could prevent analysis of the methylene bridging introduced during the chloromethylation reaction.

The ability to synthesize anion exchange resins with precise control over the crosslinked polymers would significantly reduce the structural problems associated with methylene bridge formation. To achieve this, a method to analyze the chloromethylation process is required. Herein, a method is described for the solid-state NMR characterization of methylene bridging in $^{13}$C-labeled PS-DVB resins that relies on the functionalization of the chloromethylated resin at ambient temperature so as not to induce additional crosslinking.

**EXPERIMENTAL**

**Materials**

PS-DVB (6 wt % DVB) resin was provided by The Dow Chemical Company. $^{13}$C-Labeled paraformaldehyde ($^{13}$C, 99.4%) was obtained from Aldrich and all reagents were used as received.

**Preparation of Chloromethylated PS-DVB**

To a 25-mL 3-necked flask fitted with an overhead stirrer and a thermometer was added $^{13}$C-labeled paraformaldehyde (1.23 g, 39.65 mmol, 4.47 equiv), MeOH (1.60 mL), and H$_{2}$O (0.87 mL). The suspension was heated to 80 °C for 10 min. The solution was then cooled to 35 °C and to the flask was added an addition funnel fitted with a reflux condenser. To the funnel was added chlorosulfonic acid (2.67 mL, 40.2 mmol, 4.52 equiv), which was added to the reaction mixture dropwise over 4 h such that the internal temperature of the reaction was maintained at 35 °C. The PS-DVB resin 1 (0.94 g, 8.88 mmol, 1 equiv) was then added. After the copolymer was allowed to swell for 10 min, a solution of FeCl$_{3}$ (0.096 g, 0.59 mmol, 0.066 equiv) in H$_{2}$O (0.14 mL) was added. The suspension was stirred for 4 h at 35 °C, at which time the stirring was stopped and the suspension was allowed to cool to 25 °C over 10 min. The suspension was filtered through a course frit and then washed with MeOH (2 × 50 mL), H$_{2}$O (2 × 50 mL), MeOH (2 × 50 mL), CH$_{2}$Cl$_{2}$ (2 × 50 mL), MeOH (2 × 50 mL), H$_{2}$O (2 × 50 mL), MeOH (2 × 50 mL), CH$_{2}$Cl$_{2}$ (2 × 50 mL), and Et$_{2}$O (2 × 50 mL). The beads were air-dried on the frit for 30 min and then under vacuum at room temperature overnight to yield chloromethylated resin 2 (1.11 g). ELEM. ANAL.: C: 77.8%, H: 6.4%, Cl: 15.0%.

**Preparation of Reduced PS-DVB**

To a suspension of 2 (0.525 g) in THF (24 mL) at room temperature was added hexadecyltributylphosphonium bromide (0.112 g, 0.220 mmol) followed by L-Selectride (1.0 M, 24.0 mL, 24.0 mmol), dropwise. After 71 h, the suspension was cooled to 0 °C and then MeOH (20 mL) was added. After stirring for 1 h, the suspension was filtered and the resin was washed with MeOH (2 × 20 mL), H$_{2}$O (2 × 20 mL), MeOH (2 × 20 mL), and CH$_{2}$Cl$_{2}$ (2 × 20 mL). The beads were air-dried on the frit for 20 min and then under vacuum at room temperature overnight to yield 3 (0.360 g). ELEM. ANAL.: C: 89.9%, H: 7.7%, Cl: 0.6%.

**Instrumentation and Analysis**

Fourier transform infrared (FTIR) spectra were acquired on a Nicolet iS10 spectrometer with a diamond ATR accessory. Each spectrum was obtained with 32 scans at a 1 cm$^{-1}$ resolution and scanning range of 4000–400 cm$^{-1}$.

$^{13}$C NMR spectra were obtained at ambient temperature on a Bruker Avance III 400WB spectrometer operating at 100.6 MHz with a 4.0 mm MAS triple resonance broadband probe. PS-DVB was spun at 14.0 kHz and resins 2 and 3 were spun at 14.5 kHz in a 4.0 mm zirconia rotor with a Kel-F cap. $^{13}$C chemical shifts were externally referenced to adamantane. CP-MAS spectra were acquired with a $^{1}$H 90° pulse length of 2.3 μs, 2 ms contact time, 3.0 s recycle delay, and ~4500–7000 transients. The acquisition time was 20.5 ms with a spectral width of 50 kHz. CP-MAS spectra were processed with 25 Hz exponential line broadening. SPE-MAS spectra were acquired with a $^{13}$C 33.3° pulse length of 0.83 μs, 33.3 s recycle delay, and ~5200–5300 transients. The acquisition time was 10.2 ms with a spectral width of 50 kHz. SPE-MAS spectra were processed with 100 Hz exponential line broadening. Tetrakis(trimethylsilyl)silane (TKS) was used as an internal standard.

Elemental analysis and chloride content were obtained from Robertson Microlit Laboratories. Chloride content was determined by titration following combustion. Samples were vacuum-dried at ambient temperature before analysis.

**RESULTS AND DISCUSSION**

The morphology of chloromethylated PS-DVB resins is dependent on a number of variables during their preparation including the initial crosslinking within the resin, chloromethylation reagent, catalyst, solvent, temperature, and reaction time. This transformation has historically been performed with chloromethyl methyl ether and a Lewis acid catalyst, but due to the carcinogenic nature of this reagent more recent procedures have migrated toward the generation of chloromethyl methyl ether in situ so as to limit exposure. A variety of formulations have been developed that rely on formaldehyde equivalents as the basis for this reagent. One of the predominant methods utilized takes advantage of the depolymerization of paraformaldehyde with chlorosulfonic acid in methanol and water.

In this study, the chloromethylation of 6 wt % crosslinked PS-DVB (1) was examined with the use of $^{13}$C-labeling at the benzylic positions. It was anticipated that $^{13}$C-labeling would allow for easier visualization of the methylenes, resulting from the potential methylenebis(ethenylbenzene) crosslinking, in the $^{13}$C NMR spectra. The resin was chloromethylated
with chloromethyl methyl ether, generated in situ from >99% 13C-labeled paraformaldehyde, and catalyzed by iron(III) chloride at 35 °C over 4 h to provide 2 (Scheme 1). Analysis of the infrared spectra of 2 confirmed that the chloromethyl functionality was installed through the presence of the chloromethyl methylene bend at 1421 cm⁻¹, the methylene wag at 1255 cm⁻¹, and the carbon–chloride bond stretch at 658 cm⁻¹ (Fig. 1). The chloromethyl groups were incorporated predominantly at the para positions as indicated from the newly formed 1,4-disubstituted aromatic carbon–carbon stretch at 1511 cm⁻¹ and the 1,4-disubstituted aromatic carbon–hydrogen out-of-plane bend at 823 cm⁻¹. This regioselectivity had previously been confirmed in both small molecules and polystyrene.  

Examination of the 13C cross-polarization magic angle spinning (CP-MAS) spectra of 2 revealed a peak representing the 13C-labeled methylenes of the chloromethyl functionality at 46.6 ppm (Fig. 2). Ford and coworkers previously showed that the methylene bridge carbons also fall within this same region; however, as the degree of crosslinking increases the linewidths of the peaks increase such that the methylene bridging is not directly observable. To complicate this region further, the naturally abundant methylenes and methines of the polymer backbone also overlay with this peak. Inspection of the 46.6 ppm signal revealed asymmetry in the form of a slight shoulder on the right-hand side. While this shoulder may have resulted from contribution of the backbone, it was postulated that methylene bridge crosslinking could also play a role.

To observe the methylene bridging, functionalization of 2 was required to remove the chloromethyl contribution from the peak at 46.6 ppm. Chloromethylated resins have previously been functionalized with a variety of reagents, but in most instances the methylene signal in the resulting products remains in this same region. Conditions had to be established to functionalize the chloromethylated resin and shift the peak in question to allow for the analysis of the methylene bridging resulting from the initial chloromethylation reaction. However, we sought to avoid the use of radical conditions and elevated temperatures due to the possibility of incorporating additional crosslinking within the resin. The reduction of chloromethylated resins was previously demonstrated by Oehme et al., although to facilitate this reaction the chloride was first converted to the iodide and subsequently reduced with lithium aluminum hydride in refluxing THF. Tsuge and coworkers then showed that this transformation could be performed with tributyltin hydride and AIBN at elevated temperatures. In an effort to find conditions that would facilitate this transformation at room...
temperature various hydride reagents, which were known to reduce the chloromethyl functionality in small molecules, were examined. It was found that with sodium borohydride and hexadecyltributylphosphonium bromide (TBHDPB), Red-Al, diisobutylaluminum hydride, lithium aluminum hydride, or lithium triethylborohydride, the carbon–chloride bond failed to reduce. Alane, lithium aluminum hydride with TBHDPB, and the ate complex derived from diisobutylaluminum hydride and n-butyllithium provided only slight reduction. L-Selectride afforded significant reduction at room temperature. To our gratification, when combined with TBHDPB, full reduction of the carbon–chloride bond was observed to give 3. The reduction was confirmed by the infrared spectra, which indicated that the chloride was removed by the absence of chloromethyl related peaks at 1421, 1255, and 658 cm⁻¹ (Fig. 3).

Examination of the ¹³C CP-MAS spectra of 3 revealed a new peak at 21.3 ppm arising from the reduction of the chloromethyl groups (Fig. 4). The remaining contributors to the peak at 42.4 ppm were the methylenes and methines of the PS-DVB backbone and any ¹³C-labeled methylene bridges present.

Elemental analysis indicated that 2 and 3 had chloride contents of 15.0 and 0.6 wt %, respectively. The 0.6% chloride loading in 3 may be due to either residual unreduced primary chloromethyl groups or from secondary benzylic chlorides that would result from the addition of chloromethyl methyl ether across residual unfunctionalized vinyl groups within the resin. The later transformation, first identified by Bootsma et al. and later revised by Sherrington and coworkers, is supported by the carbon–oxygen stretch at 1110 cm⁻¹ in the infrared spectra of 2. Even though there is no indication of residual vinyl groups in 1 (i.e., no signals resulting from the vinyl group in the infrared or ¹³C NMR (137 and 114 ppm) spectra), which are necessary to form the secondary benzylic chloride, it is believed that all PS-DVB resins contain some degree of residual unfunctionalized vinyl groups.

To determine the amount of methylenebis(ethenylbenzene) crosslinking within the resin, SPE-MAS NMR was employed with tetrakis(trimethylsilyl)silane as the internal standard (Supporting Information). Direct polarization of the carbon nucleus avoided the polarization transfer issues commonly observed in CP-MAS experiments. Since the peak at 42.4 ppm in 3 represented both the potential methylene bridges and the methylenes and methines of the PS-DVB backbone, the contribution from the backbone could be removed to reveal the methylene bridging. Since we knew that the resin was composed of 6 wt % DVB, the contribution of the polymer backbone to the signal at 42.4 ppm could be determined based on the integration of the aromatic carbons. In removing this contribution from the signal at 42.4 ppm, the ratio of the reduced methyls to methylene bridges was determined to be 15:1. Utilizing this ratio, the amount of crosslinking within the chloromethylated resin from the initial functionalization could be determined. For example, after accounting for the backbone contribution to the signal at 46.6 ppm in 2 and normalization of the ¹³C-labeled integrals, the contributions from the chloromethylstyrene and methylenebis(ethenylbenzene) were established based on the 15:1 ratio from 3 (Table 1). The amount of each component was determined based on the integration and the internal standard. To determine the unfunctionalized styrene content of the resin the total millimoles of styrene, determined from the aromatic integration, were adjusted by removing the contribution from chloromethylstyrene and methylenebis(ethenylbenzene) to account for the newly substituted aromatic rings. From this analysis of 2, it was determined that 52.5 mol % of the styrene was functionalized, which included 6.2 mol % toward the methylene bridging. This translated to 5.1 wt % of the methylenebis(ethenylbenzene)
crosslinker and brought the total crosslinking within the chloromethylated resin to about 10 wt %. However, the degree of crosslinking may be slightly lower due to the chloride content observed through elemental analysis, presumably due to residual primary or secondary benzylic chlorides, which would inflate the methylene bridge values. This analysis is significant as it demonstrates the total degree of crosslinking after chloromethylation and reveals that the initial crosslinking in the PS-DVB resin is not an accurate representation of the crosslinking found in the functionalized product.

CONCLUSIONS

By developing a new room temperature reduction of the chloromethyl functionality in chloromethylated PS-DVB resins, coupled with the use of solid-state $^{13}$C NMR, the ratio of reduced methyls to methylene bridges in 3 could be established. This ratio could then be used to determine the amount of methylene bridging in the chloromethylated resin resulting from the initial functionalization process. Through the use of this technique, the amount of methylene bridging was determined to be upward of 10 wt % in PS-DVB resins that had been chloromethylated at 35 °C, which was an increase from the 6 wt % in the initial unfunctionalized resin. The use of this methodology should enable the crosslinked polymer community to gain a better handle on the total degree of crosslinking within chloromethylated PS-DVB resins. With this method, chloromethylation conditions could be analyzed and tuned to provide a desired degree of crosslinking within the functionalized resin.

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REFERENCES AND NOTES


