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Communications to the Editor

MALDI−TOF Mass Spectral Characterization of Covalently Cationized Polystyrene

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1. Introduction. Recently, we and others developed methods whereby an organic species is covalently attached to the polymer forming an organic salt (e.g., Figure 1) to produce matrix-assisted laser desorption ionization time-of-flight (MALDI−TOF) mass spectra for polyethylene[1,2] and polyisobutylene.[3] However, an upper mass limit was observed for polyethylene (m/z 15 000). In addition, the mass moments for polyethylene and some low molecular mass (MM) polyisobutylene samples as determined by MALDI mass spectrometry (MS) were lower compared to those determined via classical methods, such as gel permeation chromatography (GPC), osmometry, and nuclear magnetic resonance spectroscopy (NMR). To determine if these MM discrepancies are due to the chemical derivatization method, covalent cationization was performed on polystyrene (PS), a well-characterized polymer by MALDI−TOF MS and traditional analytical methods.[4] This communication reports the highest polymer MM ($M_n \approx 40\,000$ g/mol or u) detected to date by MALDI analysis using chain-end functionalization for ionization.

2. Experiment. Synthesis of polystyrene via ATRP. Controlled MM PS with narrow polydispersity was prepared via atom transfer radical polymerization (ATRP), a controlled radical polymerization process by which an equilibrium between growing and dormant chains is established using a metal/ligand complex.[5,6] All reagents were purchased from Aldrich.[10] Copper(I) bromide was purified by stirring in acetic acid overnight, filtering to collect the solids, and washing with ethanol. Styrene monomer was passed through neutral alumina to remove inhibitor. All other reagents were used as received. Copper(I) bromide (Cu(I)Br, 15.7 mg, 1.10×10^{-4} mol) and styrene (15 mL, 0.13 mol) were added to a 25 mL round-bottom flask and stirred for 45 min at room temperature with argon purged through the solution. N,N,N',N'',N-pentamethyldiethylenetriamine (PMDETA, 0.023 mL, 1.1×10^{-4} mol) was added, and the mixture was stirred for an additional 15 min until the solution became homogeneous and had a yellow-green color, indicating formation of the catalyst. After removing the argon line and the vent line to atmosphere, 1-bromoethylbenzene (0.030 mL, 2.2×10^{-4} mol) was added to the flask, the flask was heated to 100 °C, and the polymerization was continued at 100 °C for 24 h (Figure 1). The product was dissolved in toluene, stirred over DOWEX ion-exchange resin overnight, filtered through neutral alumina, precipitated twice in methanol and once in hexanes, and dried in a vacuum oven for 48 h at 45 °C. Polymer conversion and Br-termination were confirmed by GPC and ^{1}H NMR analyses.

End Group Modification of Bromine with Tributylphosphine. Bromine-terminated PS (Br−PS, 36 500 g/mol, 500 mg, 1.37×10^{-5} mol) and a large excess (>10) of tri-n-butylphosphine (TBP, 26.8 mg, 0.133 mol) were dissolved in dimethylformamide (DMF, 5 mL) at 78 ± 1 °C. The reaction was allowed to proceed for 2 d, after which the polymer in hot solution was precipitated three times in cold methanol (≈200 mL), filtered, and dried in a vacuum oven overnight. PS derivatization was confirmed by ^{1}H NMR.

Gel Permeation Chromatography and Mass Spectrometry. PS MM moments were measured using a GPC system equipped with a Waters 717+ autosampler, Waters columns (guard, HR4 and HR4E, both with 5 μm bead size, with molecular mass separation ranges of 5000−600 000 and 50−100 000 g/mol, respectively) and a Waters 2414 refractive index detector against linear polystyrene standards in tetrahydrofuran (THF, 2.5 mg/mL, 1 mL/min) at 30 °C. The injection volume was 20 μL with volume fraction of 0.1% anisole as an

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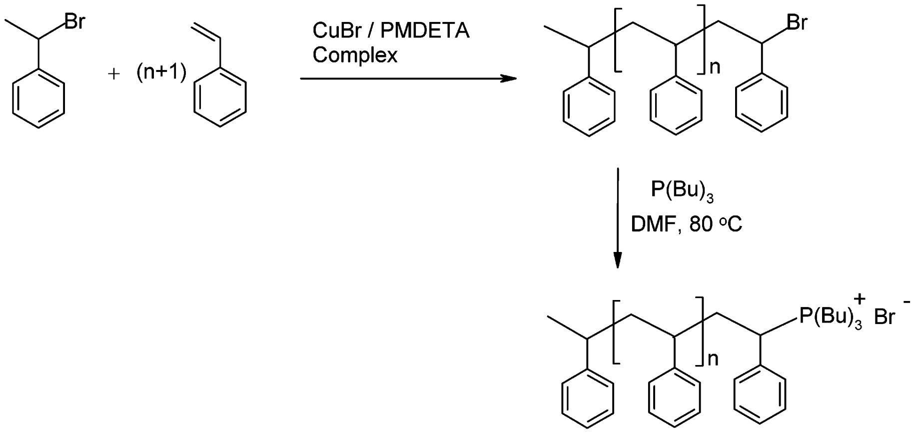

Figure 1. Synthesis of bromine-terminated polystyrene via ATRP, followed by substitution of bromine with tri-*n*-butylphosphine

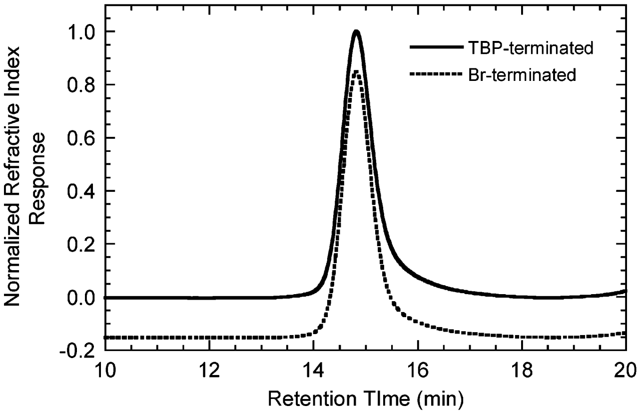

Figure 2. GPC chromatogram of 36 500 g/mol Br−PS and TBP−PS. Data were shifted vertically for clarity.

internal reference peak. The estimated expanded uncertainty of 5% on reported moments is based on choice of baseline and reference peak shift monitored over multiple injections.

The MALDI matrix, all-trans retinoic acid, and the polystyrene samples were mixed dry, 50 mg of matrix to 1 mg of polymer, respectively, and dissolved in 1 mL of THF. For the measurements using the traditional metal cationization method, silver trifluoroacetate (AgTFA) was used as the cationizing reagent in a 1:1 by volume ratio of AgTFA solution (0.5 mg/mL solution in THF) and PS/retinoic solution. All MALDI samples were deposited on the target by electrospray. The MALDI−TOF MS was performed on a Bruker (Billerica, MA) REFLEX II at a typical operating pressure of $\sim 10^{-5}$ Pa.[4] Samples were irradiated using a 337 nm N_2 laser. Mass spectra were acquired in the reflectron mode at 25 kV using delayed extraction and low-mass (i.e., matrix-ion) blanking. Each spectrum shown is the sum of 512 discrete laser shots and is shown without smoothing or background subtraction. The estimated expanded uncertainty reported for MM moments arises from choice of baseline and laser power (5%). The estimated standard uncertainty in overall signal intensity from repeatability studies is 15%.

3. Results and Discussion. Br−PS and TBP-terminated polystyrene (TBP−PS) were synthesized based on the scheme shown in Figure 1. Figure 2 shows GPC traces of the Br−PS (M_n = 36 500 g/mol, PDI = 1.14) and the polymer derivatized with TBP. GPC traces illustrate that derivatization of the Br-terminated polymer did not change the distribution shape. Since the initiator defines both end groups of the polymers, we chose 1-bromoethylbenzene, which leads to PS with a hydrogen on one end and a bromine on the other. The hydrogen end group is inert, but the bromine end group can be modified to a number of functionalities. Substituting the bromine with a trialkylphosphine produces a single positive charge on each polymer chain and allows direct MALDI MS measurement without the addition of a metal salt.[7]

As will be discussed, we observed the highest reported MM to date using covalent cationization for MALDI MS characterization. Furthermore, the molecular masses are comparable for those characterized by MALDI via traditional metal cationization (M_n = 42 310 ± 2040 g/mol) and covalent cationization (M_n = 42 010 ± 1660 g/mol) and show reasonable agreement to values obtained by GPC (M_n = 36 500 ± 1500 g/mol). The higher MM observed for MALDI MS is partially due to the choice in baseline and noise contribution from the high mass region of the MS data.[8] The results suggest that there is no inherent biasing in the covalent cationization method and that factors other than ion generation may cause disparities with mass average determined by other MM measurement techniques.

Parts a and b of Figure 3 show the full and expanded MALDI mass spectra for Br−PS and TBP−PS acquired with and without the addition of AgTFA. Data were shifted vertically for clarity. We first measured the Br−PS with no added metal salt. Since PS can be cationized by sodium and/or potassium ions that are ubiquitous, this spectrum was used as a baseline for comparison with other spectra. Each topmost spectrum of Figure 3, parts a and b, showed neither a distinct molecular distribution nor repeat units confirming that impurities did not cationize the polymer in appreciable quantities under our experimental conditions. With the addition of AgTFA, a clear signal was observed for Br−PS (Figure 3a, second spectrum). The expanded spectrum revealed a main series with a mass repeat unit of 104 ± 1 u, corresponding to one styrene repeat unit. Because of the width of the isotopic distribution and instrument factors, the end group masses cannot be determined at such high masses. Comparisons between Br−PS, with and without AgTFA, suggest the observed signal is due to polystyrene cationized by silver ion.

TBP−PS is a polymer-bound phosphonium ion; therefore, AgTFA addition was not necessary. This is demonstrated in the third spectrum in Figure 3a, which shows a well-defined series of peaks with a similar MM distribution and peak distribution as observed for the

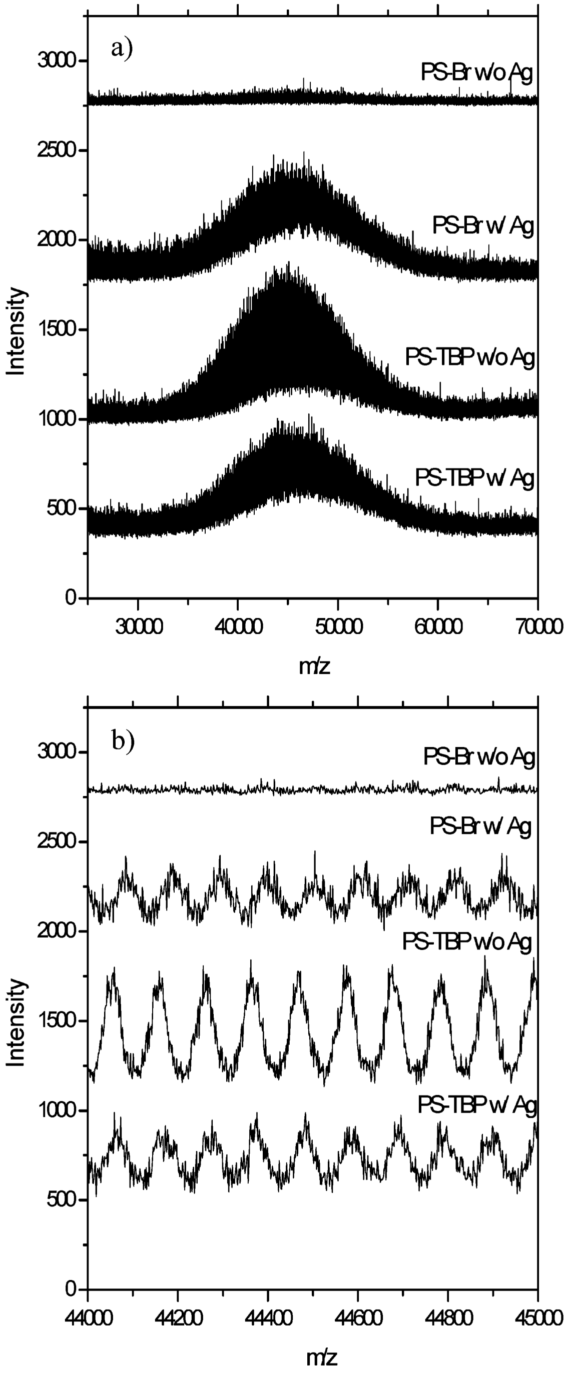

Figure 3. MALDI−TOF MS: (a) full spectra; (b) expanded spectra. Data were shifted vertically for clarity.

Br-terminated polystyrene. Upon closer inspection of the mass spectrum, the distribution contains the expected main series of peaks with mass repeat unit of 104 ± 1 u. The lower mass tail ($< m/z$ 35 000) of the TBP-terminated sample is reduced compared to the Br-terminated sample. This is likely due to the fact that laser irradiation of a Br-terminated sample may cause elimination of HBr or Br radical[9] that subsequently leads to PS fragmentation. We have observed such a phenomenon for lower mass PS samples where the instrument resolution is sufficient to identify peaks corresponding to Br/HBr loss.

Each bottom spectrum in Figure 3, parts a and b, shows the mass spectrum of TBP-terminated sample with AgTFA added. Although the full spectrum shows a distribution similar to that observed for the Br−PS with AgTFA, the expanded spectrum reveals a series of peaks with peak positions comparable to those observed for the TBP-terminated polymer with no AgTFA. This suggests that the desorption processes of this polymer in which both the metal cationization and covalent cationization are available favor the covalent cationized species.

4. Conclusions. Using MALDI MS analysis, we observed the highest MM polymer ($M_n \approx 40\,000$ g/mol) of a polymer ionized by covalent cationization. Our results suggest that the upper mass limit of 15 000 g/mol observed for covalently cationized polyethylene may be due to other polymer properties and not the covalent cationization method. The MM moments observed for PS by MALDI using both metal cationization and covalent cationization were consistent with moments determined by traditional methods. Factors observed in the MALDI MS analysis of Br−PS and TBP−PS samples will be addressed in future work.

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(10) Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by the National Institute of Standards and Technology nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

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