

MALDI-TOF MS Analysis of Chain-End Functionalized Polymers

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Recently, we and other research laboratories have developed methods whereby an organic species is covalently attached to a polymer forming an organic salt that can be analyzed by matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS).^{1,2} Here, we discuss the use of this method, which will be referred to as covalent cationization, to characterize a series of fractionated NIST polyethylene standard reference materials. Furthermore, the covalent cationization method will be compared to traditional metal cationization for a series of polystyrenes with narrow polydispersities (PD) to gain understanding of the mechanisms that govern desorption and ionization processes.

One challenge in MS analysis of saturated polyolefins is creating an intact charged macromolecule due to the lack of easily ionizable sites. Covalent cationization overcomes this challenge by attaching a charged endgroup, such as triphenyl phosphine (TPP) or other tertiary amines and phosphines, to the vinyl terminus of polyethylene (Figure 1). The MALDI-TOF mass spectrum of a polyethylene is shown in Figure 2. Each peak of the main series corresponds to an ethylene oligomer with a proton at one terminus and a TPP at the other. Although several polyethylenes were analyzed using this method, complications arise, especially at higher molecular masses (MM). The MM moments (*i.e.*, M_n and M_w) determined from MALDI-TOF MS are *ca.* 30 % lower than the values given by ¹H-NMR and light scattering. In addition, no singly-charged polyethylene species can be observed above 15 ku although ¹H-NMR confirms sufficient phosphine conversion for samples up to 32 ku. Interestingly, similar deviations in MM moment were observed by Ji *et al.* for chain end-sulfonated polyisobutylene samples.²

In order to determine that these MM discrepancies are not due to the chemical derivatization method, covalent cationization was performed on polystyrene, which can be well characterized by MALDI-TOF MS and traditional analytical methods. A series of narrow polydisperse polystyrenes (PD < 1.2) with hydrogen on one end and bromine on the other end were synthesized by atom transfer radical polymerization (Figure 3). The bromine endgroup was subsequently converted to a tributyl phosphine (TBP, Figure 3). Polystyrene synthesis was confirmed by gel permeation chromatography (GPC) and ¹H-NMR and endgroup conversion was confirmed by ¹H-NMR.

Figure 4 shows the MALDI-TOF mass spectrum of a TBP-terminated polystyrene with $M_n \approx 8000$ g/mol. Only the TBP-terminated styrene series is observed for this distribution. The MM moment determined by MALDI-TOF MS is consistent with the value given by GPC. A higher mass TBP-terminated polystyrene sample was also synthesized and analyzed by MALDI-TOF MS (Figure 5).^{1c} These results suggest that the upper mass limit observed for the covalently cationized polyethylene may be due to the physical properties of polymer and not the synthetic method.

Recently, we extended the covalent cationization effort to compare TBP-terminated polystyrenes to samples cationized by traditional metal cationization. The TBP-terminated polystyrene was compared to Br- and butyl-terminated polystyrenes. Higher signal intensity and signal reproducibility were observed for the covalently cationized samples. In addition, milder laser power was needed for the covalent cationized samples.

1. a) Lin-Gibson, S.; Bencherif, S.A.; Beers, K.L.; Byrd, H.C.M. *Macromolecules*, in press. b) Lin-Gibson, S.; Brunner, L.; Vanderhart, D.L.; Bauer, B.J.; Fanconi, B.M.; Guttman, C.M.; Wallace, W.E. *Macromolecules* 2002, 35, 7149. c) Bauer, B.J.; Wallace, W. E.; Fanconi, B.M.; Guttman, C.M. *Polymer* 2001, 42, 9949
2. Ji, H. N.; Sato, N.; Nakamura, Y.; Wan, Y. N.; Howell, A.; Thomas, Q. A.; Storey, R. F.; Nonidez, W. K.; Mays, J. W. *Macromolecules* 2002, 35(4), 1196-1199.

Figure 1

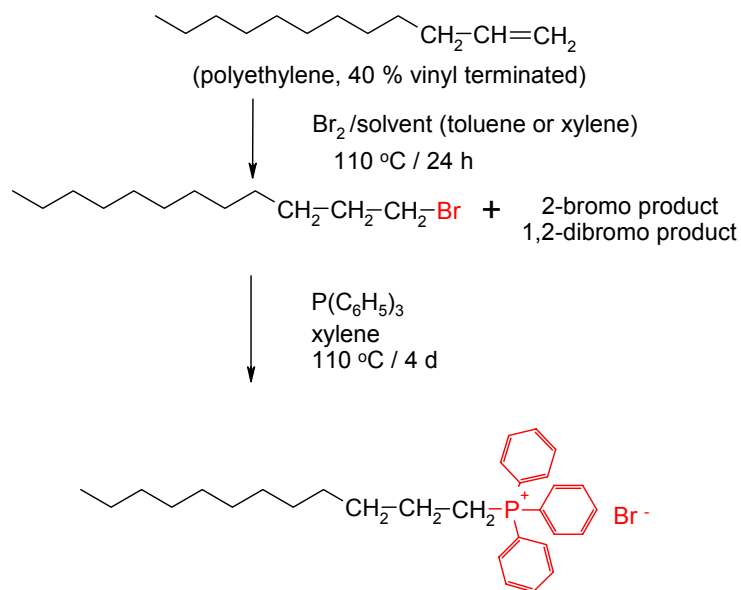


Figure 2

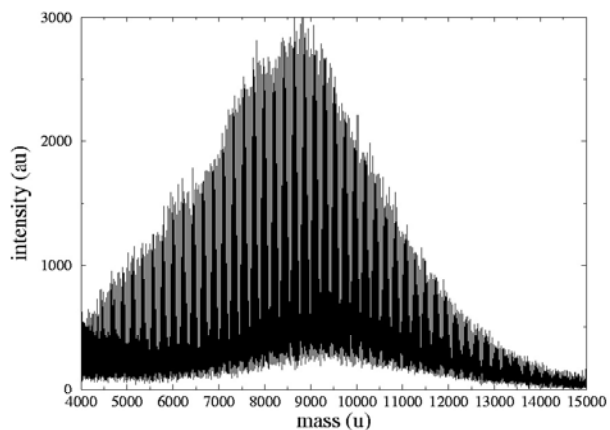


Figure 3

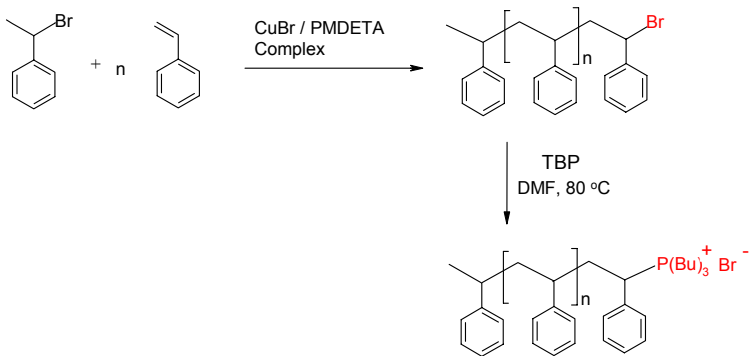


Figure 4

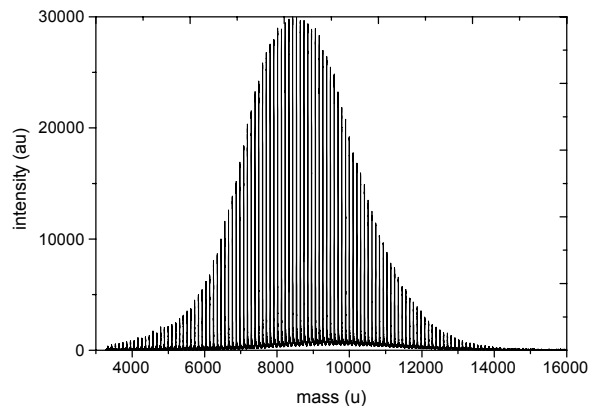


Figure 5

