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Note

Characterization of organolead polymers in trace amounts by element-specific size-exclusion chromatography

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The synthesis of interesting and significant new organometallic polymers incorporating vinylic monomers has been reported[1,2]. Conventional techniques of polymer characterization, including mass sensitive size-exclusion chromatography (SEC) can be used to estimate molecular parameters such as number- and weight-average molecular weights (M_n and M_w), molecular distribution (MWD$=M_w/M_n$), and conversion of monomer to polymer, provided the material is soluble. Such methods, however, are not designed to directly show the distribution of the metal-containing moiety in fractions of these new copolymers, a property of vital importance to their physicochemical and biological properties and utility in many applications. Parks and co-workers[3,4] have described an element-specific method for the SEC of a precise controlled-release copolymer of biocidal tributyltin methacrylate and methyl methacrylate. Using a dual ultraviolet absorption–differential refractive index (UV–ΔRI) detector coupled on-line with tin-specific graphite furnace atomic absorption spectrometry (GFAA), they obtained self-consistent tin-sensitive and mass-sensitive chromatograms. They found it essential to precondition SEC columns in order to prevent dissociation of the labile tin-bearing moeity, which affords tailored bioproperties, from the polymer chain during the chromatography[4]. Since tin-bearing cations were used in the pretreatment, this constraint necessitated injecting relatively large (5 mg) samples in order to keep the analyte absorption relatively large compared to the intensity of the background signal.

Weiss *et al.*[5] demonstrated multielement speciation of natural shale oils by means of coupled SEC–UV–GFAA. Using a 1:1 flow splitter and two GFAA instruments, they showed that at least one oil contained two iron-bearing species of different mol. weight, one of which incorporated arsenic and was chromophoric.

This paper describes new element-specific SEC studies of a lead-containing copolymer which is not subject to dissociation by the chromatographic packing surface. The result is a highly informative chromatogram requiring the injection of less than 1.0 μg of polymer, a quantity quite sufficient for UV and GFAA chromatograms but insufficient to be detected by differential refractive index, presaging potential applications for trace molecular speciation of many synthetic or natural metal(loid)-containing compounds.

EXPERIMENTAL

The analyte was prepared by copolymerization of (4-vinylphenyl)triphenyllead and octadecylmethacrylate in 5:1 molar proportions. The copolymer (12.7 mg) was dissolved in 1.0 ml of tetrahydrofuran (THF) and further diluted with THF (10 μl dissolved in 10 ml) to give a final concentration of $1.27 \cdot 10^{-5}$ g ml^{-1}. A 50-μg portion of this solution (0.635 μg) was injected into the SEC mobile phase (THF, 1.0 ml min^{-1}). Polymer fractions, separated by SEC (μStyragel* columns, pore size 10^3 A, 250 × 4.6 mm I.D.; three columns in tandem), were detected by lead specific GFAA (hollow cathode lamp operating at 217 nm) and a UV detector (254 nm, 0.0125 a.u.f.s.). Aliquots of the eluent were transferred automatically at 0.82 min intervals to the GFAA furnace to obtain the chromatogram shown in Fig. 1.

The SEC–UV–GFAA system has been described in detail[6]. The SEC μStyragel column was calibrated with polystyrene standard samples[6] to correlate the elution volume of analyte fractions with the estimated molecular weight.

RESULTS AND DISCUSSION

Fig. 1 displays the SEC–UV–GFAA chromatogram of the polymer, and MW assignments based on polystyrene standard samples. The calculation of M_n, M_w, and MWD is based on the elution volumes corresponding to the individual GFAA spikes and the measured height[6]. Based on the number average- and the weight average-molecular weights (4000 and 9000 daltons, respectively) the MWD is 2.25. The conversion of lead-containing monomer to polymer is 93.9%.

A striking feature of the coupled UV–GFAA chromatograms is the absence of UV absorptivity in the high polymer fraction, whereas the low-MW fraction (190 daltons), apparently unreacted monomer, absorbs very strongly. Given such loss of optical properties on polymerization, there remains only the lead specific GFAA signals for quantitation of polymer parameters. Mass-sensitive differential refractive index chromatography would provide supplementary information. The latter, however, would require a quantity of this analyte higher by three orders of magnitude than that actually used.

Very importantly, sample recovery (as lead) after injection was complete, indicating no retention or dissociation on the packing. For two consecutive injections, sample recoveries of 109.8 and 95.6% were calculated based on integration of all observed peaks in the GFAA chromatogram, and compared to the measured absorptivity of stock solution (taking the average of seven consecutive spikes, having a relative standard deviation of 3.2%).

The SEC–UV–GFAA method thus is capable of characterizing trace quantities of an organometallic polymer, such as may be obtained during preliminary stages of synthetic research. The requirements for successful characterization include polymer solubility in a solvent which is compatible with the column packing; absence or pre-

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* Certain commercial materials and equipment are identified in this paper in order to specify the experimental procedures. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

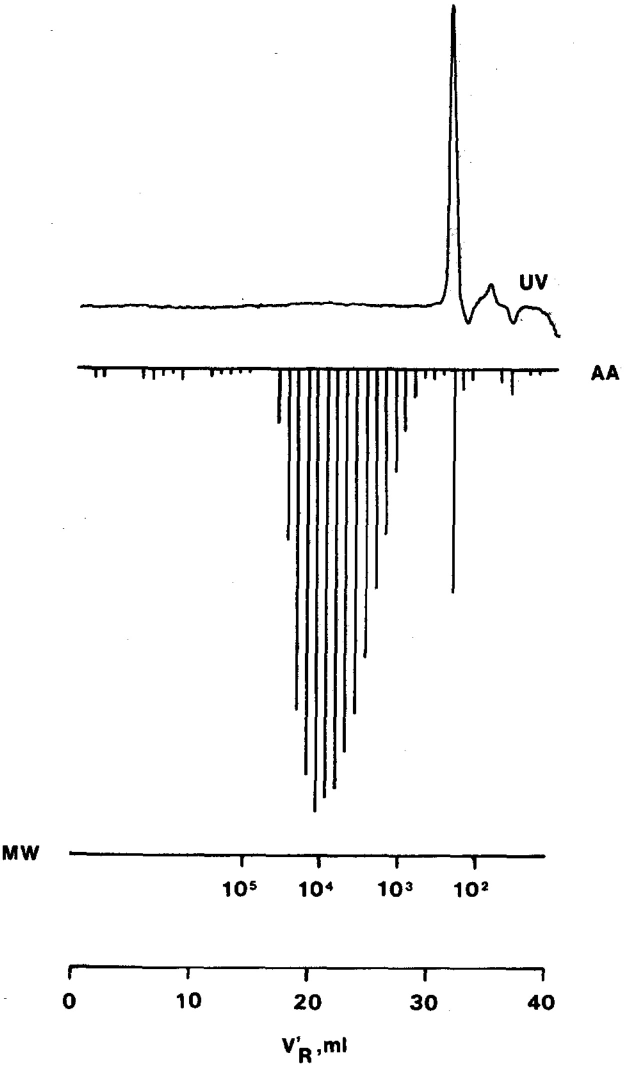

Fig. 1. SEC–UV–GFAA chromatogram of a 5:1 copolymer of 4-(vinylphenyl)triphenyllead and octadecylmethacrylate. Eluent, THF; flow-rate, 1.0 ml min^{-1}. Injected volume, 50 μl. Injected analyte, 0.635 μg.

vention of polymer decomposition on column packing materials, and an element-specific detector for the incorporated metal. Finally, the method demonstrated here for macromolecular lead is readily extended to multimetallic macromolecules as shown by Weiss *et al.*[5].

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REFERENCES

1 J. E. Sheats, *J. Macromol. Sci. Chem.*, A15 (1981) 1173.
2 C. E. Carrahar, Jr., J. E. Sheats and C. U. Pittman (Editors), *Organometallic Polymers,* Academic Press, New York, 1978.
3 E. J. Parks, F. E. Brinckman and W. R. Blair, *J. Chromatogr.*, 185 (1979) 563.
4 E. J. Parks, W. F. Manders, R. B. Johannesen and F. E. Brinckman, *J. Chromatogr.*, 351 (1986) 475.
5 C. S. Weiss, E. J. Parks and F. E. Brinckman, in W. H. Lederer and R. J. Fensterham (Editors), *Arsenic: Industrial, Biomedical, Environmental Perspectives,* Van Rostrand Rheinhold, New York, 1983, pp. 309–326.
6 E. J. Parks and F. E. Brinckman, in D. H. Lewis (Editor), *Controlled Release of Pesticides and Pharmaceuticals,* Plenum Press, NY, 1981, pp. 219–238.