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POLYMER ADSORPTION CHROMATOGRAPHY WITH EVAPORATIVE LIGHT-SCATTERING DETECTION

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SUMMARY

Poly(alkyl acrylate) and poly(alkyl methacrylate) homopolymers and copolymers are eluted from silica with toluene-2-butanone solvent gradients. The polymers are separated by liquid-solid adsorption chromatography according to their chemical composition and not by molecular weight. Evaporative light-scattering monitors polymers that may be difficult to detect by spectrophotometry and also permits the use of good polymer solvents that are themselves strongly absorbing. This extends the application of column liquid chromatography to a broad range of synthetic polymers that previously were amenable only to thin-layer methods.

INTRODUCTION

The use of adsorption chromatography to obtain unique fractionations of high-molecular-weight synthetic polymer distributions (*e.g.*, compositional, comonomer unit sequence, stereochemical) has been limited by at least three factors: (1) lack of a simple method for quantitative detection of materials without a suitable chromophore, (2) the limited number of good polymer solvents that are also suitable for chromatography, and (3) the necessity of solvent gradients for most practical liquid chromatographic polymer separations. As a result, most examples given are thin-layer separations of vinyl addition polymers (see reviews¹⁻⁴) except for a few column gradient separations of homopolymers⁴⁻⁸ and copolymers⁹⁻¹² containing UV-absorbing groups. Application could be considerably broader if detection were available for column chromatography that permitted the use of solvent gradients with good polymer solvents such as aromatic hydrocarbons, aliphatic ketones, heterocyclics, acetamides and formamides.

Detection schemes in which the solvent is stripped (typically by evaporation) prior to detection of the eluate offer one alternative to spectrophotometric detection for gradient elution that is well suited for intrinsically nonvolatile synthetic polymers. A recent resurgence of interest in one detector that removes the solvent prior to detection, the evaporative light-scattering detector, has resulted in improved understanding of operating principles, new instrument designs and examples of new applications¹³⁻¹⁷. This detector atomizes eluent into a gas stream with a nebulizer, evap-

orates the solvent from the resultant droplets by passing them through a heated tube, and measures the light scattered by an aerosol consisting of the nonvolatile components. These detectors are characteristically rugged, stable and inexpensive. Additionally, the light scattered by the sample aerosol generated after the solvent is removed provides a convenient approximation of sample mass. This paper describes evaporative light-scattering detection of polymers not containing a chromophore suitable for UV detection that have been separated by adsorption chromatography according to their chemical composition.

EXPERIMENTAL

The evaporative light-scattering detector was manufactured by Applied Chromatography Systems (Bedfordshire, U.K.). The characteristics of this instrument have been described^{15,16}, as well as modifications to the original instrument and the use of a postcolumn-predetector switching valve for the eluent to prevent fire or explosion¹⁵. The evaporator tube was kept at 40°C, and the nebulizer nitrogen pressure was 20 p.s.i. Polymer samples were eluted from a 250 × 4.6 mm I.D. Hibar II column packed with LiChrosorb Si 60 (5 μm, Merck). Samples were injected as 10 μl of *ca.* 1 mg/ml polymer dissolved in mobile phase with composition of initial gradient conditions. Toluene and 2-butanone were HPLC distilled-in-glass grade (Burdick & Jackson).

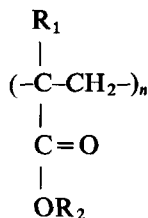
Poly(methyl methacrylate) (PMMA, $M_w = 93\,300$, $M_n = 46\,400$), poly(ethyl methacrylate) (PEMA, $M_w = 340\,000$, $M_n = 126\,000$), poly(butyl methacrylate) (PBMA, $M_w = 320\,000$, $M_n = 73\,500$), poly(methyl acrylate) (PMA, $M_w = 30\,700$, $M_n = 10\,600$), poly(ethyl acrylate) (PEA, $M_w = 125\,000$, $M_n = 38\,600$), poly(butyl acrylate) (PBA, $M_w = 119\,000$, $M_n = 33\,000$) and poly(2-ethylhexyl acrylate) (PEHA, $M_w = 124\,000$, $M_n = 47\,900$) were purchased from Scientific Polymer Products (Webster, NY, U.S.A.). Copolymers of styrene and methyl acrylate (PS-co-MA) were prepared by free-radical bulk polymerization in 25-ml glass vials sealed with PTFE-lined screwtops at different monomer ratios and isolated after polymerization to low conversion (less than 10%) by drawing out into methanol as described in ref. 10. From molar feeds of 80, 60, 40, and 20% styrene with 0.2 mole% AIBN initiator, the following polymer compositions (as determined by combustion analysis for C, H, O) and polystyrene-equivalent molecular weights (as measured by size-exclusion chromatography (SEC) were obtained: 81.5% styrene (S), $M_w = 130\,400$, $M_n = 78\,300$; 71.3% S, $M_w = 151\,700$, $M_n = 93\,600$; 58.4% S, $M_w = 198\,800$, $M_n = 119\,300$; 41.2% S, $M_w = 233\,700$, $M_n = 133\,000$. A similar compositional series of poly(methyl methacrylate-co-methyl acrylate) was prepared and isolated in identical fashion. Characterization was limited to molecular-weight determination by SEC: 80 mole% S in feed, $M_w = 267\,600$, $M_n = 134\,700$; 60 mole% S in feed, $M_w = 305\,400$, $M_n = 149\,300$; 40 mole% S in feed, $M_w = 417\,500$, $M_n = 236\,800$; 20% S in feed, $M_w = 471\,000$, $M_n = 253\,700$.

RESULTS

Previous workers have demonstrated that normal-phase gradient elution from small-pore-diameter adsorbents can effectively yield separations based on the chem-

ical composition of a polymer, independent of its molecular weight, provided that the solution dimensions of the polymer coil are larger than the pore entrance diameter (*e.g.*, see ref. 8 and references therein). This is particularly advantageous for the separation of copolymers according to compositional distribution⁹⁻¹². The polymer should be soluble in all mobile phase compositions spanned by the solvent gradient.

The homopolymers used in this investigation have the general structure



where R_1 is H in poly(alkyl acrylates) and CH_3 in poly(alkyl methacrylates) and R_2 is methyl, ethyl, butyl or 2-ethylhexyl. Figs. 1 and 2 contain examples of separations of methacrylate and acrylate homopolymers. The toluene-2-butanone solvent gradient could not be used with UV absorption, refractive index (RI) or dielectric constant detectors; the solvent response of these detectors either is inherently too large to subtract electronically from the analyte signal or is changing over too broad a

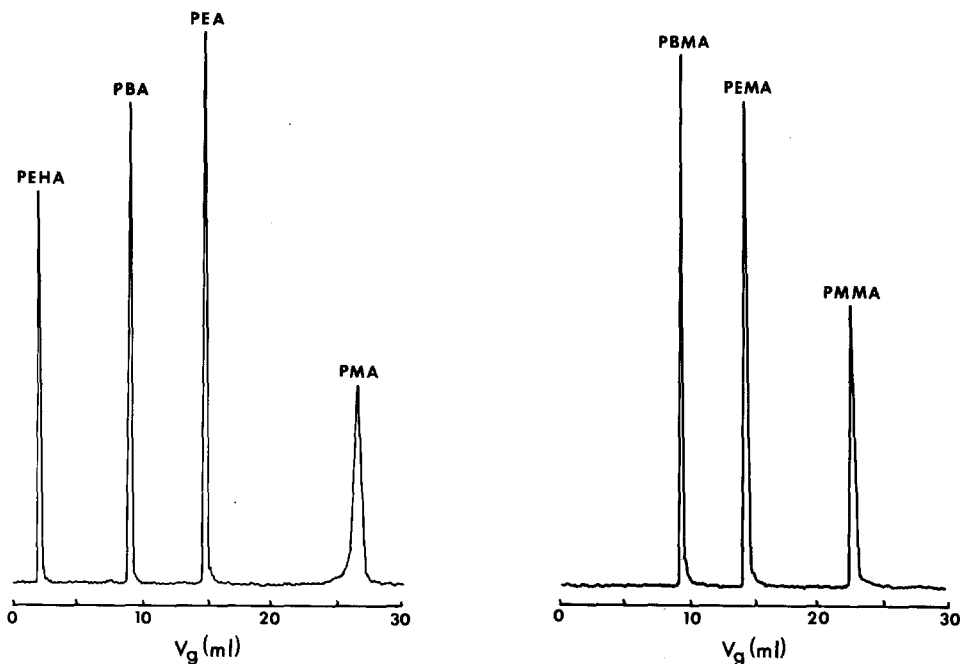


Fig. 1. Poly(alkyl acrylates). Volumetrically linear solvent gradient from 98:2 (v/v) toluene-2-butanone to 100% 2-butanone in 30 min at a flow-rate of 1.00 ml/min.

Fig. 2. Poly(alkyl methacrylates). Conditions as in Fig. 1.

range during solvent programming to maintain a flat baseline. Toluene is an excellent low-solvent-strength eluent for these polymers, and 2-butanone is both a good polymer solvent and a sufficiently strong displacer for locally adsorbed polymer ester groups. Retention increases with decreasing pendant chain length, as predicted from solvent-displacement theory¹⁸. Narrow peak widths are obtained despite large differences in molecular weights and molecular-weight distributions among samples. Tailing is normally observed at flow-rates higher than 1 ml/min. This is a characteristic of the poor mass transfer of macromolecules and is not an artifact of the detector, which in practice has extremely low dead volume¹³. Fronting of the PMA peak (Fig. 1) is a consequence of a fraction of material with molecular weight low enough to cause significant molecular-weight dependence on elution⁸.

Two examples will demonstrate the versatility of the toluene-2-butanone gradient in the separation of copolymers according to chemical composition, relatively independent of molecular weight, when used with evaporative light-scattering detection. The tetrachloromethane-methyl acetate gradient separations of poly(styrene-co-methyl acrylates) reported by Teramachi *et al.*¹⁰ were repeated with the toluene-2-butanone gradient. Similar results were obtained; retention increased with increasing methyl acrylate comonomer content (Fig. 3). The increase in peak broadening with increasing methyl acrylate content is a natural consequence of differences in copolymerization reactivity ratios, resulting in monomer drift and accompanying broadening of the copolymer compositional distribution with increasing conversion into polymer. Teramachi demonstrated that the theoretical chemical compositional distributions of random copolymers calculated from kinetic theory of copolymerization fit the compositional distributions determined by high-performance liquid chromatography (HPLC) of low-conversion samples. Similar calculations of the theoretical compositional distributions (given in ref. 10 and references therein) of these PS-co-MA polymers yielded slightly better fits to the copolymer elution profiles than the original example given in ref. 10, most likely because of reductions in extra-column effects and the use of smaller stationary-phase particles in this study. The original example of PS-co-MA fractionation by HPLC also used UV detection, which monitors only styrene comonomer. The error introduced in the generation of compositional distributions from detection that monitors absorption of only one monomer unit is not known.

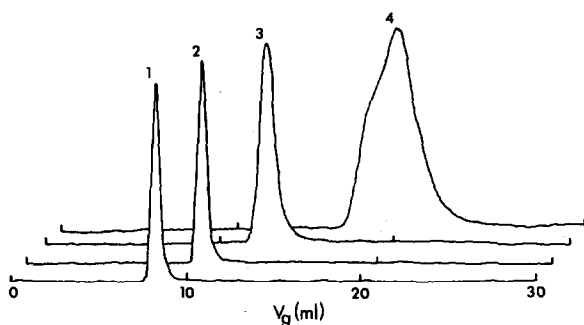


Fig. 3. Poly(styrene-co-methyl acrylates). Volumetrically linear solvent gradient from 98:2 (v/v) toluene-2-butanone to 50:50 (v/v) in 20 min at a flow-rate of 1.00 ml/min. As mole% S in copolymer: 1 = 81.5; 2 = 71.3; 3 = 58.4; 4 = 41.2.

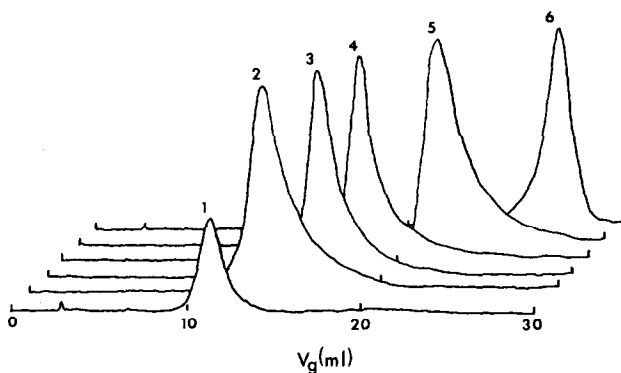


Fig. 4. Poly(methyl methacrylate-co-methyl acrylates). Volumetrically linear solvent gradient from 50:50 (v/v) toluene-2-butanone to 25:75 (v/v) in 25 min at a flow-rate of 1.00 ml/min. As mole% methyl methacrylate in polymerization feed: 1 = 100 (PMMA); 2 = 80; 3 = 60; 4 = 40; 5 = 20; 6 = 0 (PMA).

Similar compositional separations using toluene-2-butanone gradient elution of poly(methyl methacrylate-co-methyl acrylates) (Fig. 4) were made possible with the evaporation light-scattering detector. A somewhat shallower gradient than used for PS-co-MA samples is needed to separate copolymers consisting of comonomers that differ only by the presence or absence of a backbone methyl substituent. Increasing retention with increasing methyl acrylate content is again consistent with solvent-displacement theory for adsorption chromatography, primarily because methyl groups are weakly adsorbed to silica but must displace a large area of adsorbed solvent¹⁸. The fact that these polymers show any difference in retention at all is evidence that functional groups near or on the polymer backbone do participate in the adsorption process, despite evidence previously presented for polystyrene oligomers that shows that tilted adsorption conformations favor pendant-group contact¹⁹.

DISCUSSION

A previous paper has shown that response of the evaporative light-scattering detector depends on the density and RI of the aerosol particles¹⁵. These parameters can differ substantially among polymers and may result in as much as twofold difference in detector signal output. For copolymers, the responses of all chemical compositions may not be equivalent, thereby complicating quantitative measurements of compositional distributions, although simple corrections are possible if the RI and the density of the copolymers can be measured or calculated (see discussion in ref. 15). In addition, the detector response is sigmoidal with concentration, the actual dependence being highly dependent on the particle size distribution generated by the nebulizer. This particle size distribution is dependent on solvent properties such as surface tension and density that are changing during solvent programming. Despite these complications, evaporative light-scattering detection is equally effective as (although less sensitive than) spectrophotometric detection in determining compositional distributions of copolymers in which none or only one of the monomers absorbs radiation in an accessible region (e.g., PS-co-MA). It is clearly applicable to

a larger variety of polymers with a greater number of chromatographic solvents. The errors introduced in obtaining the quantitative response described above can be significant but are normally tolerable for most polymer separation problems, particularly compared with the results (or lack of) obtained from the existing detection alternatives. The methodology presented is particularly useful for characterization of polymer blends, grafting procedures and syntheses of block copolymers in which mixtures of homopolymer and copolymer can be formed.

The examples given here are adsorption separations of synthetic polymers. An example of the detection of poly(*n*-butyl acrylate) eluted from a resin-based reversed-phase column with an aqueous ammonium acetate–tetrahydrofuran solvent gradient^{1,5} demonstrates that evaporative light-scattering detection can be applied equally well to liquid chromatographic separations of synthetic polymers regardless of whether the separations are claimed to be by reversed-phase mechanism^{20–22} or precipitation and redissolution^{23,24}, which up to now have been limited primarily to polymers containing styrene monomer units.

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