Table IV. Results of the Seven-Component Stability Study in Passivated Stainless Steel Canister with 170 ppmv of Water

compound	stability ratio (exptl/control) day 0	day 1	day 4	day 7	day 14
1,2-dichloro-1,1,2,2-tetrafluoroethane (ECD)	0.98	1.05	1.09	1.01	1.05
acetone	0.99	0.98	0.98	0.88	0.76
1,1-dichloroethylene	1.00	1.06	1.03	1.02	1.07
1,1,2-trichloro-1,2,2-trifluoroethane (ECD)	1.02	0.88	0.94	1.00	0.86
1,4-dioxane	0.53	0.36	0.31	0.29	0.23
toluene	0.96	1.00	0.98	0.98	0.84
chlorobenzene	0.99	1.00	0.99	1.00	1.05

stability for toluene and chlorobenzene in the 18-component stability studies. This suggests that the stability of these two compounds may be a function of the water vapor concentration.

Table IV shows the compound stabilities of the seven-component standard in the passivated stainless steel canister. Initial stability ratios for six of the seven compounds were between 0.96 and 1.02. 1,4-Dioxane has an initial stability ratio of 0.53, and a steady decrease to 0.23 was found over 14 days of storage. A small but steady decrease in the stability ratio with time was found for acetone. A linear correlation between stability ratio and time was found for acetone at 1.7% loss per day with a correlation coefficient of 0.99 and for 1,4-dioxane at a 1.6% loss per day with a correlation coefficient of 0.79. The similar slopes found for both of these compounds suggest a common mechanism for the loss. Both 1,4-dioxane and acetone are proton acceptors and electron pair donors and would form hydrogen bonds with available protons or Lewis acid–base adducts with metals. Aluminum, being an unusually strong Lewis acid, is an especially good electron acceptor and would have a strong affinity for acetone and 1,4-dioxane, which is confirmed by the poor recovery of these compounds in the aluminum canister.

CONCLUSIONS

The applicability of using aluminum canisters to collect ambient-level air samples depends on the reactivity of the compounds of interest and the concentration of water in the sample. Compounds with only slightly polar properties and lower volatiles (bp > 60 °C) are unstable in both dry unpassivated and passivated aluminum canisters. To prevent a large initial loss of these compounds, it is estimated that the concentration of water in the canister sample must be greater than approximately 500 ppmv (1.6% relative humidity at 25 °C). Summa passivation of the aluminum surface slightly lowers the amount of compound lost initially in dry samples and requires slightly less water to completely passivate the surface. For polar oxygenated compounds such as acetone and 1,4-dioxane, aluminum canisters are more reactive than the passivated stainless steel and should therefore not be used to sample for polar organic compounds.

From the results of this study, the selected organic compounds showed no increase in stability when collected and stored in aluminum as compared to those collected and stored in stainless steel canisters. The hydrocarbons and halogenated hydrocarbons tested were found to be stable for more than a week if levels of water were greater than 500 ppmv.

Further work is needed to find an effective passivation process that would both eliminate the need for water in the sample and provide a stable surface for collecting the polar organic compounds.

Registry No. CFC114, 76-14-2; CFC113, 76-13-1; aluminum, 7429-90-5; stainless steel, 12597-68-1; vinyl chloride, 75-01-4; 1,3-butadiene, 106-99-0; bromoethane, 74-83-9; trichlorofluoromethane, 75-69-4; methylene chloride, 75-09-2; chloroform, 67-66-3; 1,2-dichloroethane, 107-06-2; 1,1,1-trichloroethane, 71-55-6; benzene, 71-43-2; carbon tetrachloride, 56-23-5; 1,2-dichloropropane, 78-87-5; trichloroethylene, 79-01-6; toluene, 108-88-3; 1,2-dibromoethane, 106-93-4; tetrachloroethylene, 127-18-4; chlorobenzene, 108-90-7; ethylbenzene, 100-41-4; *o*-xylene, 95-47-6; acetone, 67-64-1; 1,1-dichloroethylene, 75-35-4; 1,4-dioxane, 123-91-1.

LITERATURE CITED

(1) Harsch, D. E. *Atmos. Environ.* **1980**, *14*, 1105.
(2) Westberg, H. H.; Holdren, M. W.; Hill, H. H. Analytical Methodology for the Identification and Quantification of Vapor Phase Organic Pollutants. Final report the Coordinated Research Council on CRC-APRAC Project No. CAPA-11-71, Report No. 82-13-5, January, 1982.
(3) Oliver, K. D.; Pleil, J. D.; McClenny, W. A. *Atmos. Environ.* **1986**, *20*, 1403.
(4) Jayanty, R. K. M.; Cooper, S. W.; Decker, C. E.; Von Lehmden, D. J. *J. Air Pollut. Control Assoc.* **1985**, *35*, 1195.
(5) Allen, J. M.; Jayanty, R. K. M.; von Lehmden, D. *Anal. Chem.* **1987**, *59*, 1882–1884.

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Separation of Ethyl Methacrylate–Butyl Methacrylate Copolymers by Liquid Adsorption Chromatography with an Ultraviolet Absorption Detector

Sadao Mori

Department of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie 514, Japan

INTRODUCTION

Although molecular weight averages and a molecular weight distribution (MWD) of a homopolymer can be measured by size exclusion chromatography (SEC), those of a copolymer cannot be obtained accurately without knowing the chemical composition distribution (CCD) of the copolymer (*1*). Therefore, the measurement of a CCD is required before calculating molecular weight averages and a MWD of the copolymer in order to obtain accurate data.

The separation of styrene (S)–methyl methacrylate (MMA) random copolymers by high-performance liquid adsorption chromatography (LAC) has been reported in our previous papers (*1*–*6*), and the technique was applied to the separation of styrene–alkyl methacrylate and styrene–alkyl acrylate copolymers (*7*) and S–MMA block copolymers (*8*), respectively. Fractionation by LAC gave a CCD, and a real MWD has been obtained by SEC followed by LAC of SEC fractions (*5*).

Besides our work, several attempts have been reported for the separation of copolymers according to composition by high-performance liquid chromatography (HPLC): e.g., S–MMA (*9*, *10*); S–methyl acrylate (*11*); S–acrylonitrile (*12*); and S–butadiene (*13*). Similar to our work, these reports utilized

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an ultraviolet (UV) absorption detector to monitor the copolymers in the effluent from a column. Solvents used in the literature as one component of the mobile phases were chloroform and tetrahydrofuran, and they were opaque at wavelengths below 245 nm. Therefore, only the styrene absorption bands of 255 or 260 nm, where a unit such as MMA and acrylonitrile was transparent, were employed to detect the copolymer concentrations in the effluent.

1,2-Dichloroethane (DCE) is transparent at wavelengths over 230 nm and polymethacrylates and polyacrylates exhibit UV absorption at short wavelengths. Therefore, the combination of DCE and a UV detector will make possible the measurement of chromatograms of methacrylate and acrylate homopolymers and copolymers which are almost transparent over 245 nm. In the present report, homopolymers of ethyl methacrylate (EMA) and *n*-butyl methacrylate (BMA) and their copolymers were separated by using a mixture of DCE and ethanol as the mobile phase, and the polymers in the effluent from a column were detected by using a UV detector at a wavelength of 233 nm.

EXPERIMENTAL SECTION

LAC measurements were performed by using the same LAC system reported previously (*3*). Silica gel with a pore size of 30 Å was packed in 4.6-mm-i.d. × 50-mm-length stainless-steel tubing. A detector was a variable-wavelength ultraviolet (UV) absorption detector. Samples used in this experiment were poly(ethyl methacrylate) (PEMA) and poly(*n*-butyl methacrylate) (PBMA) homopolymers and EMA–BMA copolymers. These samples were prepared by solution polymerization in benzene at a low degree of conversion. The composition of EMA–BMA copolymers was indicated as mole percent monomer in feed as follows: EMA–BMA I (25%–75%), II (50%–50%), III (75%–25%).

Solvents used as the mobile phase were DCE and ethanol. Elution was performed by a linear gradient elution mode. The initial mobile phase (A) was a mixture of DCE and ethanol (99.0:1.0 (v/v)), and the final one (B) was (90.0:10.0 (v/v)). The composition of the mobile phase was changed linearly from 100% (A) to 100% (B) in 20 min. Samples were dissolved in the initial mobile phase (A) and the injection volume of the sample solutions was 0.1 mL. The sample solutions were injected 1 min after the start of gradient. The flow rate of the mobile phase was 0.5 mL/min. The column was maintained at 60 °C.

Safety consideration: Dichloroethane is a suspected carcinogen. Researchers should exercise appropriate caution when handling this reagent. Effective ventilation is essential to perform LAC. Dissolution of sample polymers in DCE and the filtration of the sample solutions have been done in a draft.

RESULTS AND DISCUSSION

UV Spectra. PEMA and PBMA were dissolved in DCE and the UV spectra of the polymer solutions were measured with DCE as a reference solvent. PEMA and PBMA have UV absorption at the short wavelength region and the foot of their absorption bands can be observed near 230 nm. The absorbance at the wavelength 229 nm for DCE was 0.90, and the baseline of the chromatogram monitored at this wavelength was a little bit noisy. Therefore, the wavelength of 233 nm was selected as the compromise of absorbances between DCE and the homopolymers. As shorter wavelengths were preferable for the detection of these homopolymers and copolymers in the effluent from the column, a wavelength such as 230 nm can be used for to monitor samples of lower concentration.

Elution. When chloroform in the mobile phase was replaced to DCE, much ethanol was required to elute styrene–methyl methacrylate copolymers from a column (*3*). Therefore, the final mobile phase (B) in this experiment contained 10% ethanol. The increase of the ethanol content in the mobile phase of DCE–ethanol and/or the decrease of the column temperature was effective to elute the homopolymers and the copolymers retained in the column. These phenomena were similar to the system of chloroform–ethanol as the mobile phase.

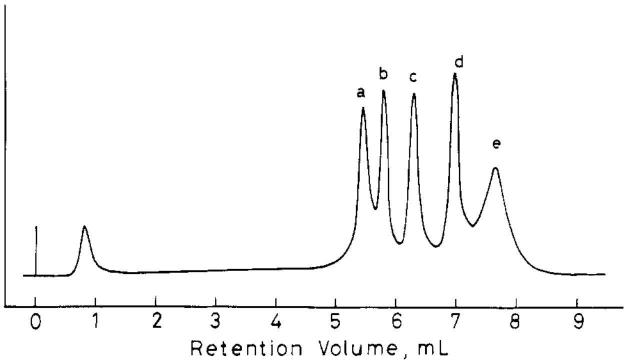

Figure 1. Chromatogram of EMA–BMA copolymers, PEMA, and PBMA: column temperature 60 °C; sample, (a) PBMA, (b) EMA–BMA copolymer I, (c) II, (d) III, (e) PEMA; sample concentration, ca. 0.01% each; detector, 233 nm, 0.16 absorbance unit full scale; gradient, 100% A to 100% B in 20 min.

PBMA eluted first and PEMA last. EMA–BMA copolymers eluted between the two homopolymers and the copolymers having more BMA eluted earlier. Figure 1 is the chromatogram for a mixture of PEMA, PBMA, and their copolymers. The retention volumes of the copolymers and PEMA increased with increasing column temperature except PBMA which was almost unchanged with column temperature. The peak widths of the polymers were also unchanged with column temperature. Therefore, the resolution between two peaks was improved at higher column temperature.

Although the possibility of the separation of alkyl methacrylate copolymers and alkyl acrylate copolymers according to the composition was predicted in the previous paper (*7*), where mixtures of chloroform/ethanol were used as the mobile phase, there was no possibility of monitoring the chromatograms of these copolymers with conventional detectors, such as UV, infrared, or refractive index detectors. When DCE replaced chloroform in the mobile phase, monitoring the concentrations of these copolymers in the effluent from a column became possible with a conventional UV detector and the prediction was demonstrated.

When tetrahydrofuran or chloroform is used as one component of the mobile phase, it is not possible to measure the chromatograms for methacrylate and acrylate homopolymers and their copolymers using a UV detector, because these polymers and copolymers have no UV absorption at 254 nm. There was only one report so far in the literature on the separation of a mixture of alkyl methacrylate and alkyl acrylate homopolymers and copolymers (*14*), where a solvent-evaporative mass detector (an evaporative light-scattering detector) was used to detect the polymers in the effluent.

Mourey (*14*) used mixtures of toluene and 2-butanone as the mobile phase. Both solvents have UV absorption and cannot be used with a UV detector. Toluene and 2-butanone are good solvents for acrylate and methacrylate homopolymers and copolymers. Toluene is a low-solvent-strength eluent for these polymers and 2-butanone is a displacer for adsorbed polymers on the silica gel. In our separation system, DCE and ethanol are not chromophores over 230 nm, and a conventional UV detector can be employed and a special detector or a detection system is not required. DCE is a good solvent for the homopolymers and the copolymers and ethanol is a nonsolvent for these polymers. DCE is a low-solvent-strength eluent for these polymers and ethanol is a strong displacer for adsorbed polymers on silica gel. Although ethanol is not a good solvent for these polymers, the displacement of adsorbed polymers on silica gel with ethanol took place with increasing ethanol content in the mobile phase. In this point, the separation mechanism of our system may be different from Mourey's system and other adsorption chromatography.

Detection schemes in which the mobile phase is stripped prior to detection of the eluate have the advantage of the use of good polymer solvents that are themselves UV absorbing. However, Mourey's system is not capable of obtaining the chromatographic fractions for the use of other purposes and of introducing the effluents directly into a SEC system. Our system overcomes these disadvantages of his system.

LITERATURE CITED

(1) Mori, S. *J. Chromatogr.* **1987**, *411*, 355–362.
(2) Mori, S.; Uno, Y.; Suzuki, M. *Anal. Chem.* **1986**, *58*, 303–307.
(3) Mori, S.; Uno, Y. *Anal. Chem.* **1987**, *59*, 90–94.
(4) Mori, S.; Uno, Y. *J. Appl. Polym. Sci.* **1987**, *34*, 2689–2699.
(5) Mori, S. *Anal. Chem.* **1988**, *60*, 1125–1128.
(6) Mori, S. *Anal. Sci.* **1988**, *4*, 365–369.
(7) Mori, S.; Mouri, M. *Anal. Chem.* **1989**, *61*, 2171–2175.
(8) Mori, S. *J. Appl. Polym. Sci.* **1989**, *38*, 95–103.
(9) Danielewicz, M.; Kubin, M. *J. Appl. Polym. Sci.* **1981**, *26*, 951–956.
(10) Glöckner, G.; van den Berg, J. H. M. *J. Chromatogr.* **1986**, *352*, 511–522.
(11) Teramachi, S.; Hasegawa, A.; Shima, Y.; Akatsuka, M.; Nakajima, M. *Macromolecules* **1979**, *12*, 992–996.
(12) Glöckner, G.; van den Berg, J. H. M.; Meijerink, N. L. J.; Scholte, T. G.; Koningsveld, R. *Macromolecules* **1984**, *17*, 962–967.
(13) Sato, H.; Takeuchi, H.; Suzuki, S.; Tanaka, Y. *Makaromol. Chem. Rapid Commun.* **1984**, *5*, 719–722.
(14) Mourey, T. H. *J. Chromatogr.* **1986**, *357*, 101–106.

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CORRECTION

Theory for Cyclic Staircase Voltammetry for First-Order Coupled Reactions

Mary Margaret Murphy, John J. O'Dea, Dieter Arn, and Janet Osteryoung (*Anal. Chem.* **1990**, *62*, 903–909).

Figure 10 should be as follows: