

Note

Multi-mode liquid chromatography of polystyrenes on Partisil PAC*

SHIH-TSE LAI*^{**} and LOUIS SANGERMANO

Rockwell International, Semiconductor Products Division, Analytical Laboratory, 4311 Jamboree Road, Newport Beach, CA 92660 (U.S.A.)

and

CHIH-KUANG CHOU and DAVID C. LOCKE

Chemistry Department, The City University of New York, Queens College, Flushing, NY 11367 (U.S.A.)

(First received November 13th, 1984; revised manuscript received January 30th, 1985)

Our recent studies of the multi-mode behavior of chemically bonded phases¹⁻⁶ in liquid chromatography (LC) have emphasized the overriding importance of the eluent composition. These studies demonstrate that the same chemically bonded phase can behave as a reversed-phase substrate, a normal-phase adsorbent, and a size-exclusion medium, depending on the precise mobile phase composition.

We demonstrate here that Partisil PAC, a polar bonded phase, also behaves as a multi-mode LC stationary phase for the separation of polystyrenes. Partisil-10 PAC is made by permanently bonding an alkyl chain containing both secondary amino and cyano groups (ratio 2:1) to silica gel⁷.

EXPERIMENTAL

High-performance liquid chromatography

Either a Varian 8500 liquid chromatograph or a Micromeritics 7500 liquid chromatograph was used with a 25 cm × 4.6 mm I.D. Whatman Partisil-10 PAC (10 μm) column. The void volume (V_0 , 3.3 ml) used in the calculation of k' was determined from the retention volume of carbon tetrachloride with *n*-hexane as mobile phase. The UV detection wavelength was set at 260 nm. The isocratic mobile phase compositions (ϕ) and flow-rates are given in the figure captions.

Fluorescence

A Perkin-Elmer 650-10S fluorescence spectrophotometer was used with a Perkin-Elmer Model 650-0151 10-μl micro-cell and a Perkin-Elmer Hitachi 057 *x-y* recorder. The cell also functions as a stopped-flow cell for taking spectra of eluting peaks. For continuous monitoring, the wavelength of excitation was 270 nm and emission was read at 320 nm. The emission wavelength corresponds to excimer emission of styrene oligomers¹. Fluorescence detection is *ca.* 10³ times more sensitive than UV absorption.

* This work was presented in part at the 1983 Pacific Conference on Chemistry and Spectroscopy³, Pasadena, CA, U.S.A., October 26, 1983.

** Address for correspondence: 25815 Southbrook, El Toro, CA 92630, U.S.A.

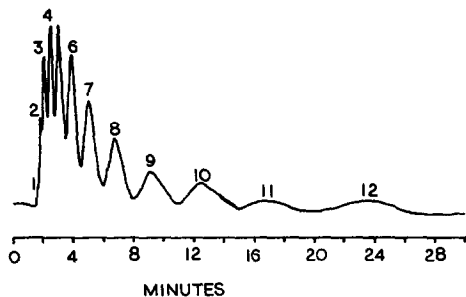


Fig. 1. Separations of polystyrene standard PS800 (average molecular weight 800) in methylene chloride–isooctane (1:12, v/v); isocratic elution; flow-rate, 3 ml/min; UV detection, 254 nm.

RESULTS AND DISCUSSION

Figs. 1 and 2 illustrate typical chromatograms of styrene oligomers on Partisil PAC with UV and fluorescence detection, respectively, in methylene chloride–isooctane (1:12, v/v). It is clear that styrene oligomers (PS800) to at least the degree of polymerization of 12 can be separated, the elution order being that of increasing degree of polymerization. In methylene chloride–isooctane, these oligomers elute as a single peak.

Fig. 3 shows that the elution order of a mixture of polystyrene standards with average molecular weight ranging from 800 to $1.8 \cdot 10^6$ depends on the eluent composition. In 2:3 methylene chloride–isooctane, the elution order is that of increasing molecular weight, *i.e.* the adsorption chromatography elution order; the higher molecular weight polystyrenes do not elute in a reasonable time because of their low solubility. Increasing the proportion of methylene chloride increases the solubility and thus significantly reduces the retention times of the oligomers. Indeed, with a 45:55 ratio, all these polystyrenes elute together. However, with a 1:1 ratio, the elution

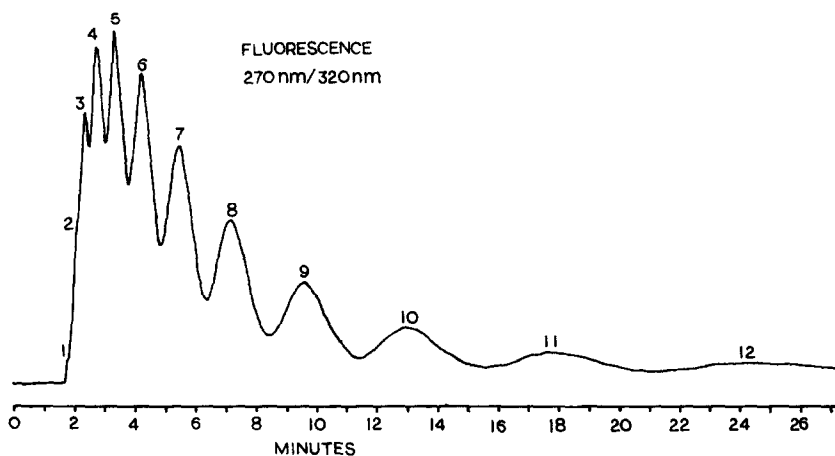


Fig. 2. As for Fig. 1, except: fluorescence detection, with an excitation wavelength of 270 nm, and an emission wavelength of 320 nm.

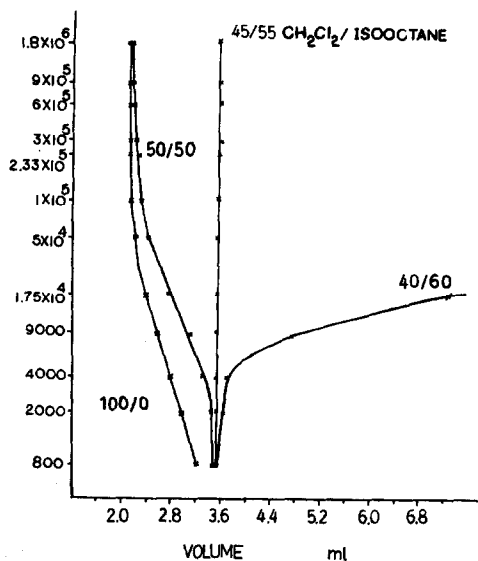


Fig. 3. The plot of log MW vs. retention volume of polystyrene polymers at different mobile phase compositions.

order is reversed: the higher molecular weight polystyrenes elute first, *i.e.* the size-exclusion order. A typical size-exclusion plot of log retention vs. molecular weight is obtained for high percentage of methylene chloride. Thus, a critical mobile phase composition (ϕ_c) exists between these two modes of LC separation². Below ϕ_c , the column acts as an absorbent, and macromolecules elute in order of decreasing solubility³; above ϕ_c , the mobile phase is strong enough to eliminate the solute-sta-

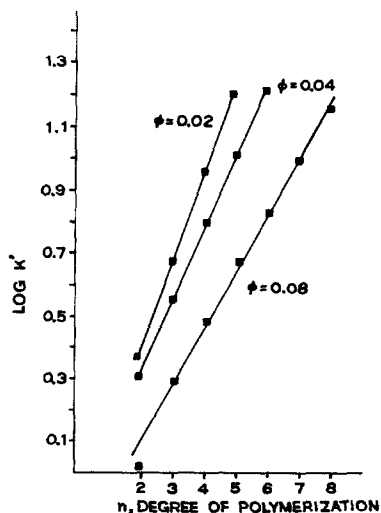


Fig. 4. The plot of log k' of styrene oligomers vs. the degree of polymerization (n).

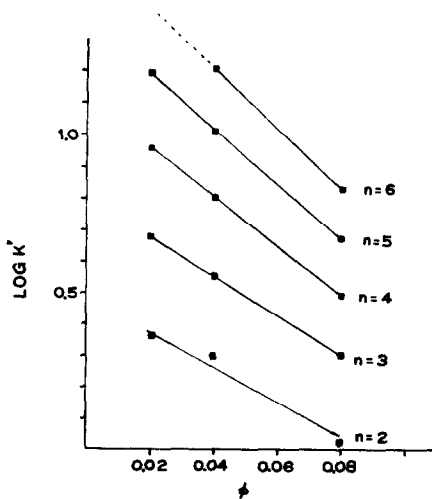


Fig. 5. The plot of log k' of styrene oligomers vs. the mobile phase composition (ϕ).

tionary phase interactions, and the column functions as a size-exclusion medium.

Figs. 4 and 5 show that the retention of styrene oligomers is related linearly to the degree of polymerization, n , and the mobile phase composition, ϕ . For poor solvent eluents, the retention behavior of styrene oligomers on Partisil PAC can be accounted for in terms of the competition between the adsorptivity of the chemically bonded phase and the solubility of oligomers in the mobile phase. This correlation can be expressed as

$$\log k' = (A - B\phi) + (C - D\phi)n \quad (1)$$

where A , B , C and D are constants. That eqn. 1 holds for styrene oligomers on Partisil PAC extends our previous observations; *i.e.* for isocratic elution the retention of styrene oligomers on phenyl-bonded and octadecyl-bonded phases⁵, of epoxy Novolac resins on a phenyl-bonded phase⁹, and of polyethylene glycol oligomers^{10,11} and polypropylene glycol oligomers¹² on phenyl-bonded phase all obey eqn. 1.

For a fixed composition of mobile phase, ϕ is a constant, and eqn. 1 becomes a Martin-type equation (as depicted in Fig. 4):

$$\log k' = U + Vn \quad (2)$$

where $U = A - B\phi$ and $V = C - D\phi$. For any individual oligomer peak, n is a constant and eqn. 1 can be rearranged to the same form as the Snyder formulation (as depicted in Fig. 5):

$$\log k' = \log k_s - s\phi \quad (3)$$

where $\log k_s$ is the extrapolated value of $\log k'$ in the pure poorer solvent, and $\log k_s = A + Cn$, and $S = B + Dn$. Thus eqn. 1 is a general expression for the isocratic retention of oligomeric series. Both the Martin equation and the Snyder equation are special cases of eqn. 1.

REFERENCES

- 1 S.-T. Lai and D. C. Locke, *J. Chromatogr.*, 252 (1982) 325.
- 2 S.-T. Lai and D. C. Locke, *ACS 13th Northeast Regional Meeting, Hartford, CT, U.S.A., June 28, 1983*.
- 3 S.-T. Lai, C.-K. Chou and D. C. Locke, *1983 Pacific Conference on Chemistry and Spectroscopy, Pasadena, CA, U.S.A., October 26, 1983*.
- 4 S.-T. Lai, L. Sangermano and D. C. Locke, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 7 (1984) 158.
- 5 S.-T. Lai, L. Sangermano and D. C. Locke, *J. Chromatogr.*, 312 (1984) 313.
- 6 L. Sangermano, S.-T. Lai, W. P. Ng, T. Stealey, M. M. Nishina, C.-K. Chou and D. C. Locke, *26th Rocky Mountain Conference, Denver, CO, U.S.A., August 6, 1984*.
- 7 *Columns on the Arts and Science of Chromatography*, Whatman, Clifton, NJ, U.S.A., Vol. 5, No. 1, October-November 1979, p. 1.
- 8 D. W. Armstrong and R. E. Boehm, *J. Chromatogr. Sci.*, 22 (1984) 378.
- 9 S.-T. Lai and L. Sangermano, *J. Chromatogr.*, 321 (1985) 325.
- 10 S.-T. Lai, L. Sangermano and D. C. Locke, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 7 (1984) 494.
- 11 S.-T. Lai, L. Sangermano and D. C. Locke, *1984 Pacific Conference on Chemistry and Spectroscopy, Sacramento, CA, U.S.A., October 12, 1984*.
- 12 S.-T. Lai and L. Sangermano, *36th International Pittsburgh Conference on Analytical Chemistry and Spectroscopy, New Orleans, LA, February 28th, 1985*.