Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Multimode Phenyl-Bonded Phase Liquid Chromatography of Phenyl-Containing Room Temperature Vulcanizeable Silicone Raw Materials and Polystyrene Polymers Using UV and Fluorescence Detection

Shih-Tse Lai[a]; Louis Sangermano[ab]; David C. Locke[c]
[a] ANALYTICAL LABORATORY SEMICONDUCTOR PRODUCTS DIVISION, ROCKWELL INTERNATIONAL, NEWPORT BEACH, CALIFORNIA [b] Hughes Aircraft Co., Los Angeles, California
[c] DEPARTMENT OF CHEMISTRY, QUEENS COLLEGE THE CITY UNTVERSfTY OF NEW YORK, FLUSHING, NEW YORK

To cite this Article Lai, Shih-Tse , Sangermano, Louis and Locke, David C.(1985) 'Multimode Phenyl-Bonded Phase Liquid Chromatography of Phenyl-Containing Room Temperature Vulcanizeable Silicone Raw Materials and Polystyrene Polymers Using UV and Fluorescence Detection', Separation Science and Technology, 20: 7, 513 — 521
To link to this Article: DOI: 10.1080/01496398508068234
URL: http://dx.doi.org/10.1080/01496398508068234

SEPARATION SCIENCE AND TECHNOLOGY, **20**(7 & 8), pp. 513-521, 1985

Multimode Phenyl-Bonded Phase Liquid Chromatography of Phenyl-Containing Room Temperature Vulcanizeable Silicone Raw Materials and Polystyrene Polymers Using UV and Fluorescence Detection

---

SHIH-TSE LAI* and LOUIS SANGERMANO†

ANALYTICAL LABORATORY
SEMICONDUCTOR PRODUCTS DIVISION
ROCKWELL INTERNATIONAL
NEWPORT BEACH, CALIFORNIA 92660

DAVID C. LOCKE

DEPARTMENT OF CHEMISTRY
QUEENS COLLEGE
THE CITY UNIVERSITY OF NEW YORK
FLUSHING, NEW YORK 11367

Abstract

A phenyl-containing room temperature vulcanizeable (RTV) silicone raw material and polystyrene polymers can be separated on a phenyl-bonded phase LC column using both UV and fluorescence detections. The multimode LC behavior was observed for both the RTV silicone raw material and the polystyrene polymers. This means that the same chemically bonded phase can have different elution behaviors under different mobile phase environments. In pure tetrahydrofuran (THF) eluent, size exclusion behavior is observed for both samples. In THF/H_2O gradient elution, polymers are retained and elute according to their solubility in the mobile phase.

---

*To whom correspondence should be addressed at Mass Spec Lab, Analytical Service Center, American Technology & Ventures, AHSC, 2132 Michelson Drive, Irvine, California 92715.

†Present address: Hughes Aircraft Co., P.O. Box 92919, Bld. S33, MSC 339, Los Angeles, California 90009.

0149-6395/85/2007-0513$3.50/0

Modern liquid chromatography can provide useful information in many industrial applications of polymers including inspection of starting raw materials, control of reaction process, quality assurance of finished products, and even the failure mechanism of the malfunction parts. For example, in semiconductor products application, Lai and Shepard (*1*) used the size exclusion chromatography (SEC) technique to demonstrate that the higher the molecular weight of poly(methyl methacrylate) (up to approximately 1,000,000) and the narrower the molecular weight distribution (MWD), the more sensitive the resist. In composite material application, Jones et al. (*2*) indicated that a correlation of the satisfactory parts and their MWDs could be used to inspect the starting raw material of epoxy resins. In areospace application, Hagnauer (*3*) demonstrated that reversed-phase high performance liquid chromatography (HPLC) could be used to characterize different blends of epoxy resins, and Ranganathan (*4*) showed that a 5 · μm Si column with UV detection could be used as a quality control tool to inspect room temperature vulcanizeable (RTV) silicone raw materials.

Recently, several studies (*5–11*) have indicated that the same chemically bonded phase can behave as normal-phase absorbents, reversed-phase substracts, or a molecular sieve, depending on the composition of the mobile phase. As pointed out by previous studies, polystyrene polymers can be used as model compounds for other types of oligomer separations (*12, 13*), and recent work (*14*) has shown that fluorescence detection is a selective detection for the LC elution of polystyrenes. In this contribution we show that the multimode LC behavior of the chemically bonded phenyl phase can be demonstrated by the elution of polystyrene polymers, and a practical application of multimode LC of a phenyl-containing RTV silicone raw material is shown using a phenyl-bonded phase column with both UV and fluorescence detection.

EXPERIMENTAL

Size Exclusion Chromatography

The size exclusion chromatographic system included a Waters Associates 6000A solvent delivery system, a Perkin-Elmer LC75 spectrophotometric detector, four Waters Associates μStyragel columns (500, 10^3, 10^4, and 10^5 Å), and a HP 85 microcomputer with Nelson Analytical GPC software. The UV detection wavelength was set at 260 nm. A Beckman 157 fluorescence detector was used in fluorescence detection, and the excitation wavelength was set at 254 nm and the emission wavelength was set at 316 nm. The mobile phase was THF at a flow rate of 1 mL/min.

Polystyrene Standards

The polystyrene standards were purchased from Perkin-Elmer. Polystyrene standards ranging from PS 800 to 6.12×10^5 and benzene were used to construct a linear MW calibration curve.

HPLC

The HPLC system included a Perkin-Elmer 3B 2/2 pump, a Beckman 165 variable wavelength detector, a Beckman 157 fluorescence detector, a Perkin-Elmer Sigma 10B chromatographic data station, and a 25 cm × 4.6 mm Excaliber Spherisorb S5P (5 μm) phenyl-bonded phase column (Applied Science). The UV detector was set at a wavelength of 260 nm. The fluorescence detection was set at an excitation wavelength of 254 nm and an emission wavelength of 316 nm.

Fluorescence

A Perkin-Elmer 650-10S fluorescence spectrophotometer was used with a Perkin-Elmer Hitachi 057 x-y recorder. The excitation wavelength was set at 232 nm and the emission spectrum was recorded.

RTV

A commercial phenyl-containing RTV silicone raw material was used for the experiment. In the fluorescence emission measurement, the RTV raw material was dissolved in hexane and was filtered by a Millipore Millex-SR 0.5 μm filter unit (Bedford, Massachusetts). In the LC separations, tetrahydrofuran (THF) was the solvent used to dissolve the RTV raw material.

RESULTS AND DISCUSSION

Cross-Linked Polystyrene Gel SEC Columns

Figure 1 illustrates the fluorescence emission spectrum of a phenyl-containing RTV silicone raw material. The spectrum suggests that fluorescence detection can be used to monitor the LC elution of this RTV

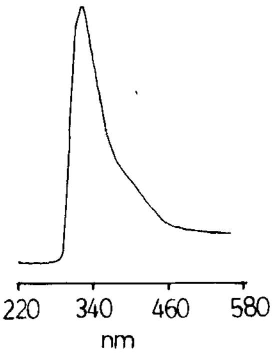

FIG. 1. Fluorescence emission spectrum of a phenyl-containing RTV silicone raw material in hexane.

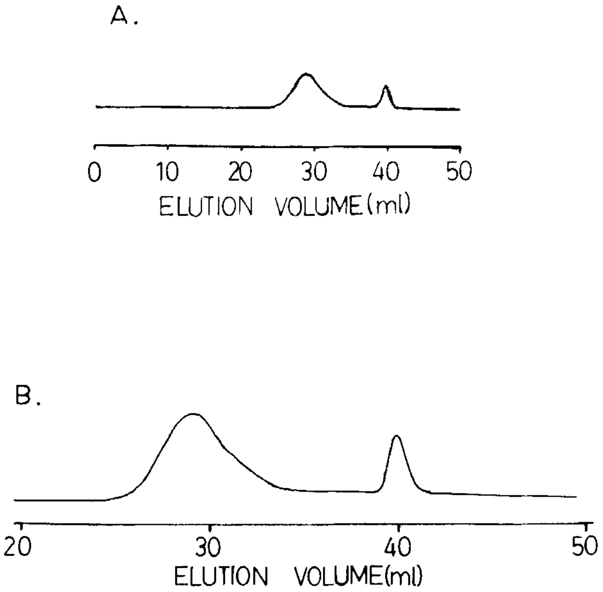

FIG. 2 (A): The SEC chromatogram of a phenyl-containing RTV silicone raw material using cross-linked polystyrene gel columns with UV detection at a wavelength of 260 nm. Mobile phase, THF; flow rate, 1 mL/min. (B): The same as (A) except for using a fluorescence detector, excitation wavelength at 254 nm, and emission wavelength at 316 nm.

silicone raw material. Figure 2 shows the SEC chromatograms of this RTV silicone raw material using both UV and fluorescence detections. These two chromatograms were obtained by using Water Associates cross-linked polystyrene gel columns. The chromatogram of fluorescence detection matches that of UV detection, except the former is more sensitive than the latter (~1000 times). The fluorescence detection technique is a selective method because only a relatively small number of compounds that absorb UV also fluoresce. The higher sensitivity of fluorescence detection, however, is an advantage for monitoring samples that can fluoresce. This is especially useful where there are a limited number of accessible samples, which is quite common in most industrial trouble-shooting applications, forensic investigations, and environmental contamination and pollution analyses.

Figure 3 is a SEC chromatogram of three polystyrene standards (PS 800, 4000, and 390000) obtained from the same organic gel column. As expected, the elution order is in the order of decreasing molecular size.

Phenyl-Bonded Phase

Figure 4 illustrates the gradient elution (THF/H_2O) of the same three polystyrene standards used in Fig. 3 on a phenyl-bonded phase column. The elution order is in the order of increasing degree of polymerization. The retention mechanism results from the competition between the selective interaction of sample solutes to the stationary phase and the solubility of the solute in the mobile phase. Figure 5 shows that the same phenyl-bonded stationary phase turns into a size exclusion column in a

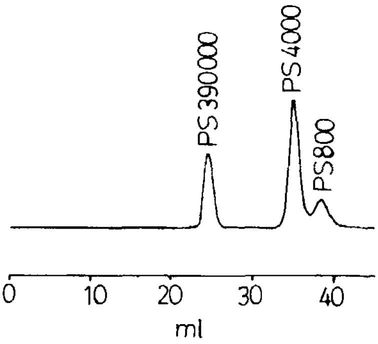

FIG. 3. The chromatographic conditions the same as for Fig. 2(A). Three polystyrene standards (PS 800, 4000, and 390000) were fractionated.

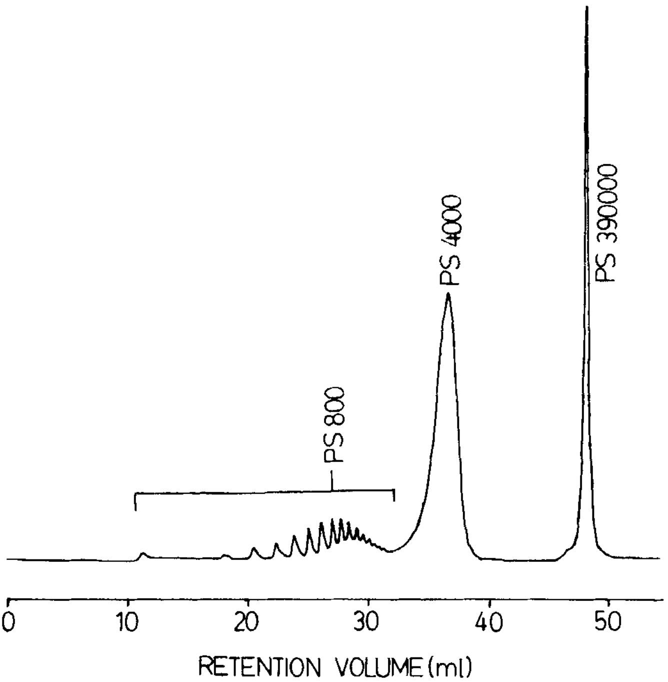

FIG. 4. The separation of PS 800, 4000, and 390000 on a phenyl-bonded phase column using a gradient elution starting from 40/60 THF/H_2O to 100% THF for 50 minutes, then maintained with pure THF. The flow rate was 1 mL/min. The fluorescence detection was the same as for Fig. 2(B).

pure THF eluent. As compared to Fig. 3, Fig. 5 demonstrates a similar SEC behavior and resolution but with a smaller elution volume. The results in Figs. 4 and 5 illustrate that two types of molecular weight distribution can be obtained from the same chemically bonded phase. One maintains the selectivity of chemical functional moiety of the solute and the stationary phase, and elutes according to the strength of the mobile phase. The other disminishes the interaction between the solute and the stationary phase, and sorts the solute molecules according to their sizes. Thus, the multimode behavior of phenyl-bonded phase LC of polystyrene polymers provides two types of information: (1) determination of molecular weight (e.g., number-average molecular weight, $\overline{M}_n$; weight-average molecular weight, $\overline{M}_w$; and polydispersity, $\overline{M}_w/\overline{M}_n$) via existing SEC calibration methods (*15*), and (2) a fine resolution chromatogram for a fingerprinting type of identification. Previous results also

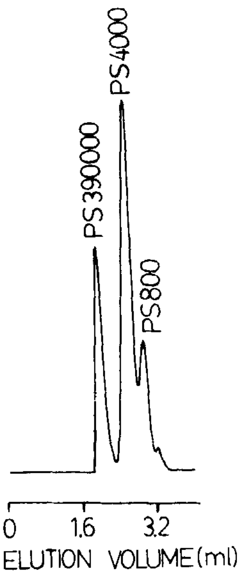

FIG. 5. The same chromatographic conditions as in Fig. 4 except for using a pure THF mobile phase at a flow rate of 0.4 mL/min with UV detection at 260 nm.

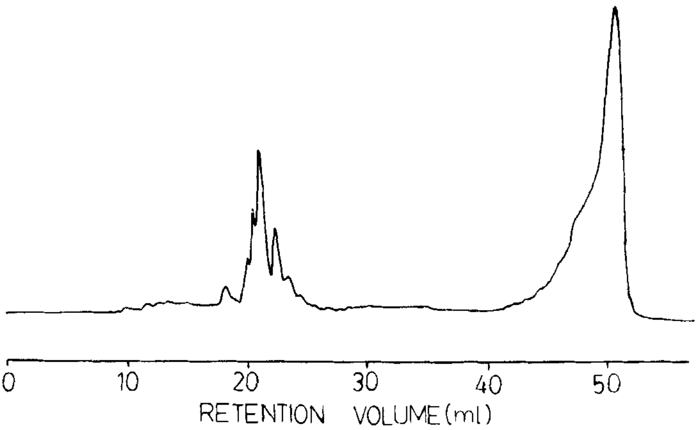

FIG. 6. The separation of a phenyl-containing RTV silicone raw material. The chromatographic conditions were the same as in Fig. 4.

showed that other types of chemically bonded phases, such as octadecyl and nitrile-bonded (*7*) phases, behaved as multimode LC substrates.

As emphasized by several previous studies (*13*, *16*, *17*), the separation of styrene oligomers on a given chemically bonded stationary phase can be used as a model for other types of oligomers such as polyethylene glycol oligomers (*18*), epoxy novolac oligomers (*19*), and polypropylene glycol oligomers (*20*). The same analogy applies to the multimode elution behavior of polystyrene polymers on the phenyl-bonded phase. Figures 6 and 7 show an application of this technique to the same RTV silicone raw materials shown in Fig. 2(A). Figure 7 is a SEC chromatogram, and is compatible to the result in Fig. 2(A). Figure 6 is the retention chromatogram of this RTV silicone raw material using the chromatographic conditions of Fig. 4. As expected and as compared to the results in Figs. 2 and 6, the elution order in Fig. 6 is in the order of increasing molecular weight, and is opposite to the elution order of SEC. The fine resolution chromatogram in Fig. 6 is useful for the inspection of batch to batch variations.

In summary, the multimode LC technique can provide information on two types of molecular weight distribution. Other advantages are: (1) the cost of chemically bonded phase columns is lower than that of SEC columns, and (2) the optimum resolution and elution time can be obtained by adjusting the gradient elution conditions.

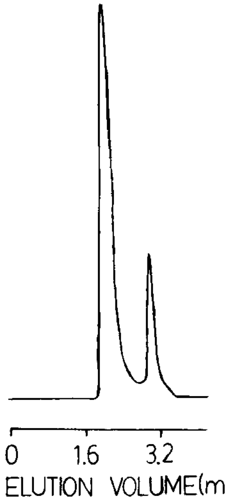

FIG. 7. The same chromatographic conditions as in Fig. 6 except for using a pure THF eluent at a flow rate of 0.4 mL/min with UV detection at 260 nm.

REFERENCES

1. J. H. Lai and L. Shepherd, *J. Appl. Polym. Sci., 20*, 2367 (1976).
2. J. F. Jones, T. T. Bartels, and R. Fountains, *Polym. Eng. Sci., 14*, 240 (1974).
3. G. L. Hagnauer, *Ind. Res. Dev., 23*, 128 (1981).
4. B. N. Ranganathan, *Liq. Chromatogr., 2*, 466 (1984).
5. D. W. Armstrong and K. H. Bui, *Anal. Chem., 54*, 706 (1982).
6. J. P. Larmann, J. J. DeStefano, A. P. Goldberg, R. W. Stout, L. R. Snyder, and M. A. Stadalius, *J. Chromatogr., 255*, 163 (1983).
7. S.-T. Lai and D. C. Locke, *Multi-mode Behavior of Chemically-bonded Stationary Phases in Liquid Chromatography*, Paper presented at the American Chemical Society 13th Northeast Regional Meeting, Hartford, Connecticut, June 28, 1983.
8. S.-T. Lai, C.-K. Chou, and D. C. Locke, *Multi-mode Liquid Chromatography of Polystyrenes on Normal Bonded PAC Phase*, Paper presented at the 1983 Pacific Conference on Chemistry and Spectroscopy, Pasadena, California, October 26, 1983.
9. S.-T. Lai, L. Sangermano, and D. C. Locke, *J. High Resolution Chromatogr. Chromatogr. Commun., 7*, 158 (1984).
10. S.-T. Lai, L. Sangermano, C.-K. Chou, and D. C. Locke, *J. Chromatogr., 324*, 436 (1985).
11. W. A. Howard, T.-B. Hsu, and L. B. Rogers, *Sep. Sci. Technol., 19*, 95 (1984).
12. S.-T. Lai, L. Sangermano, and D. C. Locke, *J. Chromatogr., 312*, 313 (1984).
13. M. A. Curtis, J. W. Webb, D. C. Warren, V. O. Brandt, F. G. Gerberich, K. B. Raut, and L. B. Rogers, *Sep. Sci. Technol., 15*, 1413 (1980).
14. S.-T. Lai and D. C. Locke, *J. Chromatogr., 252*, 325 (1982).
15. W. W. Yau, J. J. Kirkland, and D. D. Bly, *Modern Size-Exclusion Liquid Chromatography*, Wiley, New York, 1979, Chap. 9.
16. T. H. Mourey, G. A. Smith, and L. R. Snyder, *Anal. Chem., 56*, 1773 (1984).
17. S.-T. Lai, L. Sangermano, and D. C. Locke, *J. Chromatogr., 312*, 313 (1984).
18. S.-T. Lai, L. Sangermano, and D. C. Locke, *J. High Resolution Chromatogr. Chromatogr. Commun., 7*, 484 (1984).
19. S.-T. Lai and L. Sangermano, *J. Chromatogr., 321*, 325 (1985).
20. S.-T. Lai and L. Sangermano, *Phenyl-bonded Phase Liquid Chromatography of Polypropylene Glycol Oligomers Using Low Wavelength UV Detection at 190 nm*, Paper Presented at 1985 Pittsburgh Conference and Exposition on Analytical Chemistry Spectroscopy, New Orleans, Louisiana, February 28, 1985.

Received by editor January 9, 1985