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PYROLYSIS-CHROMATOGRAPHY AND PYROLYSIS-SPECTROSCOPY

City University of New York PH.D. 1983

PYROLYSIS-CHROMATOGRAPHY AND PYROLYSIS-SPECTROSCOPY

by

SHIH-TSE LAI

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City Univeristy of New York.

1983

Abstract

PYROLYSIS-CHROMATOGRAPHY AND PYROLYSIS-SPECTROSCOPY

by

Shih-Tse Lai

Adviser: Professor David C. Locke

This dissertation is in three parts: (1) Pyrolysis-Chromatography and Pyrolysis-Spectroscopy, (2) Separation of Styrene Oligomers Using High Performance Liquid Chromatography with UV and Fluorescence Detection, and (3) Multi-Mode Behavior of Chemically Bonded Phases in Liquid Chromatography.

Part One is concerned with the first report of the newly developing methods of pyrolysis-Liquid Chromatography (Py-LC) and pyrolysis-fluorescence; the comparison of stepwise Py-LC and stepwise pyrolysis-gas chromatography (Py-GC); the informative method of off-line Py-LC-MS; and Py-MS with electron impact ion source of polystyrene, which shows a fragment at mass=180 (1,2-diphenylethylene) that provides evidence of trace amounts of head-to-head microstructure.

Part Two reports the first separations of styrene oligomers on nitrile-bonded phases, PAC (1:2 ratio of nitrile- and amino-bonded phases) and alumina absorbents. Excimer fluorescence emission spectra are also observed on each HPLC fraction of lower styrene oligomers. Fluorescence detection is reported here to monitor HPLC fractionation of styrene oligomers and Size Exclusion Chromatographic (SEC) separation of Polystyrene polymers.

Part Three discusses a factor overlooked by modern LC users, the mobile phase effect. The nitrile bonded phase is used as an example to demonstrate that by changing the mobile phase alone, reversed-phase, normal phase, and size exclusion LC can be conducted on the same stationary phases.

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosphy.

7 June 1983
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PART ONE

PYROLYSIS CHROMATOGRAPHY AND PYROLYSIS SPECTROSCOPY

CHAPTER I

INTRODUCTION

Pyrolysis, literally breakdown by heat, is used to designate the process of converting a sample into another substance or substances through the agency of heat alone in an inert atmosphere. This process may produce molecules of lower molecular weight due to thermal fission [1], or less commonly may produce higher molecular weight compounds through condensation reactions of the pyrolysis products depending on the conditions chosen [2].

Pyrolytic fragmentation is not a random phenomenon, but a process which can, in principle, be predicted from thermodynamic and kinetic data. In practice, however, it is difficult to predict the pyrolysis pattern before the experiment [3]. For a given set of thermal energy parameters(such as temperature rise rate, final temperature, pyrolysis duration time, etc.), the molecular bonds in the material rupture in a statistically controlled manner, and the resultant radicals react via known mechanism to yield a reproducible product distribution [3].

As early as 1862, Williams used pyrolysis to identify the isoprene unit in rubber [4]. Since then, much effort has been put into the development of sophisticated instrumentation for

producing and analyzing the pyrolysis products, including chromatography and spectroscopy(Py-C and Py-S). Table 1 lists developments in Py-C and Py-S. Both are indirect methods of analysis in which the sample is pyrolyzed and the resultant products (pyrolyzates) are analyzed by chromatographic separation and spectroscopic measurement.

Table 1

Developments in Pyrolysis-Chromatography and Pyrolysis-Spectroscopy

1862	Identification of isoprene unit in rubber [4]
1948-1952	Indirect Pyrolysis-Mass Spectroscopy(Py-MS) [5-7]
1953	Direct Py-MS [8]
	Py-IR [9,10]
1954	Indirect Pyrolysis-Gas Chromatography(Py-GC) [11]
1955	Integrated Reaction-GC [12]
1959	Integrated Py-GC [13-15]
1960	Introduction of the term "Pyrogram" [16]
1965	Curie-Point Pyrolyzer [17,18]
1970	Py-Flame Ionization Detector [19,20]
1973	Low Voltage Py-MS [21]
	Laser Pyrolyzer [22]
	Py-FIMS(Field-Ionization Mass Spectroscopy) [23,24]
1975	Py-FDMS(Field Desorption Mass Spectroscopy) [25,26]
1976	Py-GC-MS [27,28]
1977	Py-CAMS(Collisional-Activation Mass Spectroscopy)[29,30]
	Continuous Mode Furnace Pyrolyzer [31]
	Galvanically Heated Filaments(Pulse Mode Pyrolyzer) [32]
	Py-CIMS (Chemical Ionization Mass Spectroscopy) [33]

It is clearly indicated in Table 1 that analytical pyrolysis techniques have become more sophisticated as advanced analytical instrumentation has become available. Among these methods, research activities have been heavily focused on the areas of Pyrolysis-Gas Chromatography (Py-GC) and Pyrolysis-Mass Spectrometry (Py-MS). For example, Berezhkin [34] has made a comprehensive review with 278 references on the development of Py-GC; Irwin [2] covered Py-GC and Py-MS analytical pyrolysis methods with over 500 references. A recent book by Meuzelaar et al. [35] evaluates the technique of Py-MS using a Curie-point pyrolyzer.

These techniques can be applied to characterize low molecular weight compounds as well as macromolecules. The sample to be analyzed can be gas, liquid or solid. Table 2 lists the general types of applications.

Table 2

Types of Applications of Analytical Pyrolysis Techniques

1. Fingerprint Identification
2. Composition Analysis
3. Structure Determination
4. Mechanistic and Kinetic Studies
5. Taxonomy
6. Pathology
7. Forensic Science
8. Toxicology

This part of the dissertation describes the first work on the development of the techniques of Pyrolysis-High Performance Liquid Chromatography (Py-LC) and Pyrolysis Fluorescence (Py-F). Most of the reported pyrolysis procedures in Py-GC and Py-MS were isothermal pyrolysis conditions; comparison is made here between isothermal and stepwise pyrolysis, i.e. the sample is sequentially pyrolyzed at certain temperature increments from low temperature to high temperatures. The first part of this dissertation discusses the newly developing Py-LC, including comparison of stepwise Py-LC and stepwise Py-GC, and the potential of Py-LC-MS, Py-Fluorescence, and stepwise Py-MS coupled with resistive heating probe.

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CHAPTER II

PYROLYSIS-LIQUID CHROMATOGRAPHY (Py-LC)

I. INTRODUCTION

Py-LC uses high performance liquid chromatography for the analysis of pyrolysis products. This newly developing method is designed to overcome certain limitations of Py-GC, e.g. Py-LC is able to detect thermally labile pyrolysis products and pyrolyzates highly retained on GC columns. It is worthwhile to review briefly the Py-GC methods before going into a discussion of Py-LC.

Pyrolysis followed by gas chromatographic analysis of the volatile products (Py-GC) has been used for some time as a rapid fingerprinting technique for the characterization of a diversity of synthetic organic polymers and natural polymeric materials [1,2,3]. In conjunction with high-resolution open tubular GC columns, GC-mass spectrometry (MS), and pattern recognition-type statistical evalutions of the chromatographic data, even subtle structure differences in polymer microstructure can be seen [4,5]. For example, Py-GC has been used to characterize the degree of cross-linking of copolymer of styrene and divinylbenzene [6], homopolymer blends of styrene and 2,6-dimethyl-1,4-phenylene oxide [7], the isomeric structure of styrene-acrylonitrile and styrene-methacrylate copolymers [8], the steroregularity of styrene distribution in butadiene-styrene copolymers [9], the polydispersity of methacrylate-styrene block polymers [10], the

dyad sequence in vinyl-type copolymers [11], and the tacticity of polypropylene [12].

Py-GC techniques can not only easily analyze intractable materials, but can also distinguish among simple isomeric compounds. Fanter [13] et al. showed that Py-GC could distinguish the six C_6H_{12} isomers (2-, 3- and 4-methyl-2-pentene; 2-ethyl-1-butene; 3,3-dimethyl-1-butene, and 2,3-dimethyl-2-butene), which were extremely difficult to differentiate among each other with a mass spectrometry [13]. Excellent intralaboratory Py-GC reproducibility has been demonstrated [1]. Interlaboratory reproducibility makes possible more economical qualitative and quantitative analyses, because (i) Py-GC results obtained under standard conditions can be compiled and used as reference spectra by other laboratories, and (ii) formation of a central interlaboratory data library will lower the burden and cost of building individual data libraries. The usefulness of this is clear from the results of interlaboratory tests of Py-GC methods for analyzing rubbers, which showed that 20 samples out of 23, i.e. 87%, were correctly identified [14].

Py-GC is one of the most powerful techniques to investigate polymer materials for forensic purposes. Frequently, only traces of samples are found at the scene of a crime, e.g. trace amounts of paints on the criminal's clothes or on his vehicle. Although the inorganic constituents of paints can be identified by various spectral methods, identifying polymeric constituents of the paints

using Py-GC is more meaningful than the analysis of inorganic components. Py-GC enables the forensic analyst to distinguish different paints, including paints of the same grade but manufactured at different factories. For example, Table 3 lists the ratios of acrolein/methacrolein peak heights in pyrograms of white alkyd paints produced at two different factories over 12 months [15]. Wheal [15] also demonstrated that Py-GC is more feasible than spectral analysis in analyzing paints. For example, spectral analysis identified 53 paint samples out of 190, as compared to 141 indentified by Py-GC [15]. Thus, in this case at least, Py-GC is three times as effective in identifying paints as emission spectroscopy. The use of just one peak ratio is, however, not always sufficient for identification by Py-GC. The powerfulness of Py-GC increases with the number of peak ratios used, or by using the total pyrogram as a fingerprinting identification.

Table 3

RATIO OF ACROLEIN/METHACROLEIN PEAK HEIGHTS FOR DIFFERENT BATCHES OF WHITE PAINT PRODUCED AT TWO FACTORIES [15]

Batch	Factory A	Factory B
1	0.15	0.81
2	0.15	0.64
3	0.70	0.97
4	0.15	0.47
5	0.12	0.81
6	0.12	0.99
7	0.11	0.92
8	0.13	0.62
9	0.13	0.82
10	0.14	0.54
11	0.81	0.42

As useful as these GC methods are, in general only a fraction of the sample is pyrolyzed to compounds sufficiently volatile to be eluted from a GC column; the balance could be viewed as lost information. The more complex the sample, the more likely this should be. For example, van de Meent et al. [16] found that pyrolysis of certain kerogen (insoluble carbonaceous matter) samples at 610°C in Helium produced only about 10% gas chromatographable volatiles, but 40-50% each of a dark brown condensate and a black residue. Berezhkin [2] too has urged that particular attention be paid to the identification of the heavy pyrolysis products, in order to give a more complete picture of the sample structure.

The combination of Py-GC-MS suffers the same limitation as Py-GC itself, but direct interfacing of the pyrolyzer to mass spectrometer allows, as does HPLC, one to look at higher molecular weight fractions of the pyrolyzate (e.g. ref. 17). However, LC cost far less than MS, and there are probably few MS labs willing or able to dedicate a mass spectrometer to pyrolysis studies.

The advantages of high performance liquid chromatography (HPLC) over gas chromatography are described in the following. For example, it has been postulated that only about 15% of the known compounds can be analyzed by gas chromatography; the other 85% have insufficient volatility or thermal stability. HPLC does not have these limitations. The availability of isocratic and gradient elution with a wide variety of mobile phase solvents can

provide special selectivity effects that are absent when the mobile phase is a gas. Also, HPLC can be used to analyzed a wider variety of samples such as ionic compounds, labile naturally occuring compounds, polymers, and high molecular weight polyfunctional compounds, etc. It is clear that HPLC can offer more complete information about pyrolysis products.

Py-LC, like HPLC, is of course restricted to substances detectable with available detectors, in particular at present the UV absorption detector. The technique of Py-LC would consequently be of limited use for study of the pyrolysis of for example polyethylene.

At present, a good packed column for GC is nominally 1000-3000 plates/m; capillary GC columns range from 1000 to 4000 plates/m. Therefore, the total number of theoretical plates available for separation will be less than 10,000 for packed columns, but ranging up to 600,000 plates for capillary GC columns. Exceptionally high efficiency HPLC columns (up to 40,000 plates/m) are now available. Consequently, for a 25 cm HPLC column, the total plate number is about 10,000. Clearly, the relative practical efficiency for HPLC column is less than that of capillary GC.

II. INSTRUMENTATION REQUIREMENTS

The pyrolysis unit and the HPLC are the two major components in Py-LC instrumentation. In general, for a successful analysis, the pyrolysis unit must have an accurate temperature control and high reproducibility, and a high resolution HPLC system is needed. The details are discussed in the following.

(1) Pyrolysis Unit

Reproducibility is the most important requirement of the pyrolysis unit from the points of view of both the formation of the products and the transfer of products from the pyrolyzer to the analytical device. Different pyrolyzer designs lead to different pyrolysis product distributions. Folmer [18] indeed showed that three different pyrolyzate distributions were obtained for the three types of pyrolyzers studied, i.e., flash-filament, tube-furnace and laser-type pyrolyzers. The tube furnace-type pyrolyzer gives a very complicated pyrogram, mainly because of secondary reactions which result from the pyrolysis of large quantities (grams) of sample and the large void volume. The laser pyrolysis gas chromatogram is simpler than those generated using the other two pyrolysis methods. In laser beam pyrolysis, the laser beam is focused on a small area which causes a ultra fast temperature jump; temperatures of 4000 to 10,000^{o}K have

been estimated, based on the energy distribution of emitted electrons [19]. Exposure of material to such an intense power concentration results in extensive degradation. The cooling rate of the primary pyrolysis products is reported to be almost as rapid as the rate of heating, i.e., 200-300 microseconds [20], thus minimizing secondary reactions. The main disadvantage of this method is that only samples which absorb the light of the laser beam can be pyrolyzed. This problem can be solved by adding carbon black to the sample, but mixing sample with carbon black affects the pyrolysis product distribution. Therefore, the comparison of results should only be made among samples with the same concentration of carbon black.

Both the Chemical Data Systems (CDS) resistance (flash-filament) and induction (Curie-point) heating probes offer remarkable reliability in pyrolysis duration time and temperature control, i.e., temperature rise rate and final temperature, so that under carefully controlled conditions the pyrolysis product distributions are reproducible. Because of the use of small sample sizes (microgram- mg), these two techniques also have the advantage of minimum secondary reactions. Considering maintenance, cost, minimization of secondary reactions and reproducibility of results, they are the optimal choices for the pyrolysis unit used in Py-LC.

The difference between filament and Curie point devices results from different heating mechanisms. In the CDS flash

filament-type pyrolyzer, the probe is equipped with a platinum coil, heated electrically in a circuit designed to provide accurate temperature control. Both isothermal and temperature programmed pyrolysis conditions can be controlled, as well as the pyrolysis duration time (up to 240 min), temperature rise rate (0.1°C/msec to 300°C/min) and final temperature (up to 1000°C).

In the case of the Curie-point pyrolyzer, the probe is made of a ferromagnetic material which has a Curie-point temperature (Tc) characteristic of its exact composition. When subjected to a high-frequency electromagnetic field , the probe absorbs energy and is rapidly heated. When the temperature reaches the Curie point of the ferromagnetic material, the probe becomes diamagnetic and no longer absorbs any energy, cools below Tc, is heated, and cycles back and forth a few hundredths degree below Tc. Thus the probe temperature is essentially constant at Tc, which is the pyrolysis temperature. Therefore, only isothermal pyrolysis can be conducted using this method, and the final pyrolysis temperature can be varied only by changing the composition of the metal probe. Table 4 lists the Curie points of some ferromagnetic materials [21] used in pyrolysis.

Table 4

CURIE POINTS OF SOME

FERROMAGNETIC MATERIALS [21]

Material	Composition(%)	Curie Point(^{o}C)
Fe/Co	50/50	980
Fe	100	770
Fe/Ni	30/70	610
Fe/Ni	40/60	590
Fe/Ni	49/51	510
Fe/Ni	55/45	440
Fe/Ni/Cr	48/51/1	420
Fe/Ni/Mo	17/79/4	420
Ni/Co	40/60	900
Ni/Co	67/33	660
Ni	100	358

Use of the ferromagnetic metal filament itself as a sample support is not recommended because of possible catalytic reactions.

The performance of the filament-type pyrolysis unit is a crucial factor in determining the reproducibility of pyrolytic analysis. On pyrolysis the primary bond-fission fragmentations may be produced from several temperature-dependent and competing reactions. In practice, the final product distributions depend upon the heating characteristics of the pyrolyzer. Farre-Ruis and Guiochon [22] showed that thermal fragmentation of a sample may be largely complete before the final equilibrium temperature (Teq) is reached. Thus the reproducibility relies on the pyrolyzer's temperature-time profile (TTP), which includes the temperature-rise time (TRT), total heating time and Teq. Buhler and Simon [23] demonstrated that TRT depends upon the composition of the filament, filament geometry and available power heating. They also found that the cooling rate is important because much of the sample remains inside the pyrolyzer. Volatilization of sample residues depends upon the cooling rate. Consequently, it is important to have samples experience the same TTP for reproducible results.

It has also been pointed out by several workers [2,24] that fast TRTs are prerequisites for efficient and reproducible fingerprint analytical pyrolysis. To rapidly attain the equilibrium temperature, various heating patterns have been

proposed for filament-type pyrolyzers which permit reducing the heating time to tenths and even hundredths of a second. Figures 1 and 2 are taken from Levy and Fanter's [25] work on filament temperature variation curves, derived when (i) constant voltage source is used; and (ii) constant voltage source is combined with an additional source of capacitor discharge. The TRTs of conventional filament pyrolyzers heated by a constant voltage usually range between 5-25 sec. A more sophisted system based on discharge of a large capacitor through the filament for achieving fast TRT was introduced by Levy [27]. A schematic of a recent version of the capacitor discharge is taken from Levy et. al's work [28], and shown in Figure 3. As can beeen from these curves, filament-type pyrolyzers can provide for shortening the heating time (down to 15 msec) and maintaining the sample at prefixed temperature during the experiment. Perry [26] pointed out that the sample heating curves are readily reproducible on the same pyrolyzer but not always on different pyrolyzers of the same type. This is also true for any type of pyrolyzers.

A CDS flash-filament resistance-type pyrolyzer was used for all experiments reported here for the reason of minimum secondary reactions, reproducible results, easy maintainance, and low cost.

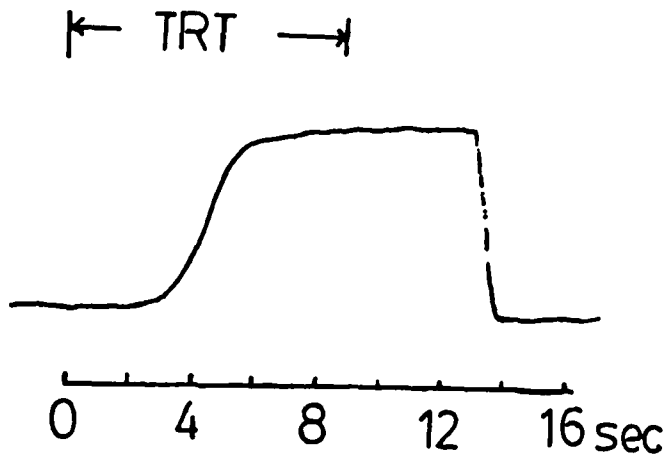

Figure 1. Oscilloscope tracings of the photomultiplier output showing the temperature-time profile of a Pt filament excited with a constant voltage source [25].

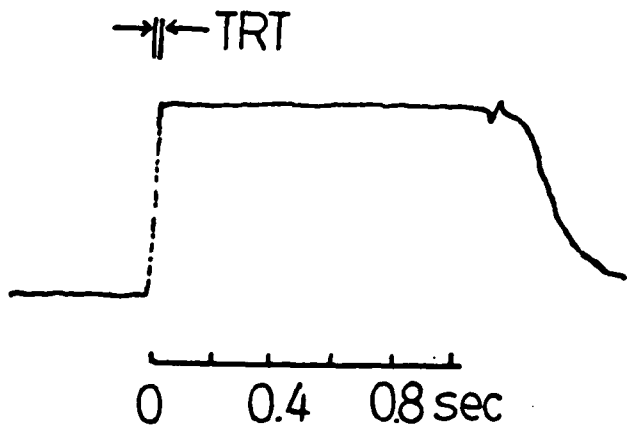

Figure 2. Oscilloscope tracings of the photomultiplier output showing the temperature-time profile of a Pt filament excited with a capacitor discharge source [45].

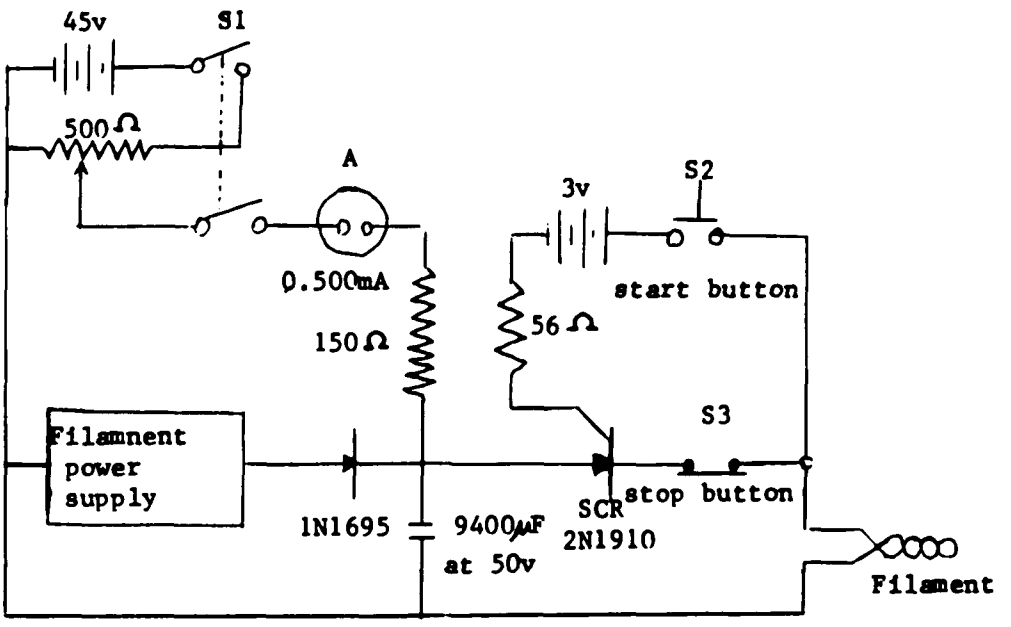

Figure 3. Schematic of the capacitor discharge circuit for rapid excitation of filament pyrolyzers [28].

(2) HPLC

Polystyrenes are used as a test polymers because well-defined molecular weight polystyrenes with narrow dispersities are commercially available. From the results of Py-GC-MS [29] and Py-MS [30], the pyrolysis products of polystyrene are known to include styrene oligomers and their derivatives. Therefore, mobile and stationary phase combinations which are suitable for the fractionation of styrene oligomers should serve as guides for finding HPLC systems useful for separating polystyrene pyrolyzates. As discussed in Part Two, styrene oligomers and therefore presumably polystyrene pyrolyzates can be separated by both normal and reversed phase LC.

At the present stage of development, the resolution of packed column LC does not rival that of open tubular GC. This problem may be ameliorated as open tubular LC columns [31] are more fully developed and commercially available. In general, the diameter of a typical open tubular LC column is less than 60 um, and in some work less than 10 um. The inside surfaces of open tubular column are either roughened by various means to build up a porous layer, or actually coated with a layer of colloidal silica, or chemically bonded with functional groups. Both theoretical and experimental aspects of open tubular column LC have been investigated by several workers [32-41]. The use of open tubular column in LC was first introduced by Pretorius and Smuts [41]. Ishii et al. [31-36] prepared both wall-coated and chemical-bonded open tubular

columns, and demonstrated their efficiency in conjunction with a micro-HPLC system. Later, Knox and Gilbert [40] discussed the theoretical optimization of open tubular columns. In order to achieve the optimum performance of such columns, ancillary equipment such as sample valves, connectors, detector, etc., must be modified significantly. In particular, Knox and Gilbert [40] estimated that the detector cell volumes must be reduced to 1 nl for a 10-um i.d. open tubular column having more than 30,000 theoretical plates, as compared to the regular ul cell volumes for UV detectors. Recently, Yang [38] introduced chemical bonded fused silica open tubular columns with 30 um bores, using a splitter-injector [38,42] and an "on-column UV detector" [38,39]. On-column detection offers an extremely small cell volume by totally excluding the void volumes from connectors. This virtually eliminates extra-column band broadening effects associated with the detector.

High resolution is the main advantage of open tubular column LC. Published chromatograms are quite impressive (e.g. 43), with very high plate numbers; however, the production rate of the plates (i.e. plates/second) is poorer than that obtained with some other types of LC columns. In addition, low sample capacity, normally less than 1ug, is a major disadvantage of open tubular column LC. Sample injection volumes of less than 2ul [31] are required for open tubular columns with i.d.'s less than 30um. This poses a major difficulty in operating open tubular columns.

New breakthroughs in injector technology and injection techniques will be necessary to reach the maximum efficiency of open tubular column LC.

The requirements for choosing column materials for open tubular column are more restricted than packed LC columns. Stainless steel, Teflon, borosilicate, soda-lime, and fused silica glasses are usually used for LC columns. Among these materials, fused silica [31] is the best choice for the following reasons. The advantages of fused silica include (i) good mechnical strength and flexibility; (ii) capability of using inlet pressures up to 800 atm enabling long open tubular columns to be used; (iii) a smooth inner surface, ensuring minimum band broadening due to wall effects [42]; (iv) chemical inertness and low trace metal content , minimizing interactions between solute molecules and the column wall; (v) high UV transmittance allowing on-column UV detection [38,39]; and (vi) surface silanol groups on the fused silica, similar to the silica absorbents used in packed LC columns, enabling formation of chemically bonded-phases, such as octadecylsiloxane, phenylsilane, cyanopropylsilane, etc.

Less mobile phases is needed in open tubular column LC because of small column elution volumes and slow flow rates (ul/min). This means more varieties of solvents can be used, including exotic, expensive and toxic solvents. Also, when solutes are to be recovered, or analyzed, by MS, the problems of evaporating solvents such as water-acetonitrile and water-methanol in

reversed-phase LC-MS can be minimized. This could provide a more practical basis for development of on-line Py-LC-MS, and Py-LC in conjunction with gas-phase ionization detectors [44,45].

Open tubular LC columns should be distinguished from both microcapillary columns and microbore columns. Microcapillary columns are loosely packed small diameter columns [46-50]; and microbore columns are well-packed columns having an i.d. at 1. mm. or less and packed with 10-um particules [51-54], or columns with conventional (2.6-4.6 mm) diameter and packed with small diameter (3-5 um) particles [55-58]. These two type of LC column systems could also be used in Py-LC. For the moment, both open tubular LC columns and microbore LC columns are not available for the present Py-LC works. However, these columns should be included in the future work of Py-LC.

III. EXPERIMENTAL

(1) Stepwise Pyrolysis

A CDS Pyroprobe 100 pyrolyzer with heated interface (Chemical Data Systems, Oxford, PA, U.S.A.) was used in all experiments. The Pyroprobe is equipped with a Pt coil 15 mm x 3.0 mm o.d. x 2.0 mm i.d., heated electrically in a circuit designed to provide accurate temperature control. Samples, in intial experiments 5.0 mg and subsequently approximately 50 ug, were loaded into a quartz sample tube 15 mm x 2.0 mm o.d., which fits inside the Pt coil and provides good thermal contact with it. The temperature rise rate of the coil is specified to be 75°C/msec although the temperature rise rate of the sample no double lags considerably behind this. Pyrolysis was carried out in a stepwise fashion, i.e. any given temperature was heated at 100°C increments from 200°C to 900°C. Heating times for the 5.0 mg samples were 4 min for pyrolysis at 200°C and 300°C, 2 min for 400°C, and 1 min for the higher temperatures; times were varied with temperature to provide comparable quantities of pyrolyzate. For the 50 ug samples, pyrolysis for 1-2 sec was found to give comparable results with less likelihood of secondary reactions occurring.

For pyrolyzate analysis by GC, the outlet of the heated interface was attached with a Swagelok fitting to a pyrolyzate

trap consisting of a 5.0 cm x 3.0 mm o.d. quartz tube filled with 45-90 um glass microbeads (Sigma, St. Louis, MO, U.S.A.), held in place with glass wool. The arrangement is depicted in Figure 4. Use of Tenax rather than glass beads allows greater retention of pyrolyzates but causes severe thermal desorption problems; the glass beads offer a compromise. The pyrolysis products were swept out of the 200°C interface with He at 100 ml/min, and collected separately at each pyrolysis temperature. Before use, the glass beads, glass wool, and quartz tubes were washed with cyclohexane-benzene (1:1) and dried at 300°C. Blank chromatograms showed no detectable organics after this treatment.

For Py-LC, pyrolyzates at each temperature were collected by bubbling the effluent from the pyrolyzer interface through a 1/16 in. O.D. stainless-steel tube into 2.5 ml of cyclohexane, as depicted in Figure 4. The pyrolysis times at each temperature were the same for Py-LC and Py-GC.

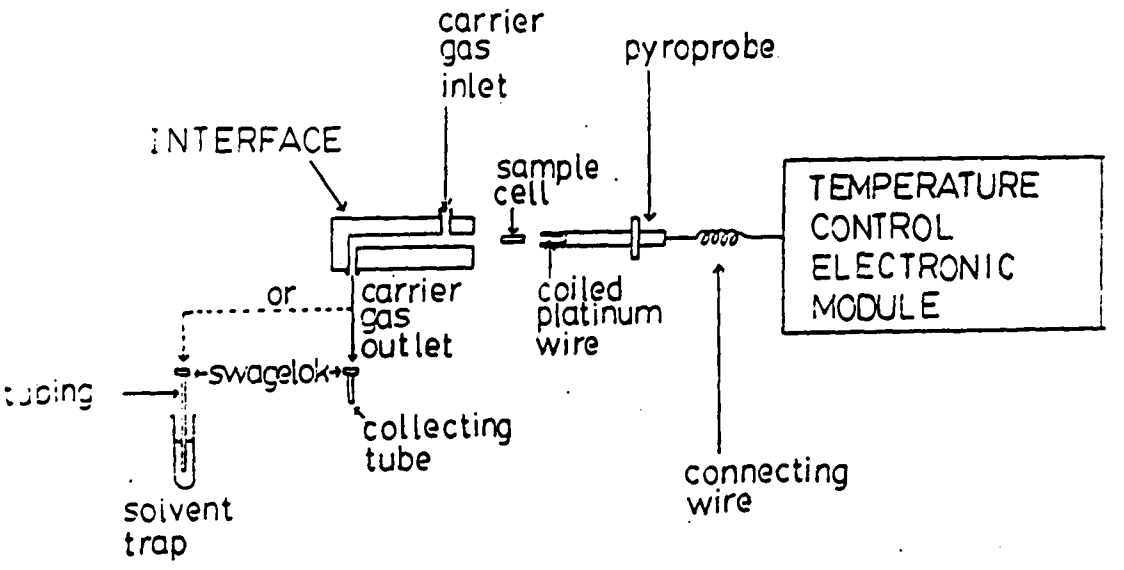

Figure 4. Schematic diagram of the instrumental arrangement using the CDS Pyroprobe 100 and heated interface with solvent trap or glass microbead collector trap.

(2) GC

A Shimadzu Mini-2 gas chromatograph with flame ionization detector (FID) was used with a 17 m x 0.25 mm i.d. open tubular glass column wall-coated with OV-101. The carrier gas was Helium at 5 ml/min. The column temperature was held initially at 36°C for 5 min after sample introduction, then programmed at 4°C/min to 250°C and held at that temperature for 50 min. To introduce samples, the column was cooled to 36°C, the injector nut removed, the glass bead-filled quartz collector tube inserted directly into the 300°C injection port, and the nut replaced. As indicated in Figure 5, a 5.0 cm x 3.0 mm O.D. quartz tube packed with glass wool was placed in the injection port between the column and the collecting tube, to prevent any loose glass beads from entering the capillary column. The guard tube, which was left in place while collector tubes were changed, also served to help protect the open tubular column from contamination and blockage by high boiling compounds in the pyrolyzate.

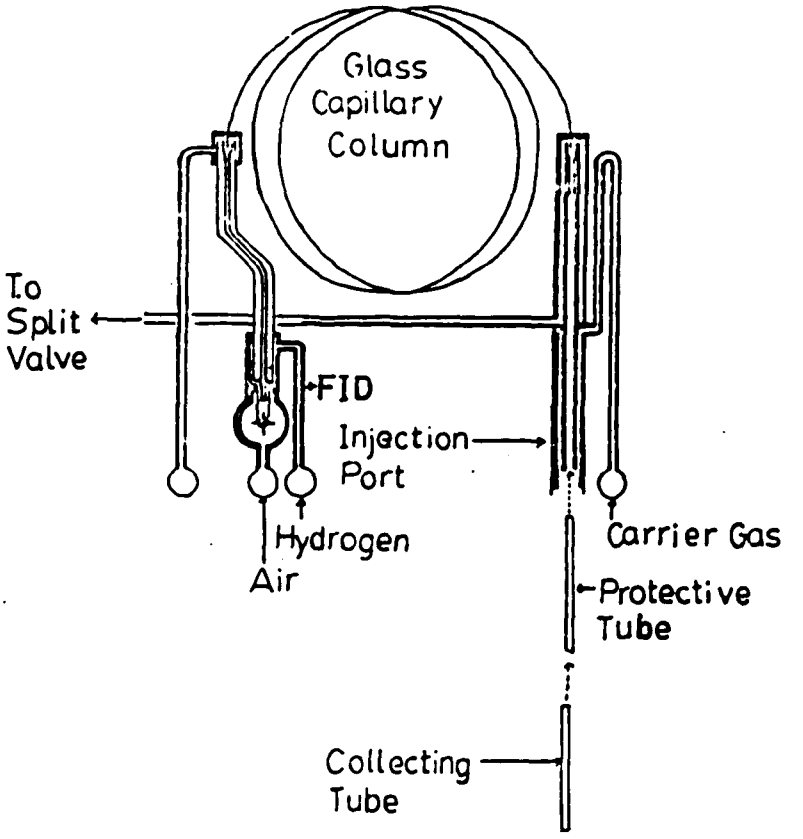

Figure 5. Schematic diagram of the GC sample inlet system. The quartz guard tube is 5.0 cm x 0.3 cm packed with glass wool. The quartz collector tube is of the same dimensions, packed with glass microbeads.

(3) HPLC

Either a Varian Model 8500 liquid chromatography or a Micromeritics 7500 liquid chromatograph was used with a 25 cm x 2 mm i.d. Micropak CH-10 column (Varian Instruments), or a 25 cm x 4.6 mm i.d. Partisil ODS column (Whatman, Clifton, NJ, U.S.A.), respectively. The eluent in either case was acetonitrile-water (90:10) at 25 ml/hr. The columns were operated at ambient temperature. The UV detectors were set at 254 nm. The LC chromatograms were obtained by injecting generally 0.5 ul aliquots of the collecting solution.

(4) Mass Spectrometry

Mass spectra were obtained through the courtesy of Dr. Field of the Rockefeller University Biotechnology Mass Spectrometric Research Resource. A DuPont 21-492 magnetic deflection mass spectrometer with a chemical ionization source was used. Isobutane was the reagent gas. The total pyrolyzate sample, dissolved in cyclohexane, was analyzed directly using programmed heating of the sample probe. The LC peaks, dissolved in aqueous acetonitrile, were extracted into 1 ml of dichloromethane, condensed to 10 ul, and analyzed using the heated sample probe.

(5) Sample

The polystyrene samples were taken from a commercially available clear plastic cup. To ascertain purity, infrared (IR)

spectra of the polymer were obtained after two different treatments. First, a sample was dissolved in cyclohexane and a film was cast on a watch-glass. The IR spectrum was taken on this film in a standard IR film holder with a Perkin-Elmer 252 spectrometer. The second IR spectrum was obtained after dissolving a sample in benzene, precipitating the polymer with methanol, and repeating this three times. The washed sample was then dissolved in dichloromethane and precipitated with methanol, again repeating this process three times. Finally the sample was washed with methanol and dried at ambient temperature, dissolved in cyclohexane, and a film cast as above. The two IR spectra were identical, and matched the standard IR spectrum of polystyrene used to calibrated spectrometers; therefore we believe this polystyrene contains no additives.

In addition, the gel permeation chromatogram (GPC) of the untreated sample shows only the rather symmetrical elution peak of polystyrene, which further confirms the purity of the sample. The molecular weights obtained by GPC are $M_w = 2.61 \times 10^5$ and $M_n = 1.01 \times 10^5$. The GPC results were obtained through the courtesy of Dr. Odian of the City University of New York.

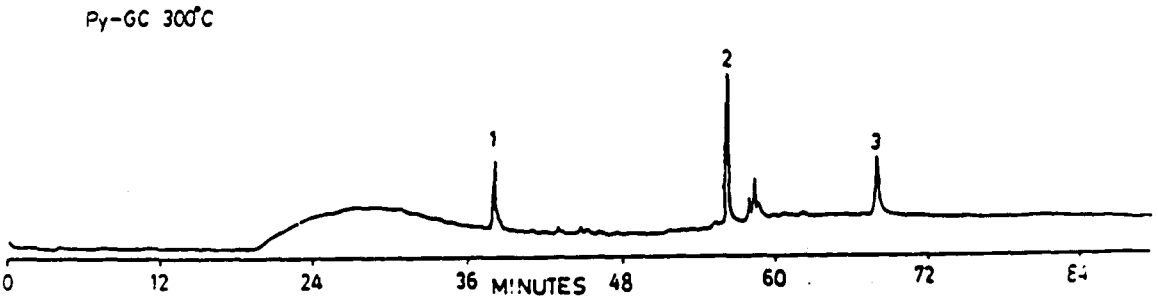

Figure 6. Py-GC chromatogram of 300°C pyrolysis products of polystyrene. Capillary GC conditions: 17 m x 0.25 mm I. D. glass column wall-coated with OV-101; 5 ml He/min; temperature programmed after initial 5 min hold at 36°C, at 4°C/min to 250°C with 50 min final hold; FID detector response set at range 10 x 8; main peaks are (1)styrene, (2) 2,4-diphenyl-1-butene, and (3) 2,4,6-triphenyl-1-hexene.

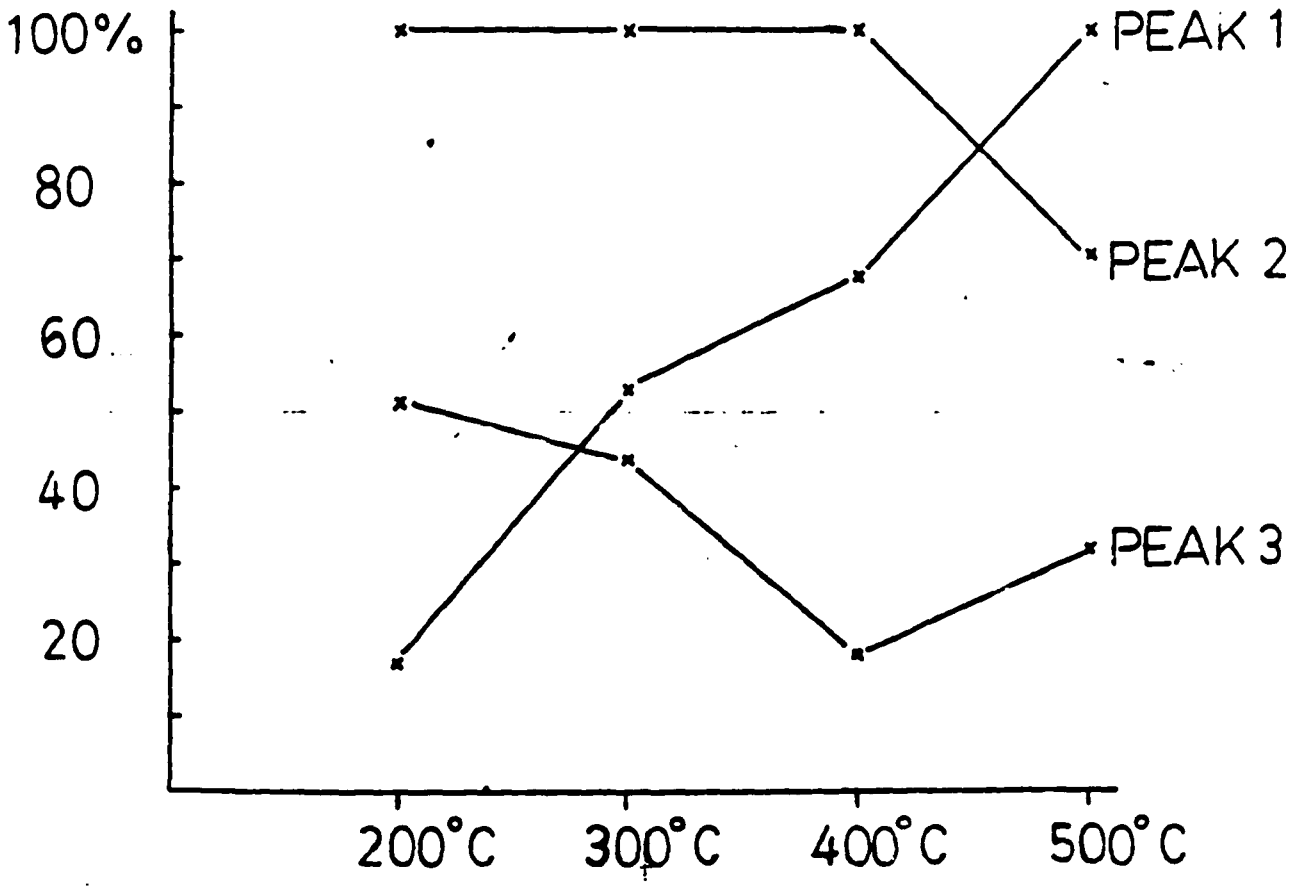

Figure 7. Relative GC peak heights of monomer, dimer, and trimer as a function of pyrolysis temperature.

IV. RESULTS AND DISCUSSION

As shown in Figures 6-10, the complexity and distribution of pyrolysis products increases with increasing pyrolysis temperatures, especially above 500-600°C. The capillary GC of the 300°C pyrolyzate is reproduced in Figure 6. The compounds evolved at the lower temperatures are probably a combination of pyrolysis products and distillates of lower molecular-weight oligomers. The broad, low peak near the start of the gas chromatograms is a spurious peak associated with the temperature program. Three major peaks, whose identification is discussed below, are observed for the stepwise pyrolyses at 200°C, 300°C, 400°C, and 500°C. The 300°C chromatogram is typical, but as shown in Figure 7, a plot of relative peak heights of the three major peaks (numbered 1, 2, and 3) at each temperature as a function of stepwise pyrolysis temperature, there are changes in the distribution of these major products; there are some minor differences as well in the minor products. Figure 8 is the gas chromatogram of the 700°C pyrolysis products, and is typical of the pyrolyses at temperature higher than 600°C. There are clear differences in the complexity and distribution of both major and minor peaks in the higher temperature pyrolyses.

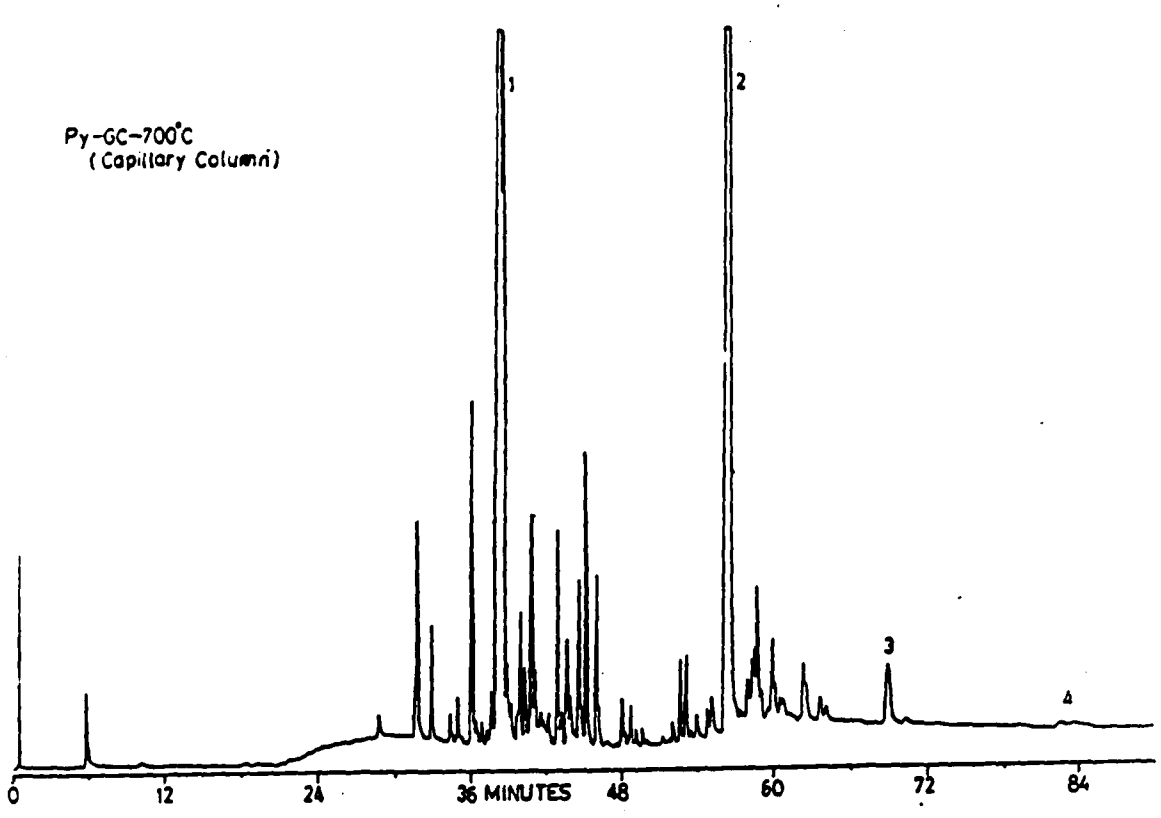

Figure 8. Py-GC chromatogram of 700°C pyrolysis products of polystyrene. Capillary GC conditions same as Figure 3. Peak 4 is 2,4,6,8-tetraphenyl-1-octene.

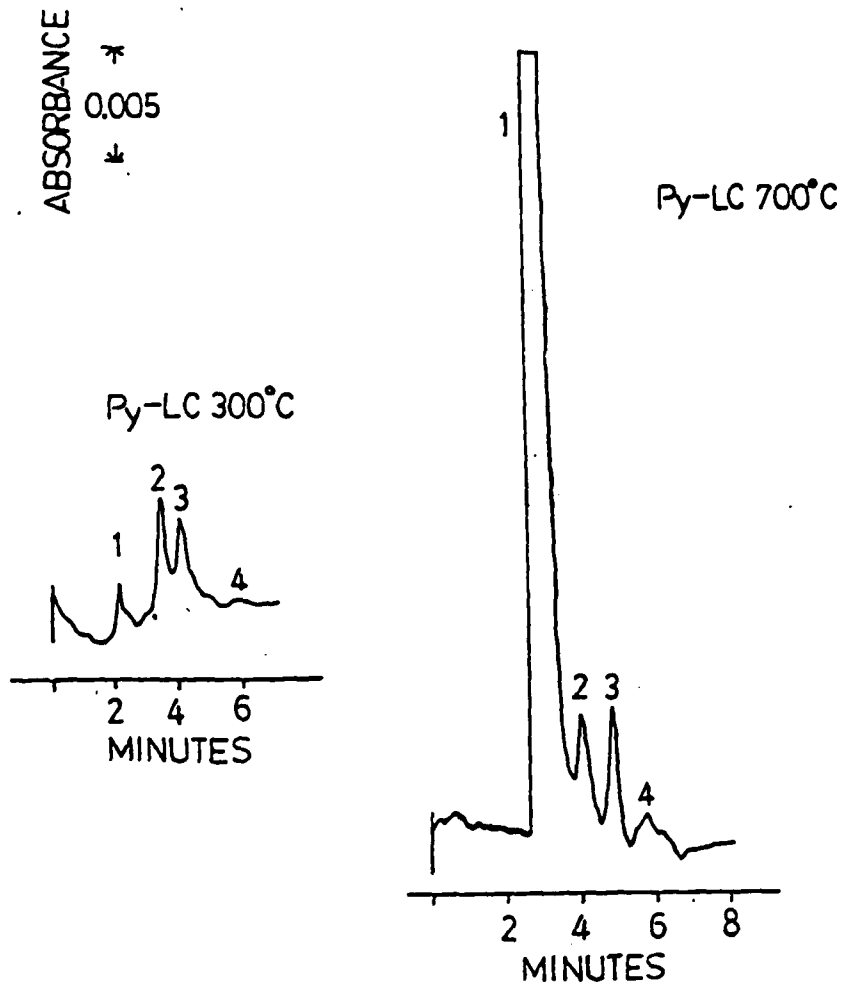

Figure 9. Py-LC chromatograms of 300°C and 700°C pyrolysis products of polystyrene. HPLC conditions: 25 cm x 2 mm I.D. Varian Micropak CH-10 reversed-phase column; 25 ml/h of acetonitrile-water (90:10); UV detector set at 254 nm; 0.5-ul sample injected.

The HPLC chromatograms of the 300°C and 700°C pyrolysis products, representative of the lower and higher temperature chromatograms, respectively, are shown in Figure 9. Peak identifications are discussed below. As in the gas chromatograms, yield and complexity increase with increasing pyrolysis temperature. The peaks eluting from the LC, however, are of higher molecular weight than those from the GC.

In stepwise pyrolysis, which involves heating the same sample sequentially to increasing temperatures, one would expect total chromatographable yield to maximize at a certain temperature as the polymer is sequentially degraded. This is in fact observed in Figure 10. We also observed the same phenomena for stepwise pyrolysis-mass spectrometry, which is described in chapter four of Part One. Relative total yields of pyrolysis products for each pyrolysis temperature from 200°-900°C at 100°C intervals were determined as follows. Pyrolysis time at each temperature was 10 sec, and pyrolysis products were trapped by bubbling through solvent traps containing 10 ml of cyclohexane. A 1-ul aliquot of each pyrolyzate solution was injected into the liquid chromatograph with a 2 ft. length of 1/16 in. O.D. stainless-steel tube replacing the LC column, using 1 ml/min of hexane eluent, and the UV detector set at 254 nm. Relative yield was assumed to be proportional to the peak height of the resulting peak. The results, in Figure 10, show increased yields above 500°C, with maximum yield near 700°C, which correlates well with the chromatographic results.

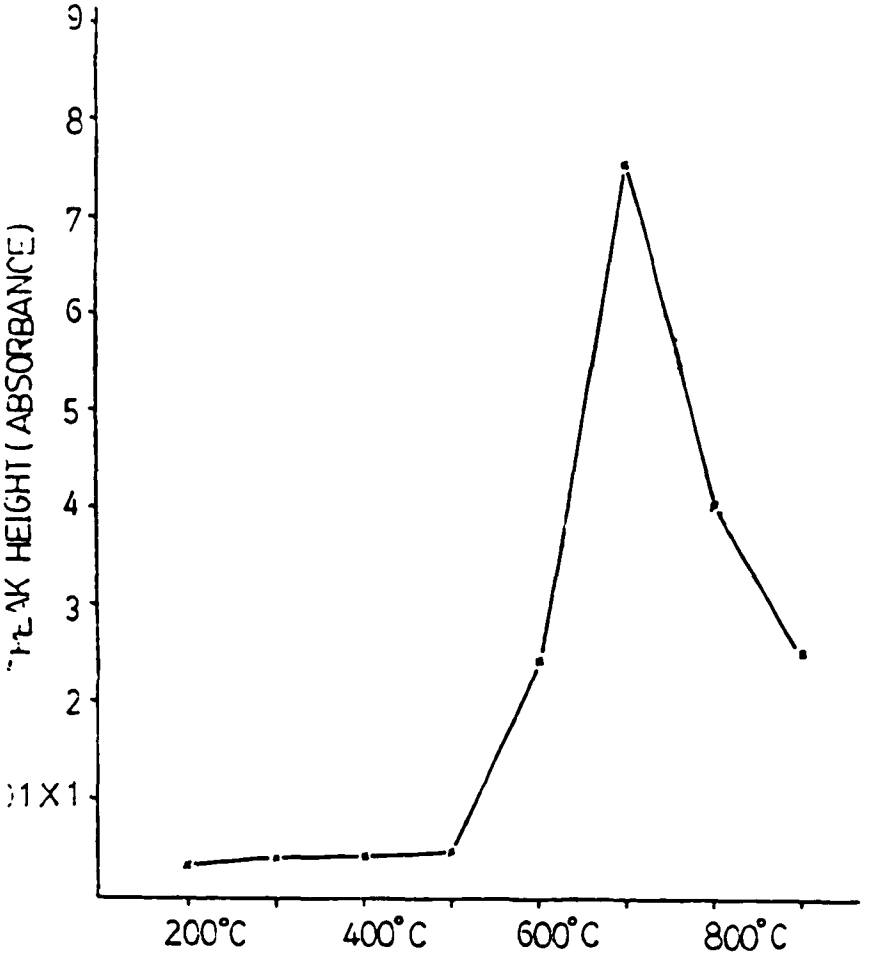

Figure 10. Total recoverable pyrolyzate yield as a function of pyrolysis temperature. See text for method of determination.

To determine whether pyrolyzate was left in the interface, 2.5 ml of cyclohexane was used to rinse out the interface and connecting tubing, following sequential pyrolysis of a polystyrene sample in the usual manner. A 0.5-ul aliquot was injected into the liquid chromatograph, giving rise to the chromatogram in Figure 11. As might be expected, there is condensation of considerable amounts of pyrolyzate in the interface. Clearly a redesign of the interface between pyrolyzer and collector is indicated. In addition, for Py-GC, the interface should be cleaned regularly to prevent artifacts in the pyrogram and to avoid loss of volatile pyrolyzate by dissolution into or adsorption onto the condensate. The criteria for the future design of the interface should include (i) rapid transfering of pyrolysis products out of heating zone, (ii) constructing the inside wall of interface with inert materials, such as glass,quartz, etc., and (iii) a easy way for frequent rinsing of the interface with solvents.

To test for quantitative transfer of pyrolyzate from the collector tube and guard tube in the GC inlet to the GC column, after a normal GC run of a 700°C pyrolyzate, the collector tube and guard tube were removed and rinsed with 10 ml of cyclohexane. A 1.0-ul aliquot was analyzed in the same fashion as described above for the determination of total pyrolysis yield as a function of temperature. About 12% of the pyrolyzate is in fact retained in the collector tube, and about 1-2% in the guard tube.

This further confirms that the LC provides access to the study of the higher molecular weight, less volatile portion of the pyrolyzates.

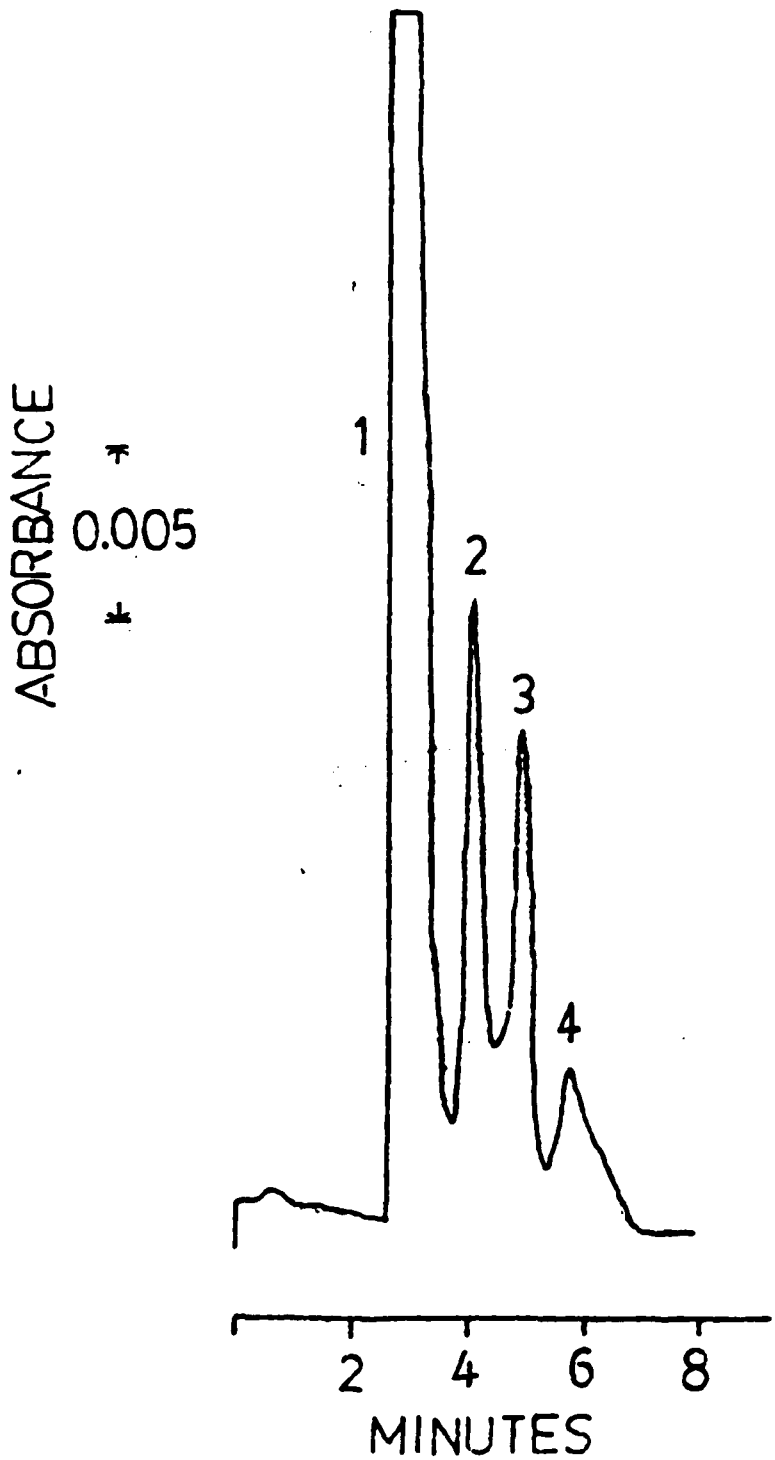

Figure 11. LC chromatogram of rinsing of heated interface after pyrolysis. Solvent: 10 ml cyclohexane. HPLC conditions as for Figure 9.

Although most of the solvent-trapping results reported here were obtained using cyclohexane, several other solvents were evaluated for efficiency of trapping. The efficiency is defined as the ratio of the weight trapped to the weight loss on pyrolysis. The latter was determined gravimetrically. The weight trapped was determined spectrophotometrically at 254 nm in the trapping solution, assuming the molar absorptivity of the pyrolyzate equals that for styrene. For cyclohexane, the trapping efficiency is 67%; one third of the pyrolysis products never reach the trap from the interface, or are not condensed in the solvent trap. Figure 12 shows the amount of 700°C pyrolyzate trapped, determined using the blank column chromatographic method described above, increases linearly with pyrolysis time; the trapping efficiency increases in the order of n-hexane, dichloromethane, cyclohexane, carbon tetrachloride, 2-propanol (IPA), and acetonitrile (ACN). The % efficiency of each solvent can be calculated from this plot and the known efficiency of cyclohexane, e.g. ACN is 80% efficient. In similar fashion, the trapping efficiencies of the glass microbead trap and a trap packed with glass wool were determined to 15% and 3%, respectively. Again, trapping efficiency must be balanced against desorption efficiency.

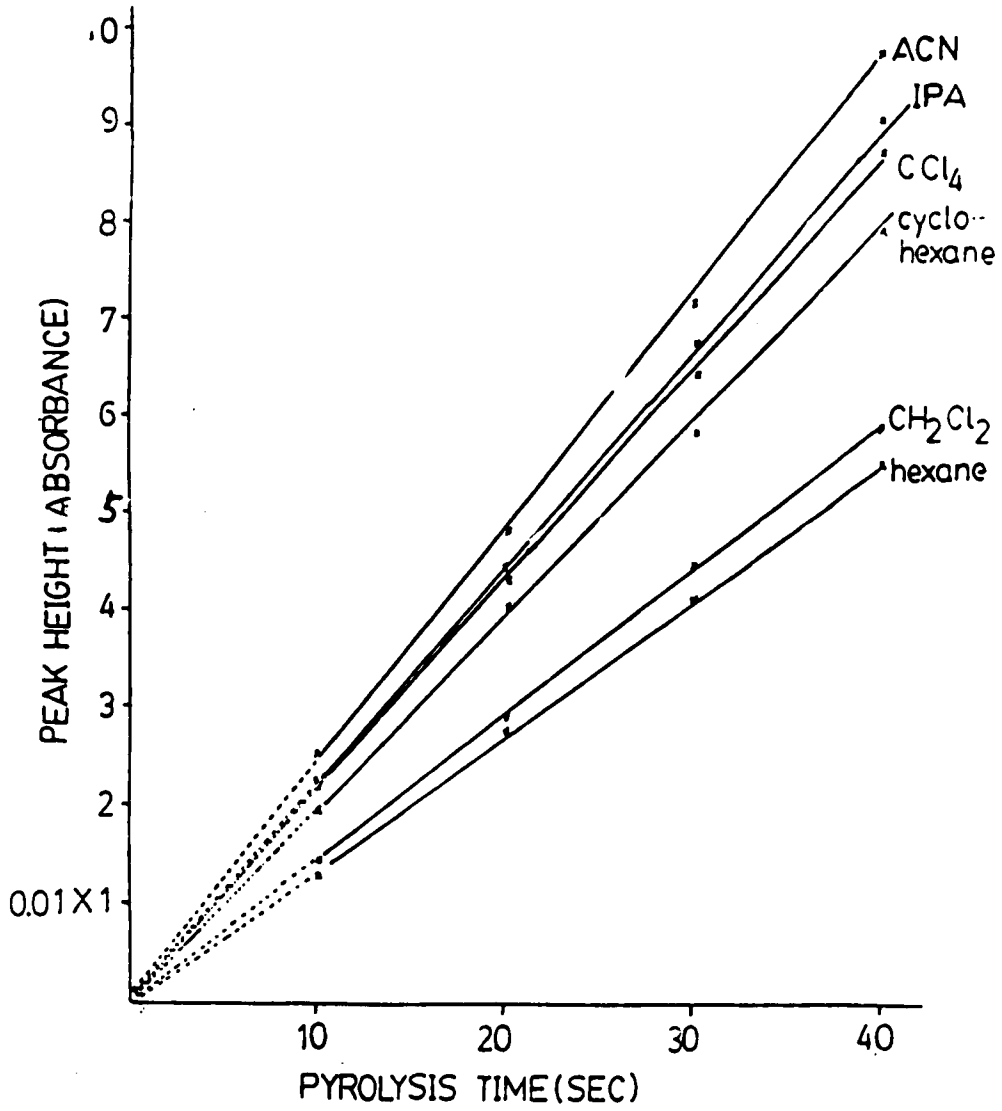

Figure 12. Trapping efficiencies of several solvents.

GC peaks were identified using retention data. The three main peaks in Figures 6 and 8 were identified by comparison with literature data [29,30] as styrene, 2,4-diphenyl-1-butene, and 2,4,6-triphenyl- 1-hexene; the styrene identified was confirmed by chromatographing pure styrene. In addition to the main peaks in the higher temperature pyrograms, compounds such as ethyl benzene and 3-phenyl-1-propene elute near styrene; 1,4-diphenyl-1-butene and 1,4-diphenyl-butane near 2,4-diphenyl-1-butene [29]. At the highest pyrolysis temperatures a small peak (numbered 4 in Figure 8) appears, probably corresponding to a quadrimer, e.g. 2,4,6,8-tetraphenyl-1-octene, but the volatility of this compound is close to or less than the limit that GC can handle.

For the LC chromatograms, GC and MS were used for peak identification. Peak 1 in Figure 9 was studied as follows. The 700°C pyrolyzate was collected in 2.5 ml of cyclohexane, a 0.5-ul aliquot injected into a glass microbead-packed collector tube, and the cyclohexane evaporated in a stream of nitrogen. The tube was inserted into the GC inlet as described above to produce the chromatogram in Figure 13A. A 0.5-ul aliquot of the same cyclohexane solution of pyrolyzate was injected into the liquid chromatograph, the first peak collected, injected into a glass microbead collector tube, and following the same procedure, the chromatogram in Fig. 13B was obtained. It is clear that the first LC peak corresponds to the first three GC peaks. Figures 8 and 13A differ in apparent sensitivity only because a smaller portion

of the pyrolyzate was analyzed in the latter case. It is also demonstrated here that Py-GC has a better resolution for the pyrolytic fragments of lower molecular weight. However, Py-LC can provide additional information for the pyrolysis products of higher molecular weight.

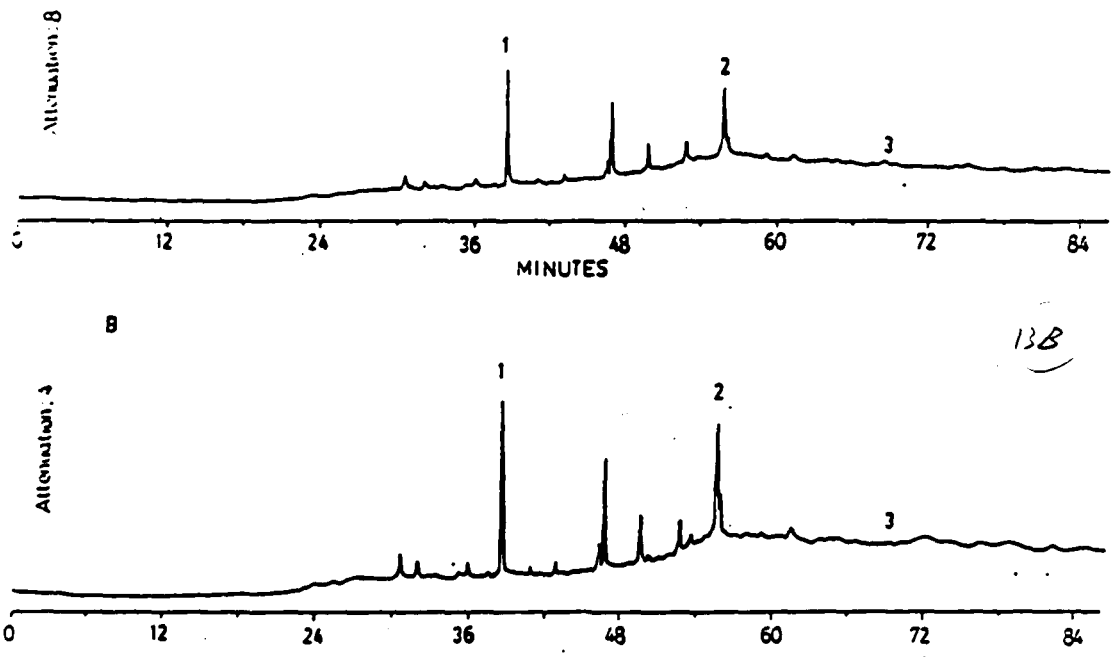

Figure 13. Pyrolysis-GC chromatogram of pyrolyzate at 700°C collected by bubbling pyrolyzer effluent through cyclohexane. (A) GC of cyclohexane solution. GC condition as of Figure 3. (B) GC of first HPLC peak of same cyclohexane solution.

Chemical Ionization-Mass Spectrometry (CI-MS) was applied to the four LC peaks and also to a sample of total 700°C pyrolyzate collected in cyclohexane. CI-MS with isobutane yields strong peaks at m/z values of M - 1, M, and M + 1 (M = mass of fragment), and relatively little fragmentation. For the total pyrolyzate, MS peaks with intensities less than 3% of the base peak were subtracted manually, and remaining peaks plausibly identified using the M - 1, M, and M + 1 peaks. Table 5 lists the compounds identified tentatively in this manner. Only one of the several possible isomers are listed, e.g. the peak at m/z = 208 could be 2,4-diphenyl-1-butene and/or 1,4-diphenyl- 1-butene and/or the 1,3- and/or the 2,3- isomer, etc. About one-third of these were identified previously [29,30]. Compounds heavier than hexaphenylundecene (mol. wt. = 613) were not observed, probably because the maximum sample probe temperature was 240°C, and in any case the mass spectral scan stopped at m/z = 700.

The mass spectra of the compounds in the LC fractions were simplified by subtracting manually peaks smaller 15% of the base peak. These are presented in Figure 14. Compounds up to quadrimer (mol. wt. = 416) were found in the first LC fraction, confirming the GC analysis. The pentamer (mol. wt. = 520) was found in the later peaks, and hexaphenylundecene in the third LC peak. Absence of the higher oligomers is probably accountable in terms of the reasons above, and in addition the total amounts of pyrolyzates diminish with increasing molecular weight; the

concentration of the higher oligomers in the later peaks may be below the mass spectral sensitivity. In any case it is clear in Figure 14 that the distribution of products shifts to higher m/z values with increasing LC retention time.

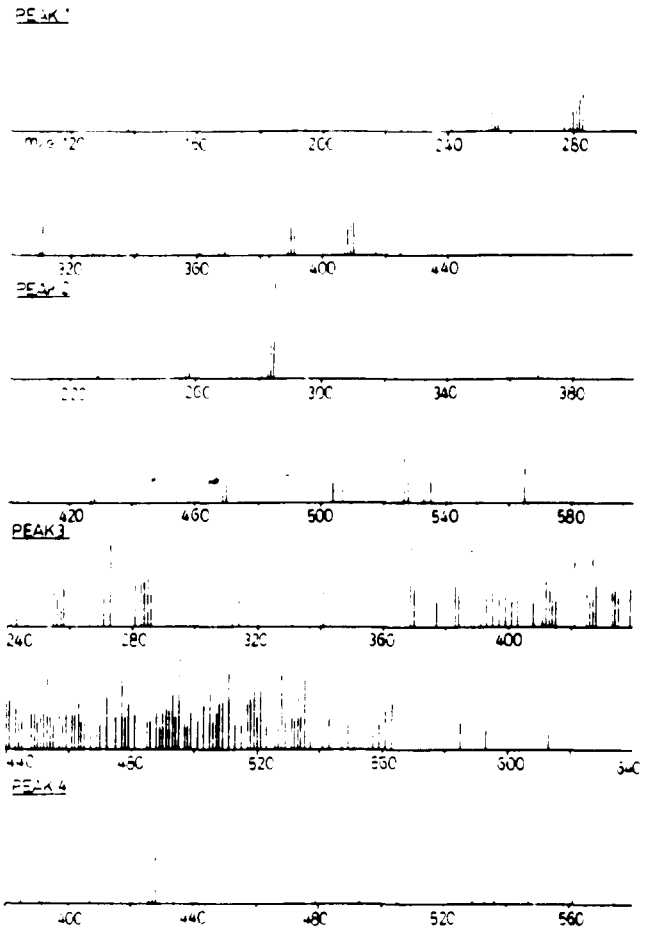

Figure 14. Simplified mass spectra of four LC peaks of 700°C pyrolysis of polystyrene.

Table 5

TENTATIVE IDENTIFICATION OF COMPOUNDS IN 700°C PYROLYZATE OF POLYSTYRENE USING CI-MS

Mol.wt.	% of Base Peak			Tentative Identification
M	M-1	M	M+1	
92	18	-	6	Toluene
104	-	-	19	Styrene
106	19	-	7	Ethylbenzene
118	41	9	8	2-phenyl-1-propene
120	8	7	7	Cumene
132	11	-	9	1-phenyl-1-butene
146	-	-	5	1-phenyl-1-pentene
160	9	-	15	1-phenyl-1-hexene
174	4	-	6	1-phenyl-1-heptene
180	7	-	4	1,2-Diphenyl·ethylene
192	6	-	12	1,3-Diphenylallene
194	12	6	73	1,3-Diphenyl-1-propene
196	73	21	4	1,3-Diphenylpropane
202	-	-	7	1-phenyl-1-nonene
206	-	7	30	1,3-Diphenyl-1,3-butadiene
208	30	10	17	2,4-Diphenyl-1-butene (Dimer)
210	17	7	11	1,3-Diphenylbutane
216	7	-	6	1-Phenyl-1-decene

220	16	-	26	2,4-Diphenyl-1,4-pentadiene
222	26	9	9	2,4-Diphenyl-1-pentene
224	9	4	9	2,4-Diphenylpentane
234	27	4	59	2,5-Diphenyl-1,5-hexadiene
236	59	13	16	2,5-Diphenyl-1-hexene
244	5	-	-	1-Phenyl-1-dodecene
250	9	-	14	1,2-Diphenyl-1-heptene
258	19	4	5	1-Phenyl-1-tridecene
264	7	11	13	1,2-Diphenyl-1-octene
270	-	-	19	1,2,3-Triphenylpropene
272	19	4	30	1,2,3-Triphenylpropane
278	6	4	9	1,2-Diphenyl-1-nonene
284	29	9	19	1,2,3-Triphenyl-1-butene
286	19	9	5	1,2,3-Triphenylbutane
292	12	-	5	1,2-Diphenyl-1-decene
296	-	-	11	1,3,5-Triphenyl-1,4-pentadiene
298	11	7	15	1,3,5-Triphenyl-1-pentene
300	15	6	9	1,3,5-Triphenylpentane
306	-	-	8	1,2-Diphenyl-1-undecene
310	11	10	43	1,3,5-Triphenyl-1,5-hexadiene
312	43	39	36	2,4,6-Triphenyl-1-hexene (Trimer)
314	36	14	35	1,3,5-Triphenylhexane
320	4	6	-	1,2-Diphenyl-1-dodecene
324	7	4	20	2,4,6-Triphenyl-1,6-heptadiene
326	20	6	13	2,4,6-Triphenyl-1-heptene

328	13	10	16	2,4,6-Triphenylheptane
334	6	-	16	1,2-Diphenyl-1-tridecene
338	10	-	9	2,5,7-Triphenyl-1,7-octadiene
340	9	-	9	2,5,7-Triphenyl-1-octene
348	-	-	7	1,2-Diphenyl-1-tetradecene
354	6	-	12	1,2,3-Triphenyl-1-nonene
358	-	7	5	1,2,3,4-Tetraphenyl-1,3-butadiene
360	5	4	-	1,2,3,4-Tetraphenyl-1-butene
362	-	-	10	1,2,3,4-Tetraphenylbutane
368	16	13	100	1,2,3-Triphenyl-1-decene
374	10	7	4	1,2,3,4-Tetraphenyl-1-pentene
382	7	4	13	1,2,3-Triphenyl-1-undecene
386	14	-	-	1,2,4,6-Tetraphenyl-1,5-hexadiene
388	-	4	9	1,2,4,6-Tetraphenyl-1-hexene
396	11	-	-	1,2,3-Triphenyl-1-dodecene
400	9	11	8	1,3,5,7-Tetraphenyl-1,6-heptadiene
402	8	-	7	1,3,5,7-Tetraphenyl-1-heptene
404	7	-	6	1,3,5,7-Tetraphenylheptane
410	20	4	33	1,2,3-Triphenyl-1-tridecene
414	7	10	9	1,3,5,7-Tetraphenyl-1,7-octadiene
416	9	-	11	2,4,6,8-Tetraphenyl-1-octene (Quadrimer)
418	11	-	-	1,3,5,7-Tetraphenyloctane
424	7	-	14	1,2,3-Triphenyl-1-tetradecene
428	55	12	14	2,4,6,8-Tetraphenyl-1,8-nonadiene
430	14	-	14	2,4,6,8-Tetraphenyl-1-nonene

432	14	-	15	2,4,6,8-Tetraphenylnonane
438	-	4	11	1,2,3-Triphenyl-1-pentadiene
442	-	4	7	2,4,7,9-Tetraphenyl-1,9-decadiene
444	7	-	17	2,4,7,9-Tetraphenyl-1-decene
448	14	7	14	1,2,3,4,5-Pentaphenyl-1,4-pentadiene
450	14	14	14	1,2,3,4,5-Pentaphenyl-1-pentene
452	14	-	-	1,2,3,4,5-Pentaphenylpentane
458	5	-	7	1,2,3,4-Tetraphenyl-1-undecene
472	5	5	5	1,2,3,4-Tetraphenyl-1-dodecene
478	23	16	32	1,2,3,4,5-Pentaphenyl-1-heptene
486	9	-	5	1,2,3,4-Tetraphenyl-1-tridecene
490	9	-	25	1,2,4,6,8-Pentaphenyl-1,7-octadiene
492	25	9	19	1,3,5,7,8-Pentaphenyl-1-octene
500	-	-	9	1,2,3,4-Tetraphenyl-1-tetradecene
504	10	4	26	1,3,5,7,9-Pentaphenyl-1,8-nonadiene
506	26	9	27	1,3,5,7,9-Pentaphenyl-1-nonene
508	27	19	11	1,3,5,7,9-Pentaphenylnonane
518	6	-	13	1,3,5,7,9-Pentaphenyl-1,9-decadiene
520	13	10	19	2,4,6,8,10-Pentaphenyl-1-decene (Pentamer)
522	19	-	-	1,3,5,7,9-Pentaphenyldecane
532	24	10	20	2,4,6,8,10-Pentaphenyl-1,10-undecadiene
534	20	14	23	2,4,6,8,10-Pentaphenyl-1-undecene
536	23	14	14	2,4,6,8,10-Pentaphenylundecane
546	7	-	15	2,4,6,8,11-Pentaphenyl-1,11-dodecadiene
548	15	13	16	2,4,6,8,11-Pentaphenyl-1-dodecadiene

554	-	9	-	1,2,3,4,5,6-Hexaphenyl-1-heptene
562	17	7	11	1,2,3,4,5-Pentaphenyl-1-tridecene
576	-	-	13	1,2,3,4,5-Pentaphenyl-1-tetradecene
582	-	-	12	1,2,3,4,5,6-Hexaphenyl-1-nonene
590	-	8	-	1,2,3,4,5-Pentaphenyl-1-pentadecene

V. SUMMARY

In general, products of pyrolysis are temperature dependent. At lower temperatures, most of the pyrolytic products are evidently the distillates, i.e. small trapped fragments. At higher temperatures, the products of pyrolytic decomposition vary with pyrolyzing temperature. For the low boiling point products (up to the elution limit of GC), stepwise Py-GC offers a series of fingerprint-type pyrograms. It is quite obvious that the pyrogram based on one temperature pyrolysis is not adequate to represent the entire picture of polymer structure. Py-LC can provide data on the higher molecular weight products. Consequently, more information of structure and the thermal degradation process can be obtained by combining stepwise Py-GC and Py-LC.

The potential of Py-LC for charactering polymers has been demonstrated here. Improving the resolution of HPLC is a major requirement for the future development of Py-LC method. We have pointed out earlier in the section II of this chapter that rapid separation and high resolution are two major advantages of microbore column LC. Thus, this should be studied in reference to Py-LC. For the moment, the small injection volume (nl) is a technical problem in open tubular column LC. However, a small injection volume is an advantage when only trace amounts of samples are available, e.g. in forensic studies.

We have also demonstrated that off-line Py-LC-MS is useful for identifying pyrolytic fragments. Consequently, the other prospect for the develpment of Py-LC is on-line Py-LC-MS system. This would be particularly useful for structure analysis and thermal degradation studies of natural and synthetic polymers.

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CHAPTER III

PYROLYSIS-FLUORESCENCE

I. INTRODUCTION

Fluorescence is a more selective analytical method than UV absorption because only a relatively small number of compounds that absorb also fluoresce. Fluorescence spectroscopy could be useful in the study of nonfluorescing polymers that produce fluorescent pyrolysis products. For example, poly(vinyl chloride) (PVC) does not fluorese; however the thermal degradation of PVC produces fluorescent compounds such as benzene and trace amount of polycyclic aromatic hydrocarbons (PAHs) [1,2]. Evidently, HCl is produced in the initial decomposition state, and benzene is subsequently formed through a six-membered transition state as the major product [1]. Fluorescence spectroscopy could also be useful in matters of environmental concern. For example, the formation of PAHs in the incineration process could be easily monitored using fluorescence detection. Similarly, 2,3,7,8-tetrachlorodioxin, which recently become a substance of major environmental concern,can evidently be formed in small but environmentally significant quantities in pyrolytic reactions from such common chemicals as the chlorinated phenols and chlorobenzenes [3,4]. Recent studies show that polychlorinated dibenzo-p-dioxins are present in fly ash emissions from municipal incinerators and industrial power facilities [5-9]. Thus

pyrolysis in an appropriate atmosphere, followed by fluorescence monitoring of the products, might provide a rapid initial testing method to determine whether a large scale incineration of certain organic compounds and polymers under various conditions is acceptable. Further identification can then be conducted through Py-LC and Py-GC methods, or GC-MS and LC-MS methods.

This pyrolysis-fluorescence technique has not until now been reported for monitoring pyrolysis processes. Here we demonstrate that the formation of fluorescent compounds during the pyrolysis processes can be quickly detected. Typically, the whole pyrolysis-fluorescnece analysis takes less than 10 min.

II. EXPERIMENTAL

(1) PYROLYSIS

Pyrolysis was carried out both in an enclosed system and a continuous flow system. For the enclosed system, about 2 mg of sample was sealed inside a glass tube (15 mm x 2.0 mm o.d.), and pyrolyzed at 400°C for 4 min, using a CDS Pyroprobe 100 pyrolyzer with a Pt coil 15 mm x 3.0 mm o.d. x 2.0 mm i.d., and a 200°C heated interface (Chemical Data Systems, Oxford, PA.). After pyrolysis, the glass tube was broken in a 5 ml isooctane solvent bath, and the solution analyzed.

In the continuous flow system, the same amount of sample was loaded into a quartz sample tube (15 mm x 3.0 mm o.d.), and pyrolyzed at 400°C for 4 min. The Pyrolysis products were swept out of the 200°C interface with the He at 30 ml/min, and collected by bubbling the effluent from the pyrolyzer interface through a 1/16 in. O.D. stainless-steel tube into 5 ml of isooctane. After pyrolysis, the pyrolyzer was cooled to ambient temperature and another 5 ml isooctane was used to rinse the interface and the remaining residue in the quartz tube. These isooctane solutions were also analyzed separately. In both systems, considered amounts of residue remained undissolved.

(2) FLUORESCENCE

A Perkin-Elmer 650-10S Fluorescence Spectrophotometer was used with a Perkin-Elmer Hitachi 057 x-y recorder. The small 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.

(3) HPLC

A Varian 8500LC was used with a Varian 25 cm x 2 mm i.d. Al-10-Micropak column for isocratic runs using 20 ml/hr of isooctane at ambient temperature. The Varian UV detector was set at 254 nm. Aliquots (1.0 ul) of the pyrolyzates of polystyrene were injected.

(4) SAMPLES

A polystyrene standard of molecular weight 1.8×10^6 from Alfa polystyrene standard kit, and samples of Porapak P and Q (Water Associates, MA) were analyzed. Porapak P is a cross-linked polymer of divinylbenzene, ethylvinylbenzene and styrene, and Porapak Q is a cross-linked polymer of divinylbenzene and ethylvinylbenzene. Divinylbenzene is used as a cross-linker for the formation of cross-linked structure for Porapaks P and Q.

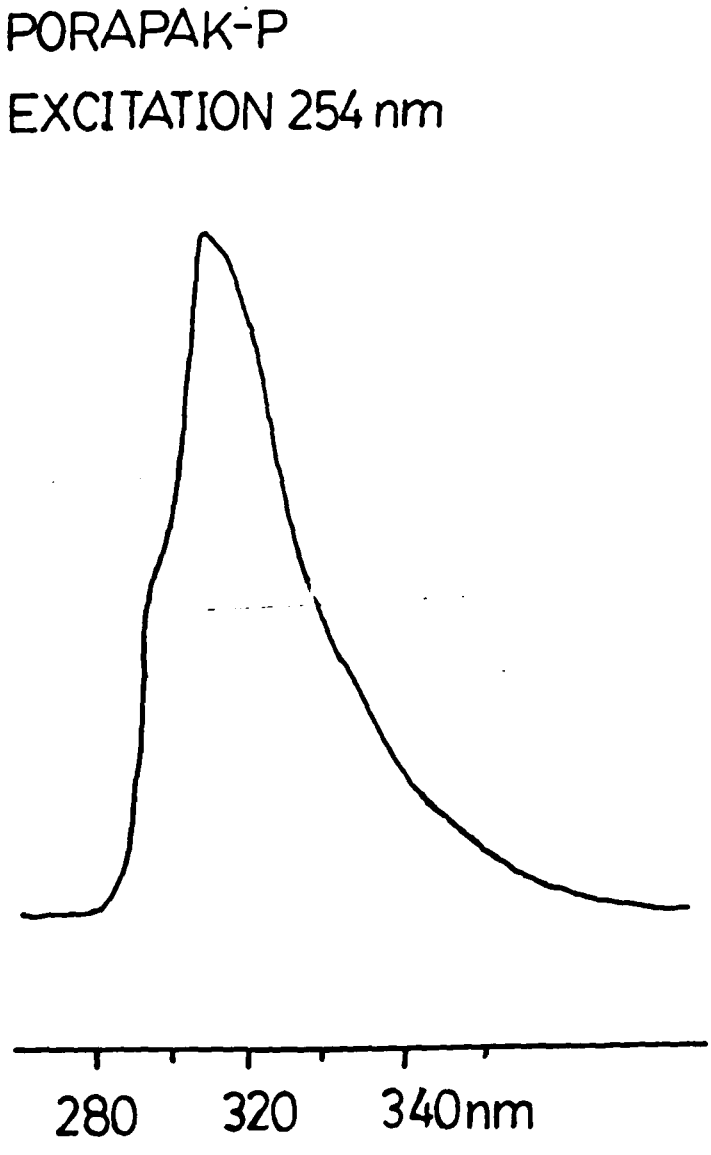


Figure 1. Fluorescence spectrum of the pyrolysis products of Porapak P at 400°C.

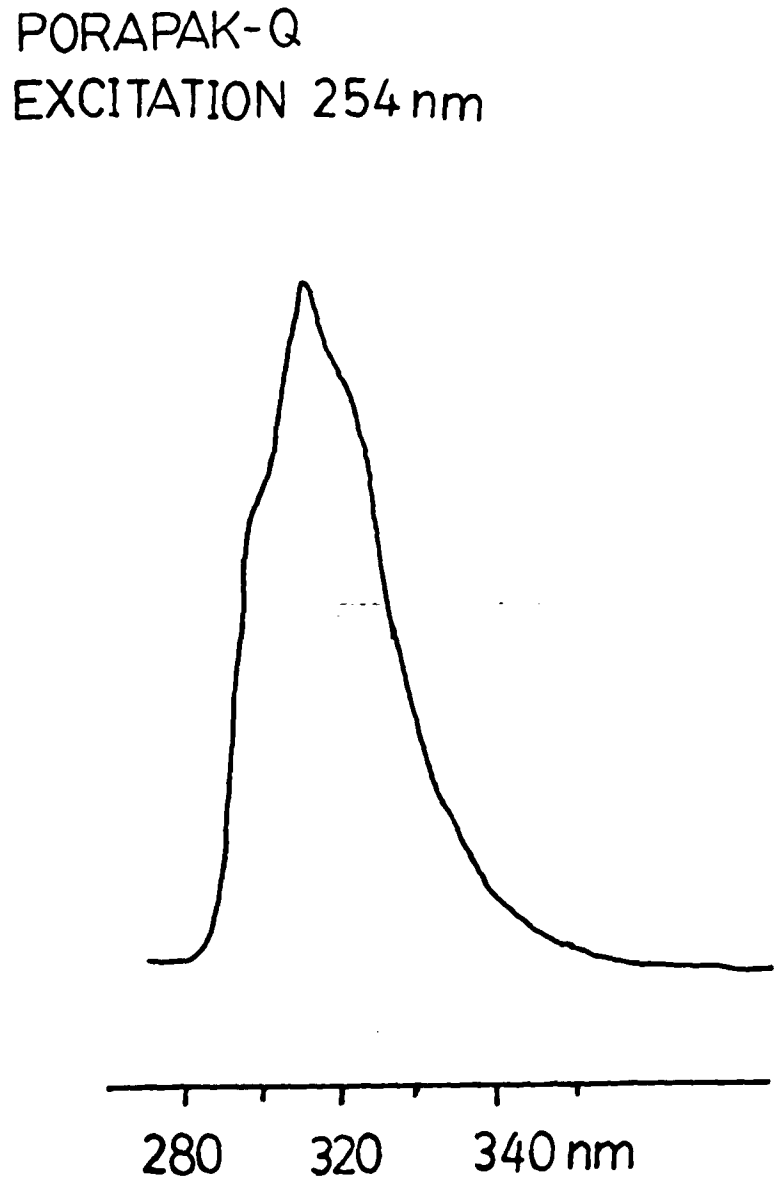


Figure 2. Fluorescence spectrum of the pyrolysis products of Porapak Q at 400°C.

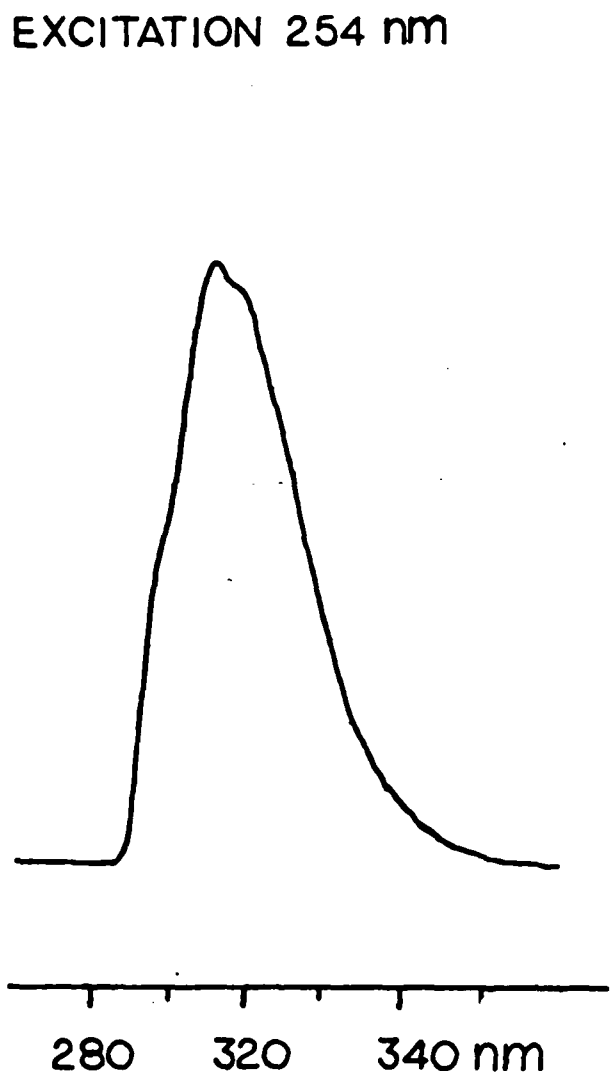
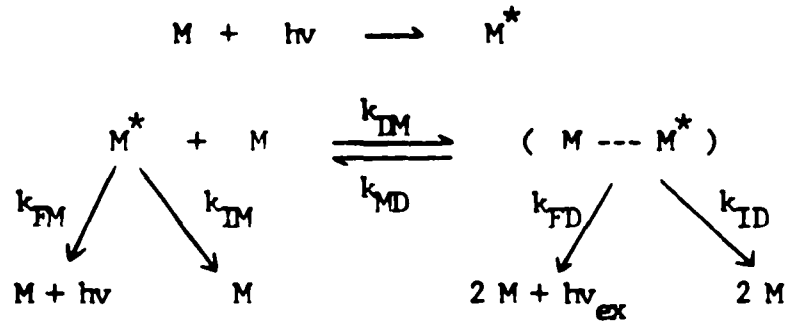


Figure 3. Fluorescence spectrum of the pyrolysis products of Polystyrene (M.W. = 1.8×10^6) at $400^{\circ}C$.

III. RESULTS AND DISCUSSION

Figures 1, 2, and 3 show the fluorescence spectra of the pyrolysis products of Porapak P, Porapak Q, and PS 1.8×10^6 using the continuous flow system. It is interesting to observe that there are two emission bands in these fluorescence spectra. The band at 290 nm corresponds to molecular fluorescence band of the pyrolysis products themselves. The band at 320 nm corresponds to excimer emission from the pyrolysis products. Excimer formation in polystyrene of high molecular weight was first reported by Yanari and Bovey [10]; small aromatic molecule excimer emission has been discussed by Birks [11]. In Part Two, excimer emission from lower molecular weight styrene oligomers [12] is disscussed. This is the first report of excimer formation in pyrolysis products of linear and cross-linked polystyrenes.

Excimer formation has been observed in a number of aromatic vinyl polymers. Birks proposed a kinetic scheme for the processes involved in the excimer formation, as depicted in the following.



k_{FM} : radiative decay of excited monomer emission

k_{IM} : nonradiative decay of excited monomer

k_{DM} : excimer formation from an excited and a nonexcited monomer

k_{MD} : excimer dissociation into an excited and a nonexcited monomer

k_{FD} : radiative decay of the excimer

k_{ID} : nonradiative decay of the excimer into two ground state monomer

The excimer emission intensity in polymers is generally expressed as the excimer to monomer intensity ratio, I_e/I_m. In general, excimer emission intensity (i) is greater for iostactic than for atactic polymers (e.g. for polystyrene [13] and poly(p-methyl styrene) [14,15]); (ii) increases with polymer concentration in solution [16]; (iii) increases in the sequence: atactic < atactic oriented < isotactic amorphous < isotactic crystallized for polystyrene at 77K [17]. (iv) increases with molecular weight (e.g. for poly(1-naphthyl methacrylate) [18]; (v) decreases with temperature [18]; (vi) decreases with solution intrinsic viscosity, as shown in Table 1 [18]; and (vii) increases on addition of either polar (MeOH) or nonpolar (cyclohexane and heptane) solvents [18] to the poly(1-naphthyl methacrylate) polymer in $CHCl_3$ solution.

In general, tacticity has an effect on the formation of excimers. This has been attributed to the formation of more stable configurations about the carbon skeleton in the isotactic form. In crystalline polymer, intrachain regularity is the determining factor for the enhanced excimer emission intensity. Excimer intensity also depends on both intrinsic viscosity and composition of solvents. This clearly indicates that chain contraction on excimer emission is important, and one can consequently conclude from (vii) that the change in excimer intensity with solvent is not due to changes in the polarity or dielectric constant of the solvent. The molecular weight

dependence of excimer emission is due to the intramolecular interaction, which means chain length is important in providing a sufficient number of chromophore-chromophore interactions. The decrease of excimer intensity at higher temperature is due to low quantum yield.

Table 1

SOLUTION AND EMISSION PROPERTIES OF

POLY(1-NAPHTHYL METHACRYLATE)

IN VARIUOS SOLVENTS [18]

Solvent	[n]	I_e/I_m
EtOAc	0.040	3.67
toluene	0.116	3.19
$CHCl_3$/	0.125	2.81
cyclohexane (1:1,v/v)		
CH_2Cl_2	0.158	2.61
$CHCl_3$	0.184	1.44

HPLC separations were conducted on the polystyrene pyrolyzates of both pyrolysis systems (including the condensates and residues of continuous flow system). Figures 4 and 5 show the chromatograms on alumina using isooctane eluent at 20 ml/hr, with UV absorption and fluorescence detection, respectively. Different pyrolysis product distributions were obtained for these two pyrolysis systems. Using the chromatogram of a styrene oligomer standard (PS 800) as a reference (Figure in Part Two), it is seen in Figures 4 and 5 that the enclosed pyrolysis system yields a product distribution of lower molecular weight. This is presumably caused by the localization of primary pyrolysis products, and because the larger pyrolytic fragments break down into smaller compounds via secondary reactions. In the continuous flow system, larger insoluble pyrolytic fragments either condense inside the interface or remaine in the quartz tube. Stopped-flow fluorescence spectra were run for each LC peak. They all have similar fluorescence spectra as seen in Figure 3; only the emission intensity varies with corresponding concentration.

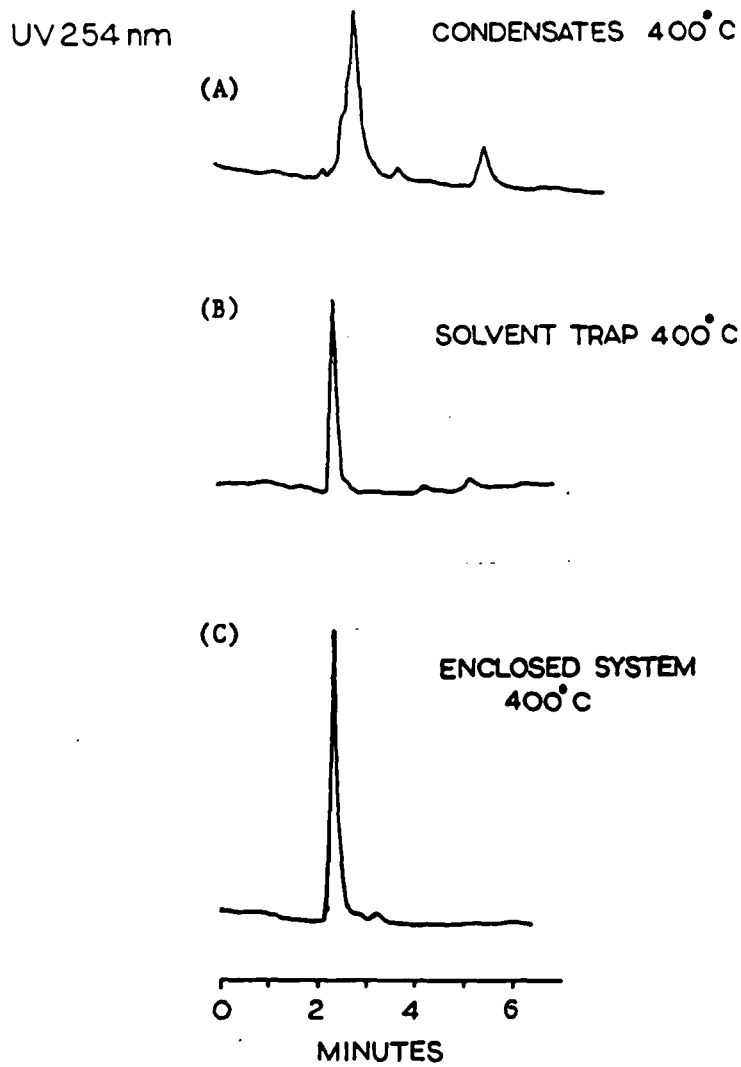


Figure 4. Py-LC chromatograms of 400°C of polystyrene; (A) the condensates left inside the smaple tube and interface and (B) the pyrolysis products trapped in 5 ml isooctane for a continuous flow system; (C) the pyrolysis products of enclosed system. UV detector: 254 nm

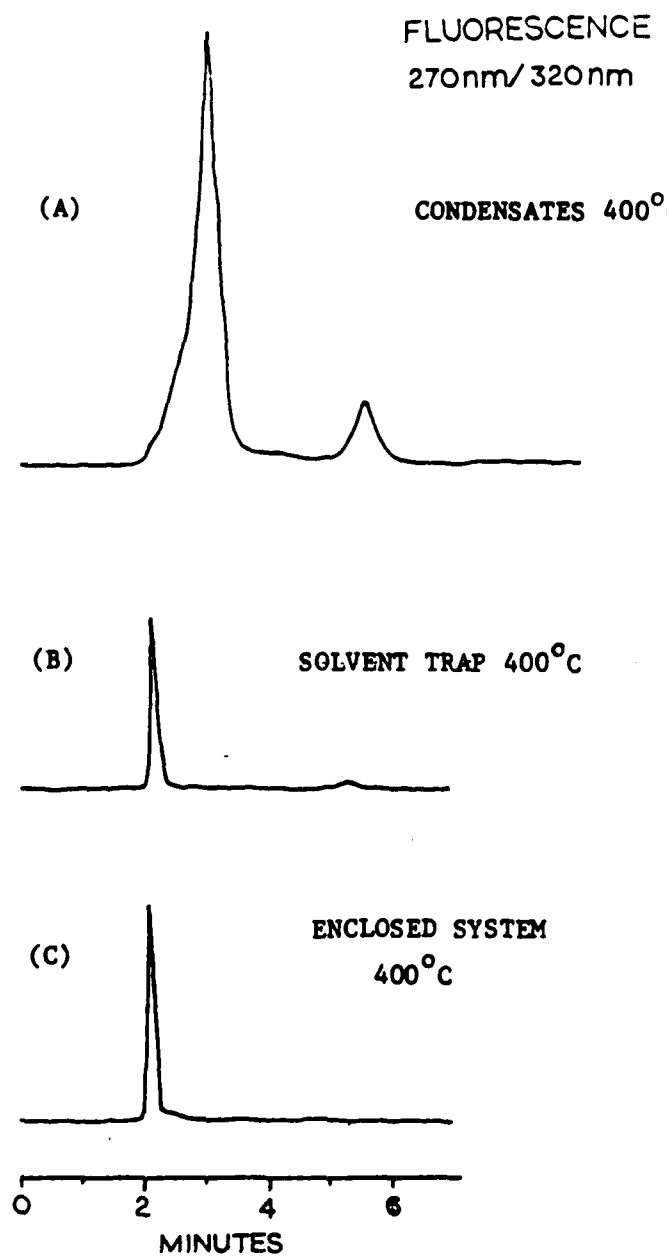


Figure 5. Py-LC chromatograms of 400°C of polystyrene. The conditions are the same as Figure 4 except using fluorescence detection.

IV. SUMMARY

Fluorescence is a sensitive and selective detection method for a limited number of polymers. However, fluorescence spectra of pyrolysis products do not give as much detailed information as for example infrared spectra. Fluorescence detection of pyrolysis products should be combined with other types of analytical methods, such as LC and GC, in order to obtain a more informative result.

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CHAPTER IV

PYROLYSIS-MASS SPECTROMETRY

I. INTRODUCTION

As mentioned in the first chapter of Part One, direct interfacing of the pyrolyzer to a mass spectrometer allows one, as does HPLC, to look at higher molecular weight fraction of the pyrolyzates. For example, Udseth and Friedman [1] used both electron impact (EI) and chemical ionization (CI) mass spectrometry to detect polystyrene evaporating from a probe filament heated at $1000^{o}/s$. They found extensive fragmentation for EI conditions, and styrene oligomers up to n=11 (n is the degree of polymerization) were detected; under CI conditions using Argon as the reagent gas, oligomers up to n=27 were detected. Attempts were made earlier [2] to study low molecular weight styrene oligomers, using a direct heated insert probe. Later, Coloff and Vanderborth [3] used laser pyrolysis and time of flight mass spectrometry for rapid analysis of degradation products. More recently, Lattimer et al. [4] used field desorption (FD) ionization to identify the styrene oligomers separated by liquid chromatography. In the field desorption method, a thin layer of the sample is placed directly onto the emitter wire. Thermal effects are reduced since no oven is

required for sample vaporization. FD involves ionization by quantum mechanical tunneling, producing mainly molecular ions, with reduced fragmentation. A piece of razor blade or a fine, activated tungsten emitter wire (10 microns) is held at a high potntial (8–14 kV) and gives positive ions. The high potential gradient (10^7 -10^8 v/cm) produced on the tips of the needles on an activated emitter in the presence of a ground plane will deform the atomic potential wall of a molecule that an electron sees to such an extent that the probability of undertunneling that wall becomes quite high. This results in a quantum mechanical tunneling effect removing an electron from the molecule without imparting much excess energy. Although FD has excellent sensitivity it can not be used directly for GC-MS but can be used for trapped samples [5]. Matsuo et al. [6] have reported FD mass spectra of polystyrene samples with molecular weight peaks at 600, 2200, 4000, and 8000. Perfluorokerosene, perfluoro-t-butylazine and perfluorotriheptyltriazine [7] are now widely used as mass references in the mass range below 1000 amu with an electron impact ion source; perfluoroalkxyphosphazines [8] up to 3700, and polyperfluoropropylene oxide [9] in the range of 3100–2000. Matsuo et al. [6] proposed the use of polystyrene as the mass reference for higher masses up to 10,000.

We have pointed out in Part One that GC is unable to detect high molecular weight, highly polar or unstable pyrolysis products. Also, the long analysis time for a capillary GC run (1

- 1.5 hr) [10,11] and lack of standard reference compounds make Py-MS an appealing method for polymer characterization.

At present, the reproducibility of the pyrolysis is still a subject of concern for Py-MS. Meuzelaar [12] listed a standard procedure (Table 1) as a basis for further work on reproducibility. Hickman and Jane [13] studied the reproducibility of three Py-MS systems; including two Curie point pyrolyzer from different manufacturer and a galvanically heated filament pyrolyzer. The mass spectrometer was tuned to produce a standard toluene spectrum enabling reproducible mass pyrograms to be obtained about six weeks. Differences were observed between pyrolysis units [13,14]. Hughes [14] recommended that the same equipment should be used for comparative analysis.

In the following section the effect of pyrolysis temperature on the abundance and reproducibility of fragments is discussed. Temperature control has an effect on the reproducibility.

Table 1

The Main Factors Governing the Long-Term Reproducibility of Pyrolysis-Mass Spectrometry [12]

A. Sample Preparation
   Cleaning method
   Solvent
   Sample size
B. Filament Heating
   Equilibrium temperature
   Temperature rise time
   Total heating time
C. Product Transfer
   Inlet temperature
   Residence time
   Surface activity
D. Mass Analysis
   Ionization
   Extraction
   Separation

II. EXPERIMENTAL

(1) Mass Spectrometry

A Varian MAT CH7 Mass Spectrometer was used for stepwise Py-MS. This mass spectrometer has an electron impact ion source (set at 70 ev), equipped with a electrically heated sample insertion probe and a 5 mm x 2 mm I.D. gold sample tube. The sample, weighing about 0.1 mg, was placed in the sample tube and inserted into the mass spectrometer. The temperature of the sample probe was quickly raised to a preselected temperature, and a mass spectral scan was started. Temperature slightly increased at the range of 5-10°C during the whole mass scanning process (about 1.5 min). The sample probe was then again quickly heated to a temperature higher, and another spectrum taken. This procedure was repeated until the spectra at subsequently higher temperatures were taken, up to 280°C for polystyrene, and 350°C for Porapak Q. Five mass spectra were taken for polystyrene (65°C, 110°C, 150°C, 210°C and 280°C); four spectra were taken for Porapak Q (145 °C, 220°C, 290°C and 350°C).

(2) Samples

Polystyrene standard PS800 and Porapak Q were used. These samples were the same as those described in the previous chapter.

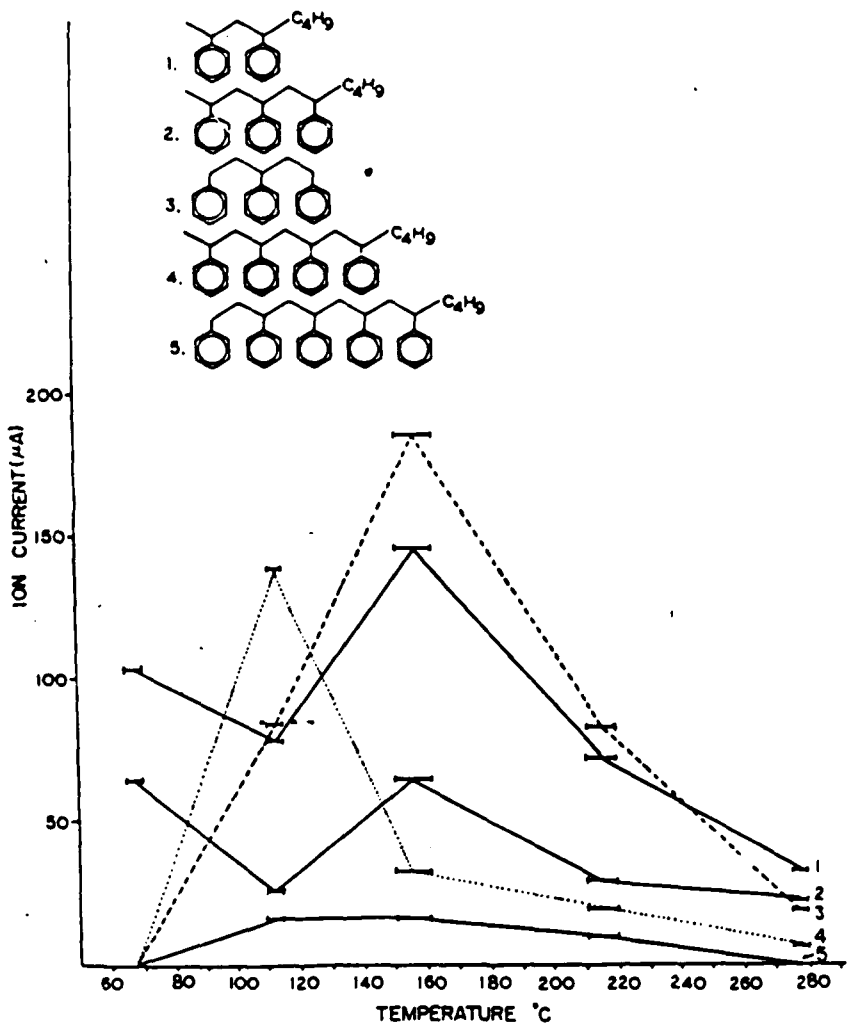

Figure 1. Mass fragment plots of polystyrene (PS800) as a function of temperature.

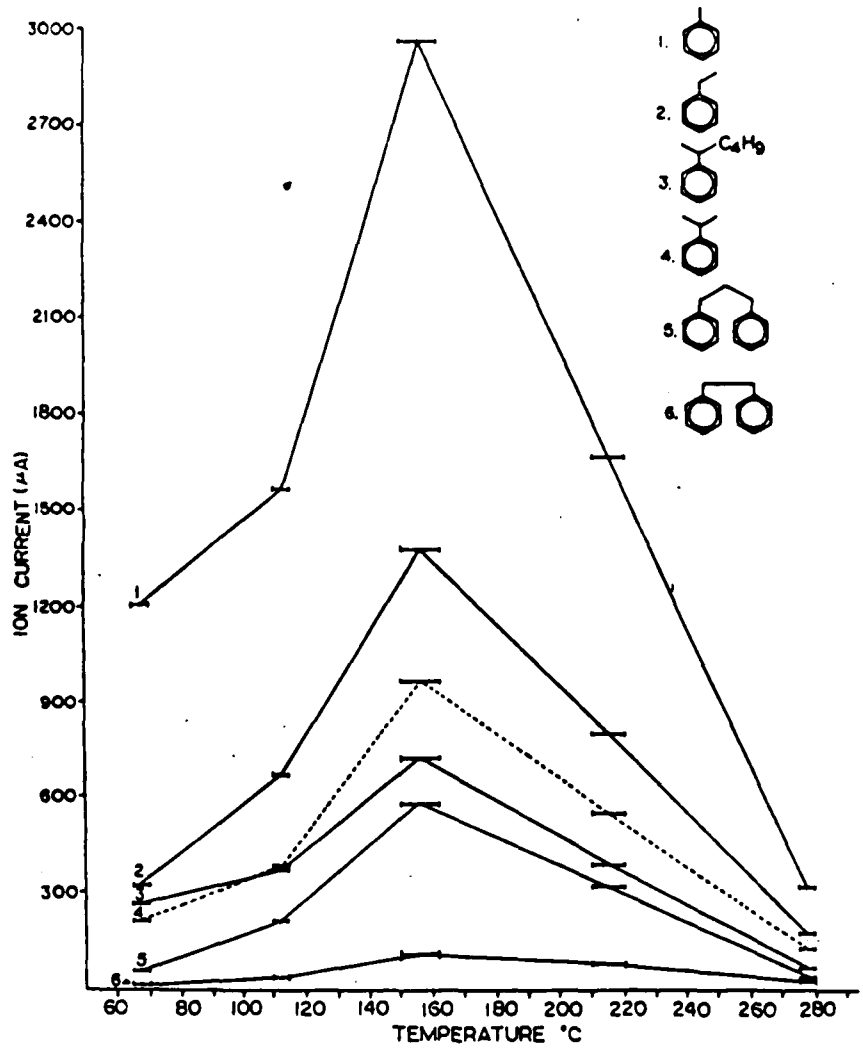

Figure 2. Mass fragment plots of polystyrene (PS800) as a function of temperature.

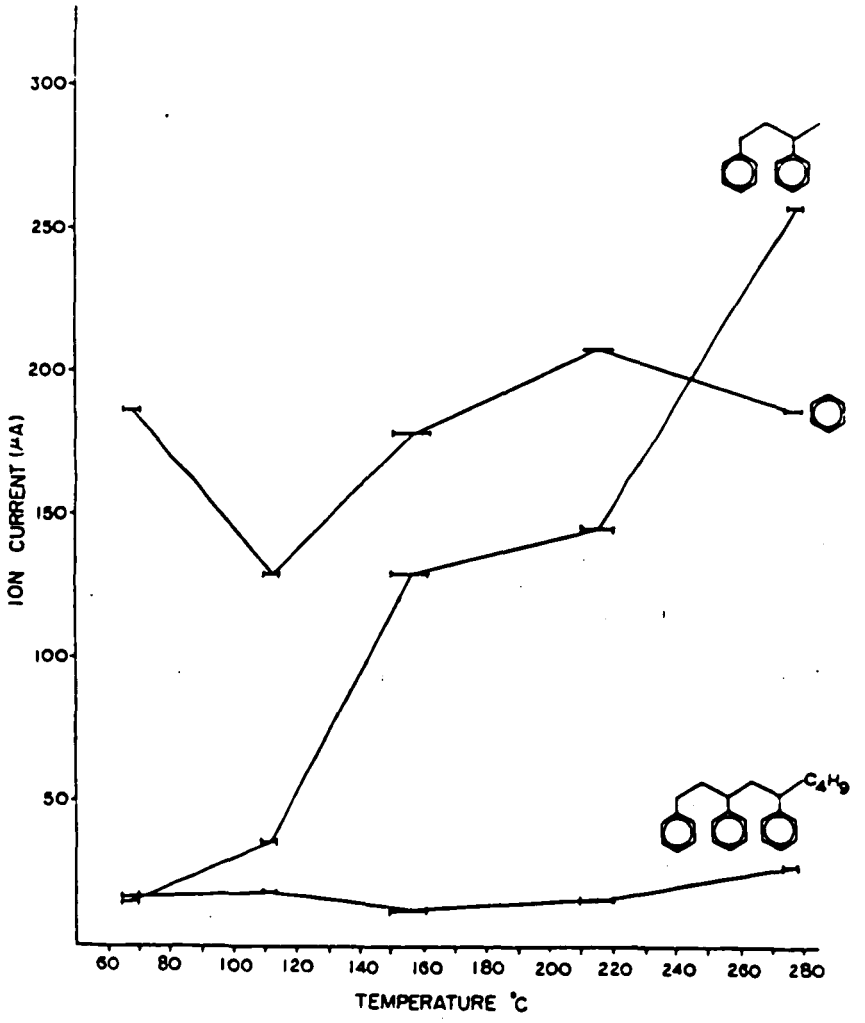

Figure 3. Mass fragment plots of polystyrene (PS800) as a function of temperature.

III. RESULTS AND DISCUSSION

Figures 1, 2 and 3 show the mass fragment plots of polystyrene (PS800) as a function of temperature. These clearly indicate that the abundance of different pyrolytic fragments differ with temperature, as did the Py-GC and Py-LC results. The abundance of fragments increases with temperature, reaching a maximum, and then declines. This is characteristic of stepwise pyrolysis; the same sample is pyrolyzed at sequentially elevated temperature, so the amount of sample diminishes at each stage. The same behavior was also observed in Py-LC and Py-GC. The mass spectra at lower pyrolysis temperatures show substantial abundance of lower molecular weight styrene oligomers. This indicates that at lower temperatures, distillation of low molecular weight compounds is a predominant process. This also agrees with our previous Py-GC results.

A series of styrene oligomer fragments are observed in these mass spectra. We also observed random scission along the carbon chain of polystyrene. An interesting fragment (M.W.=180) corresponding to 1,2-diphenyl-ethylene, is observed. The appearance of this compound is an evidence of head-to-head microstructure. The low abundance of this fragment means only a small percentage of polystyrene has head-to-head microstructure. This result substantiates previous literature data [9,14] on the microstructure of polystyrene. The fragment of M.W. 208

(2,3-diphenyl-1-butene or 1,4-diphenyl-1-butene) in the mass spectra can not, however, be used as evidence to identify head-to-head styrene dimer, because the head-to-tail styrene dimer (2,4-diphenyl-1-butene) has the same molecular weight. However, the GC retention time of these isomers are different, which has been used both in Py-GC and Py-GC-MS to distinguish head-to-head from head-to-tail microstructure of polystyrene polymers [9,14].

Figures 4 and 5 show the mass spectra of cross-linked polystyrene (Porapak Q). Pyrolysis products corresponding to random scission are observed in these spectra. All these spectra clearly indicate that pyrolysis temperature control in Py-MS is a very important factor in obtaining reproducible results, especially when the mass spectrum is taken at only one temperature. The decrease in intensity of these spectra also indicate that the quantity of sample is continuously diminished, Therefore, samples must experience a carefully controlled temperature rise rates, the same pyrolysis times and the same mass spectra scan rates, in order to give reproducible results.

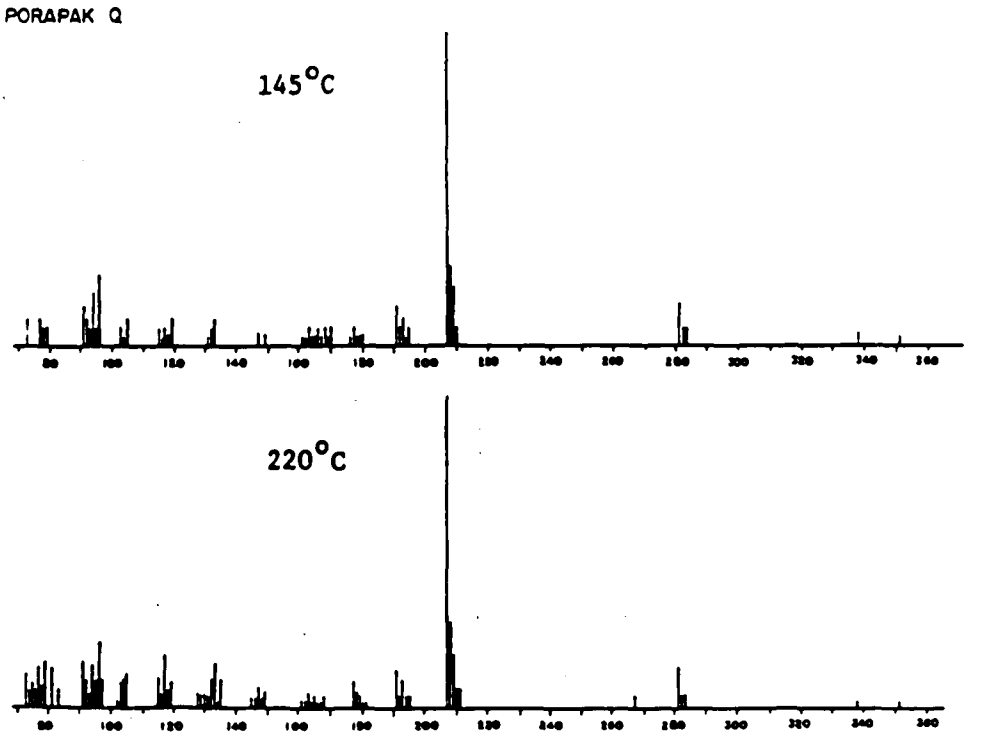

Figure 4. Py-MS of Porapak Q at 145°C and 220°C.

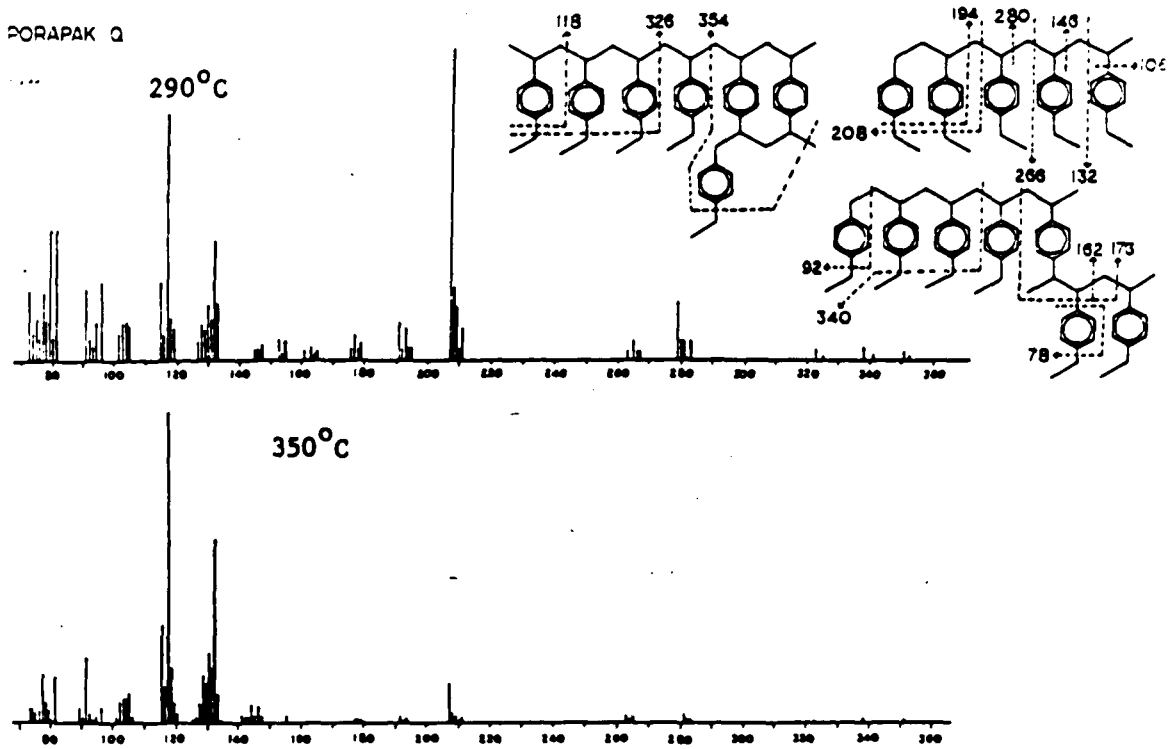

Figure 5. Py-MS of Porapak Q at 290°C and 350°C.

IV. SUMMARY

Py-MS is useful in structure analysis of polymers, especially for insoluble cross-linked polymers.

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PART TWO

SEPARATION OF STYRENE OLIGOMERS USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY WITH UV AND FLUORESCENCE DETECTION

I. INTRODUCTION

HPLC separation of styrene oligomers has been carried out using both reversed- and normal-phase chromatography, as well as size-exclusion chromatography. Snyder and Kirkland [1] presented a chromatogram of the lower styrene oligomers on a C18 reversed-phase column using a tetrahydrofuran-water gradient. Later, Kirkland [2], in evaluating a new 7-um microporous silica derivatized with octadecyl groups, showed a baseline separation of about 11 peaks in 14 min for a polystyrene standard (average molecular weight 600) (PS600) using pure acetonitrile eluent. Holt-Sackett et al. [3] analyzed the same PS600 using a 5-um silica B/5 column and a linear hexane-dichloromethane gradient. In approximately 15 min about 11 peaks appeared on top of a broad envelop. Fukuda et al. [4] separated styrene oligomers with a degree of polymerization less than 10 (essentially PS600) on a narrow-pore gel permeation column. Recently, Curtis et al. [5] investigated the use of silica and several silica-based chemically-bonded phases for separating styrene oligomers, and found that nitro- and amino-bonded phases could also separate styrene oligomers.

As mentioned in Part One, we have found that the normal nitrile-bonded phases [6], PAC (combination of nitrile- and amino-bonded phases; at 2/1 ratio), and alumina absorbents can also separate styrene oligomers. Both UV absorption and

fluorescence detectors were used; the latter has the advantage of much higher sentivity for styrene oligomers. It could also function as a more selective detector, for example for the analysis of polystyrene in copolymer blends.

As noted in chapter Three of Part One, two emission bands are observed in the stop-flow fluorescence spectra of each oligomer fraction in the HPLC chromatograms, one from regular molecular fluorescence and the second from excimer emission.

II. EXPERIMENTAL

(1) HPLC

(a) Nitrile-bonded Phases

A Varian 8500 LC was used with a Varian 25 cm x 2 mm i.d. CN-Micropak column for isocratic runs using 20 ml/h of isooctane/dichloromethane (13:1 or 12:1) at ambient temperature. Pure dichloromethane at 10 ml/h was used for some experiments. The Varian UV detector was set at 254 nm. Aliquots (1.0ul) of the polystyrene standards dissolved in dichloromethane were injected. For gradient elution using 0.77 ml/min gradients of isooctane/dichloromethane, a Micrometritics 7500 LC system was used with the UV detector also set at 254 nm.

(b) PAC Stationary Phases

A Varian 8500 LC was used with a Whatman 25 cm x 4.6 mm i.d. Partisil PXS 10x25 PAC column for isocratic run using 2ml/min of 12:1 isooctane/dichloromethane at ambient temperature.

(c) Alumina Absorbents

A Varian 8500 LC was used with a Varian 25 cm x 2 mm i.d. Al-10-MicroPak column for isocratic runs using 20 ml/hr of isooctane at ambient temperature. The Varian detector was set at 254 nm.

(2) Fluorescence

A Perkin-Elmer 650-10S Fluorescence Spectrophotometer was used with a Perkin-Elmer Model 650-0151 10-ul micro flow 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 were 260 nm or 270 nm and emission was read at 320 nm.

(3) Samples

Polystyrene standards 600 (ArRo Labs., Joliet, U.S.A.) (PS600) and 730 (U.S. National Bureau of Standards) (PS730) were supplied courtesy of Dr. Michael Dong, Perkin-Elmer Corp. Samples were dissolved in dichloromethane at a concentration of approximately 2 mg/ml. Another NBS standard polystyrene of weight-average molecular weight 1.96×10^5 ($PS2 \times 10^5$) was supplied courtesy of Dr. Arthur Woodward, City College, CUNY.

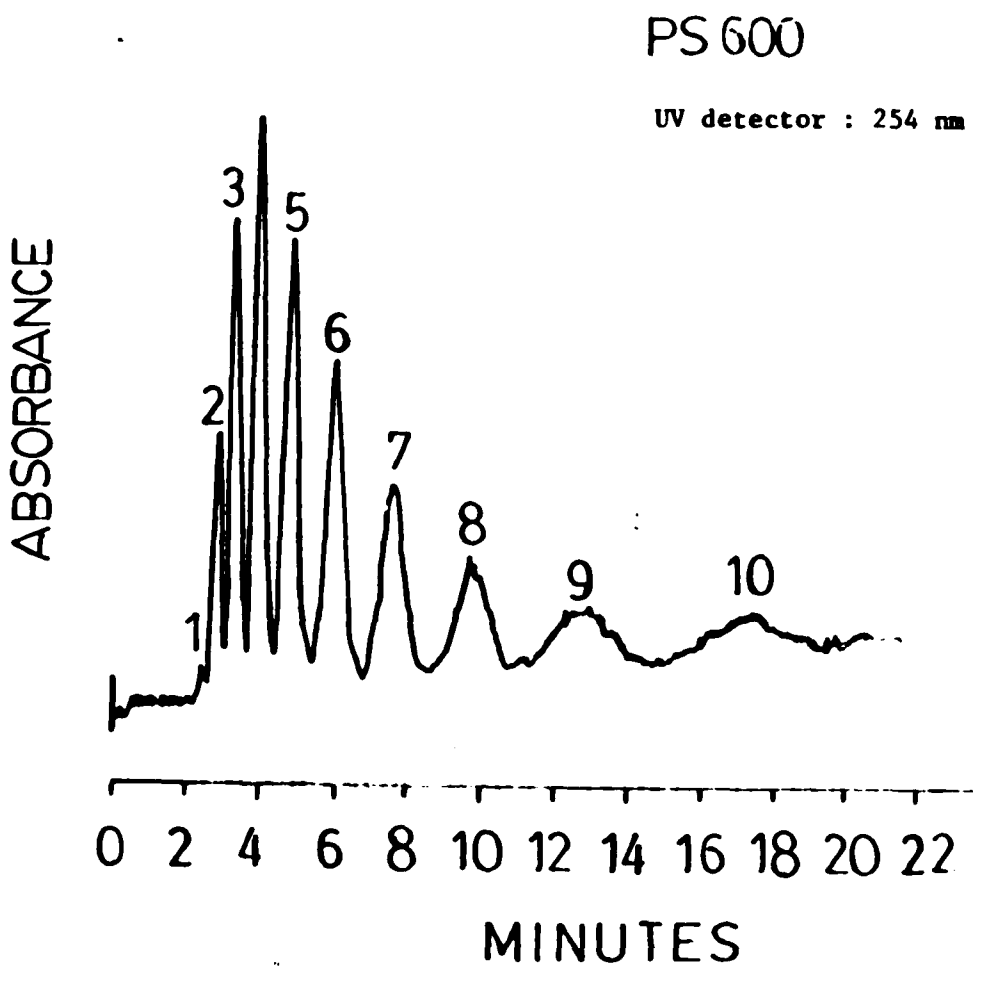

Figure 1. HPLC separation of components of polystyrene standard PS600 chromatographic conditions: CN-Micropak column, 25 cm x 2 mm i.d., 20 ml/h isooctane/CH_2Cl_2 (13/1 v/v), ambient temperature.

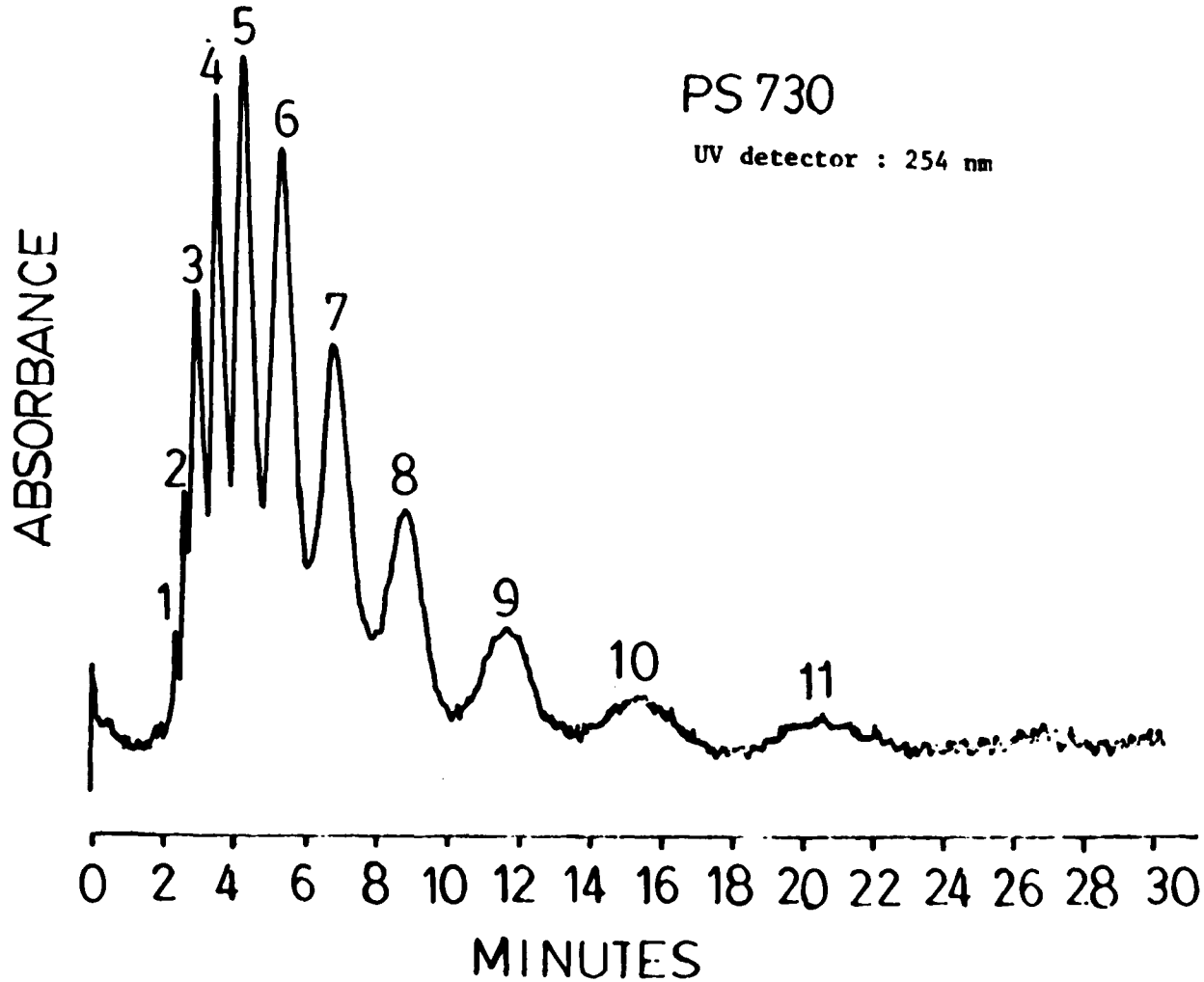

Figure 2. HPLC Separation of Components of PS730. Chromatographic conditions : same as Figure 1 except the volume ratio of isooctane/CH_2Cl_2 is 12/1.

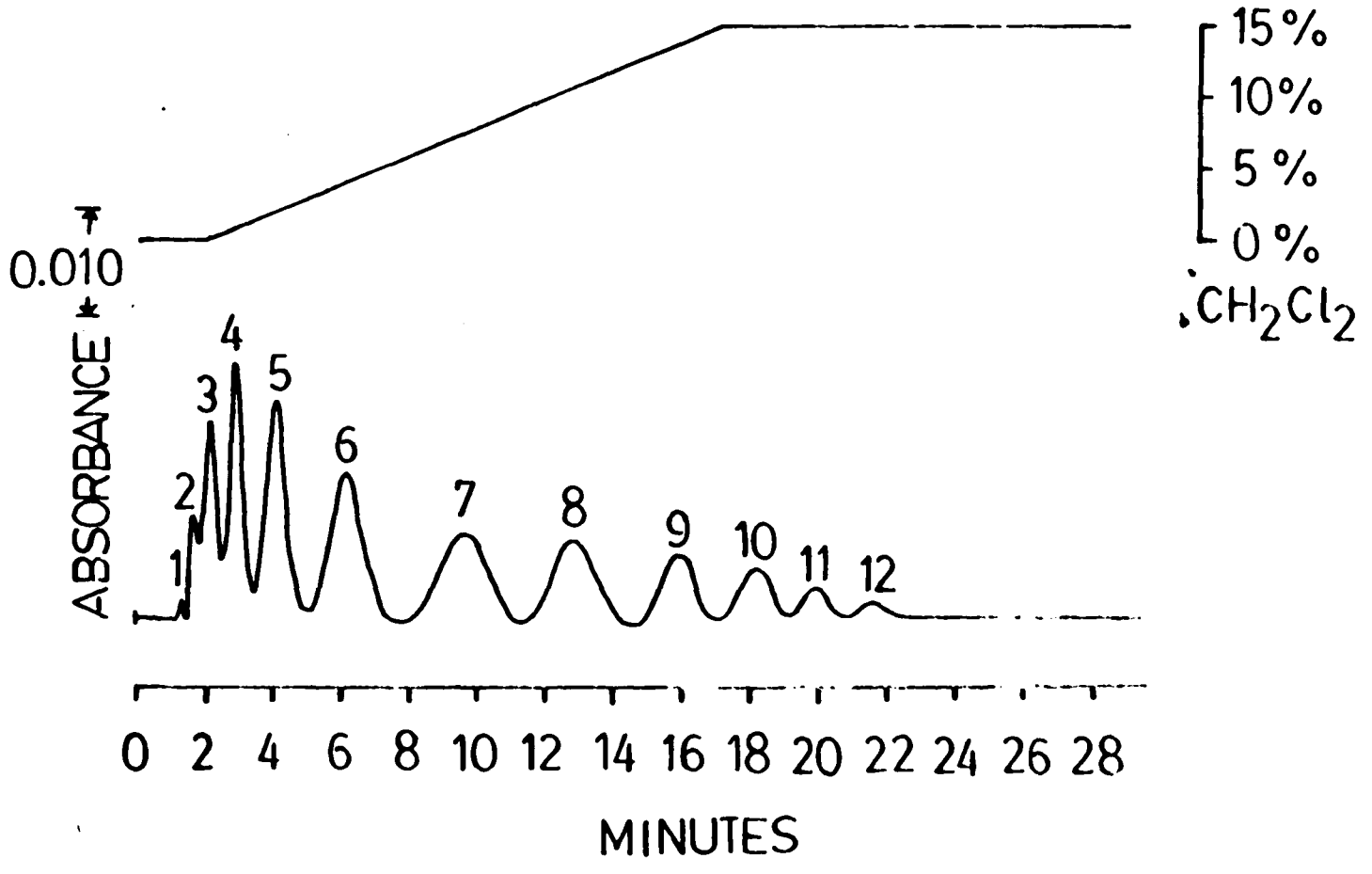

Figure 3. Gradient Elution Separation of Components of PS730. Chromatographic conditions : same as Figure 1 except using a linear gradient indicated on the figure at 0.77 ml/min.

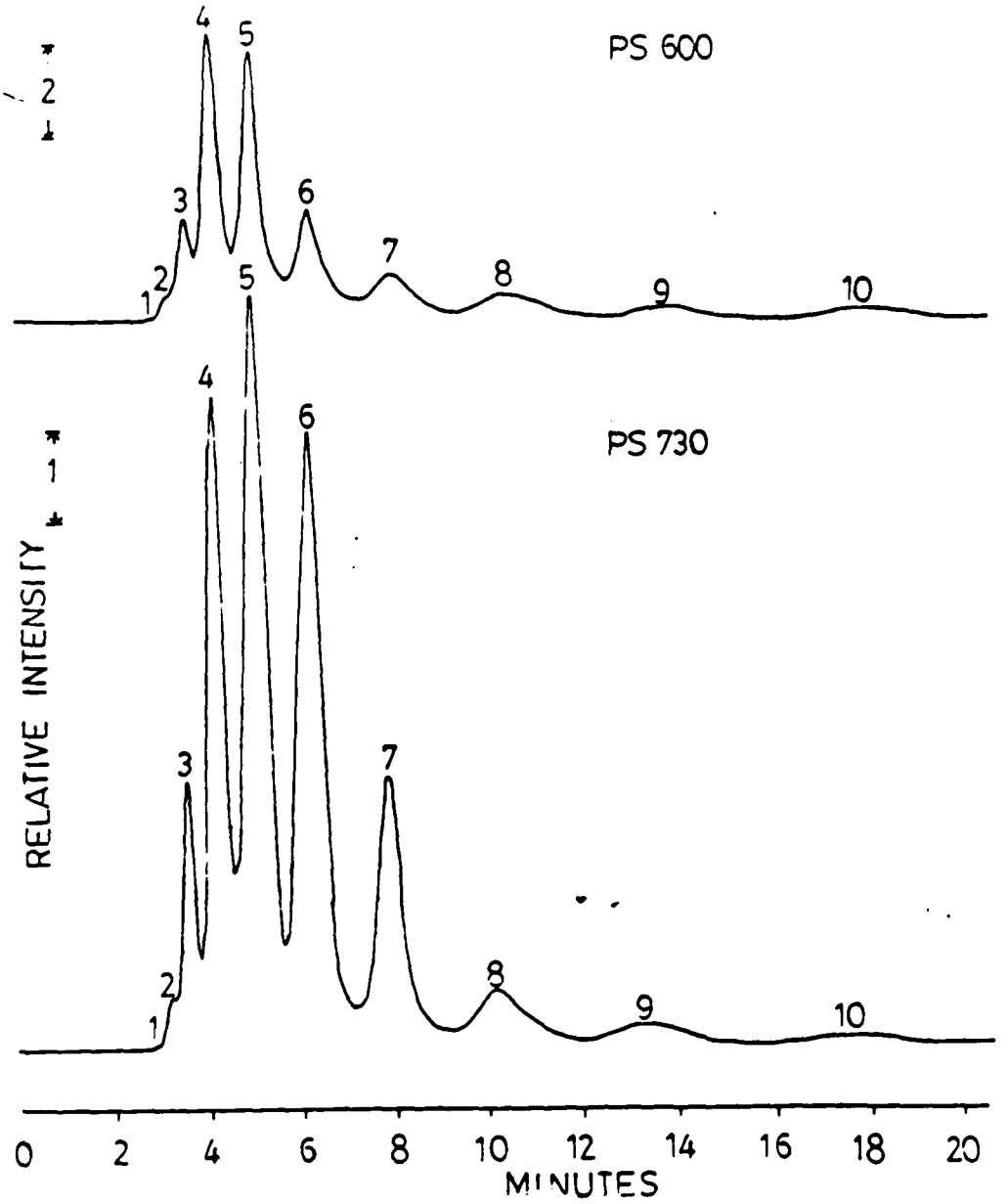

Figure 4. HPLC Separation of Components of PS600 (upper) and PS730 (lower). Chromatographic conditions : same as Figure 1 except using a fluorescence detector, wavelength of excitation, 270 nm, and wavelength of emission monitored, 320 nm.

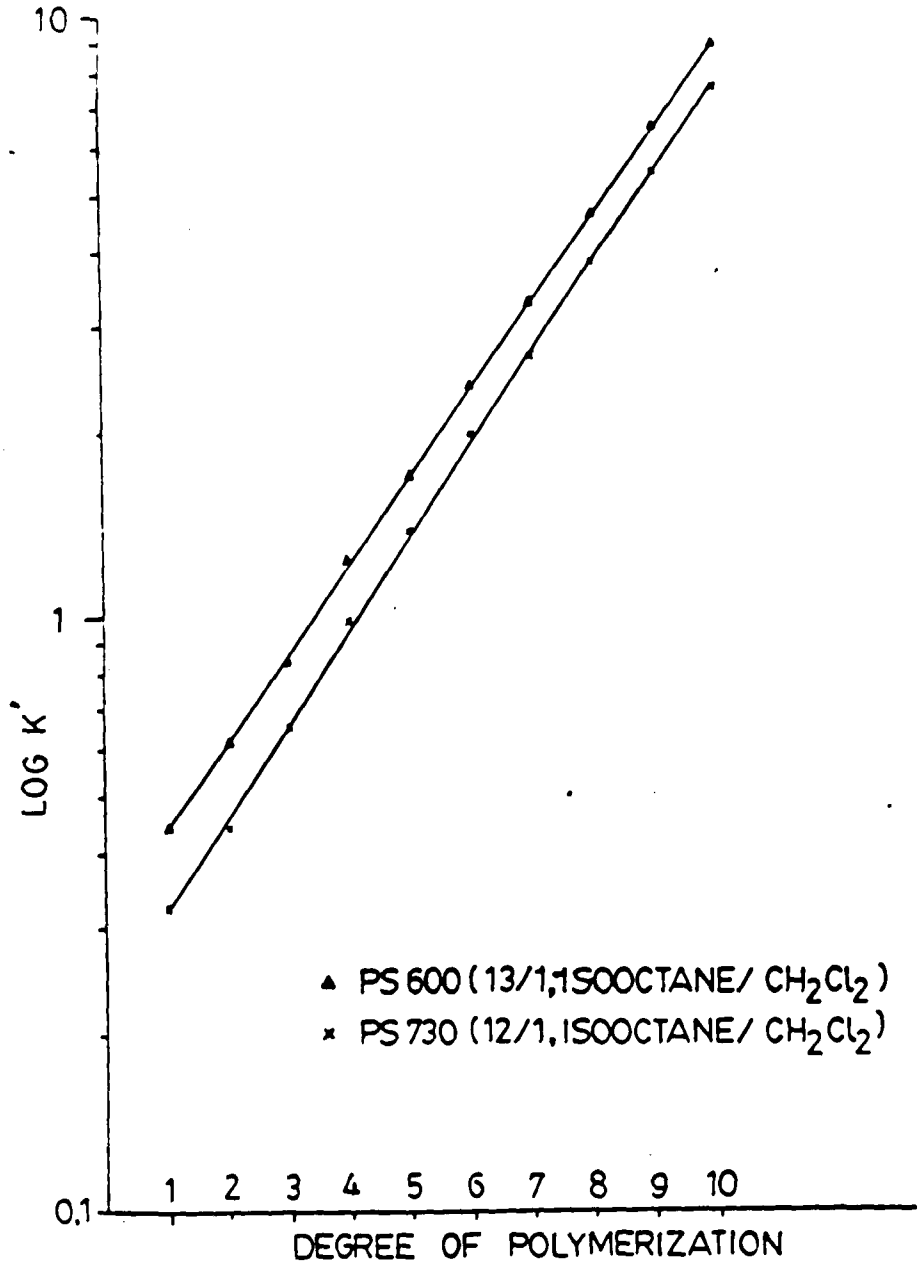

Figure 5. Log Retention as a Function of Degree of Polymerization for PS600 and PS730. Chromatographic conditions : same as Figures 1 and 2.

III. RESULTS AND DISCUSSION

(1) Nitrile-bonded Phases

Figures 1 and 2 are typical chromatograms of PS600 and PS730, respectively, using nitrile-bonded phases and the UV detector at 254 nm. In Figure 1, the eluent was isooctane-dichloromethane (13:1); in Figure 2 a 12:1 volume ratio was used. One can surmise that solvent programming would improve the separation, which is demonstrated in Figure 3 for PS730 with a 15-min linear gradient from 0 to 15% (v/v) dichloromethane in isooctane. Resolution is better at the front end, and an additional peak emerges from the noise (degree of polymerization n=12), compared to the isocratic chromatogram. Convex gradients produce slight improvements in resolution.

The fluorescence detector was used to obtain the chromatograms in Figure 4. The upper chromatogram in Figure 4 is for PS600 and the lower for PS730. The signal-to-noise ratio is increased by a factor of 10^3 over the UV detector. The eluent in both chromatograms was isooctane- dichloromethane (13:1). The tallest peak in the PS600 chromatogram corresponds to the tetramer of styrene; that in the PS730 is the pentamer.

For both standards the plot of log capacity factor (k') (isocratic) vs. degree of polymerization is the expected straight line, as shown in Figure 5. The upper line, for PS600, was

obtained with isooctane dichloromethane (13:1); the lower, for PS730, corresponds to the 12:1 mixture. These lines ultimately converge; the differential solubility between the two solvents decreases with increasing degree of polymerization, as might be expected. From Figures 3 and 5 it is evident that isocratic elution can handle oligomers with a range of degree of polymerization of about 10; k' varies by a factor of about 50 over this range. Oligomers of higher molecular weight but covering this range could be similarly resolved by increasing the proportion of dichloromethane in isooctane. With gradient elution, however, a far wider range can be separated.

The separation of styrene oligomers on the nitrile bonded phase using dichloromethane-isooctane eluents was described above. That this separation is the result of some weak but specific interaction between the styrene oligomers and the nitrile group is suggested from Figures 4 and 5 of Part Three. As the concentration of the weakly polar dichloromethane increases, it is able to displace through mass action the specifically adsorbed polystyrenes in the sample (a polystyrene standard of average molecular weight 800 (PS 800)); at a concentration of about 20% dichloromethane, the oligomers elute more or less together at a retention time exceeding the interstitial volume of the column. Retention based on a specific interaction is a reasonable hypothesis in view of the use of acetonitrile as an entrainer solvent in extractive distillation separation of aromatic from

saturated hydrocarbons; Orye and Prausnitz [7] have suggested a charge-transfer type interaction between aromatic hydrocarbons and acetonitrile. Indeed, the limiting activity coefficients of aromatics in acetonitrile are substantially lower than those of simple alkanes [8]. Since it is the nitrile group in acetonitrile that is the active part of the molecule, one could reasonably expect a similarly interaction between a chemically-bonded group with a terminal -CN and aromatic hydrocarbons such as the styrene oligomers.

It is interesting to observe that with pure dichloromethane eluent the nitrile-bonded column acts as a size exclusion medium. The solvent is sufficiently polar to overwhelm any selective solute-stationary phase interactions, and the bonded moiety largely eliminates active surface hydroxyl sites on the silica. The microporous silica then separates on the basis of molecular size. This is demonstrated in Figure 6 where a mixture of the PS2 x 10^5 and PS730 standards in dichloromethane was cleanly separated. A higher resolution separation could presumably be achieved with a column longer than the 25 cm one used here.

Stopped-flow fluorescence spectra were obtained for each peak in the PS600 and PS730 chromatograms. Here, the excitation wavelength was set at 260 nm rather than the 270 nm used in Figure 4, in order to reduce the influence of scattered light on the fluorescence band at 290 nm. The bands at 290 nm correspond to molecular fluorescence of the oligomers themselves. The bands at

320 nm most evident for the taller chromatographic peaks correspond to the emission of polystyrene excimers, i.e. emission from an excited state dimer of styrene oligomer. This is the first report of excimer emission for lower styrene oligomers. Excimer emission is concentration-dependent; thus the excimer band is most pronounced for the oligomers with degrees of polymerization of 3-7 in Figures 7 and 8. This also accounts for the differences in the relative peak heights for the earliest and later peaks between the UV and fluorescence detector chromatograms; the latter was set to measure excimer emission to reduce the background from scattered light. Further discussion of excimer formation was given in Chapter Three of Part One.

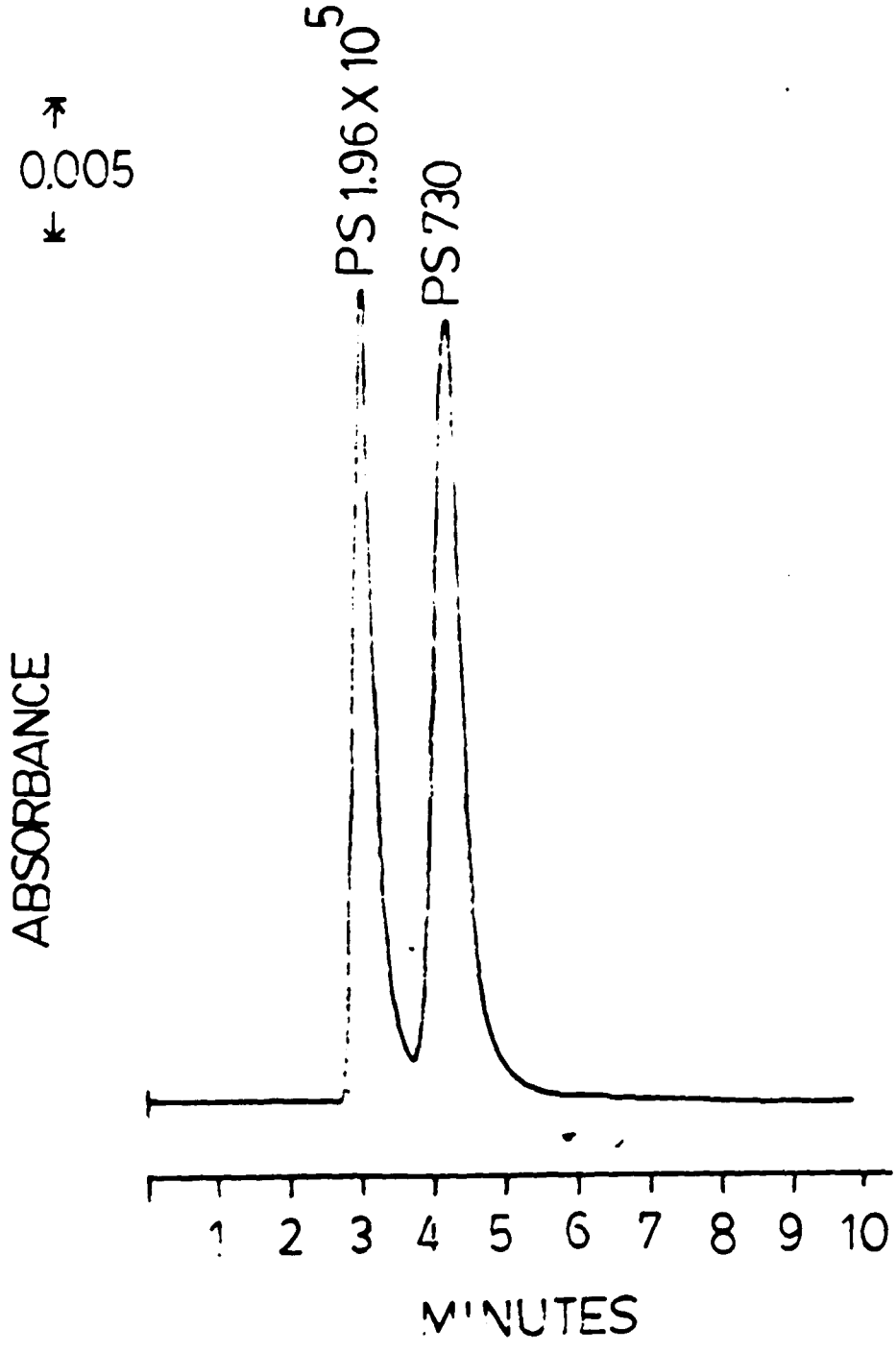

Figure 6. CN-Phase Function as a Size Exclusion Column in CH_2Cl_2 towards PS2x10^5 and PS730. Chromatographic conditions : same as Figures 1 except eluent is pure CH_2Cl_2 at 10 ml/h.

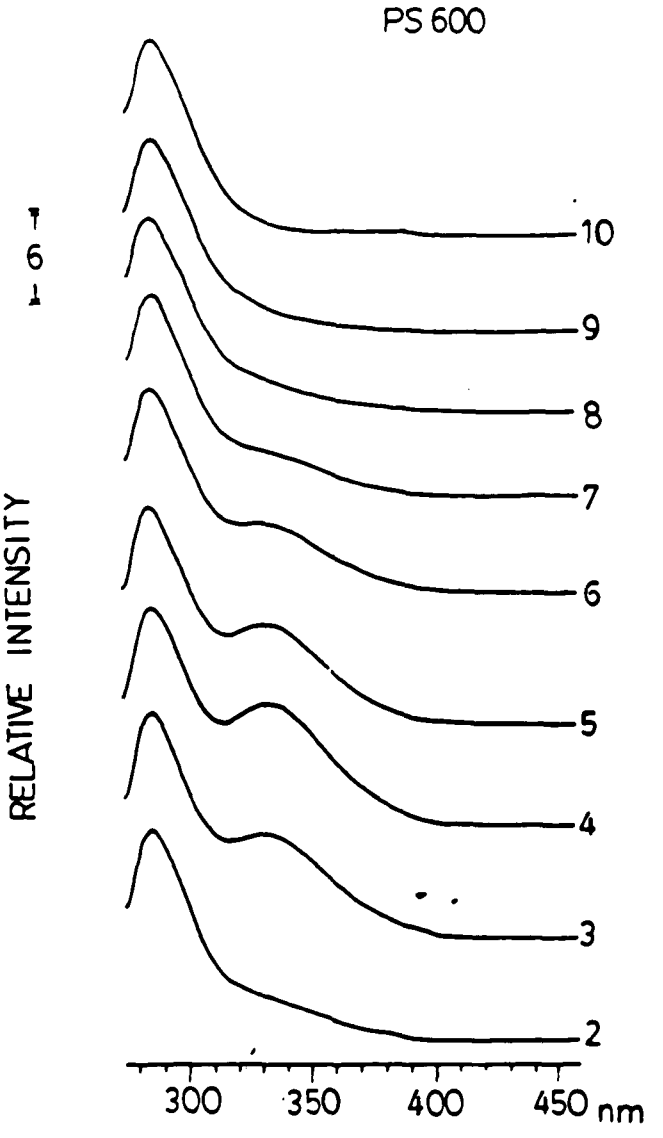

Figure 7. Stopped Flow Fluorescence Spectra of Each Peak in the Chromatogram of PS600. Chromatographic conditions : same as Figure 4. Excitation wavelength, 260 nm.

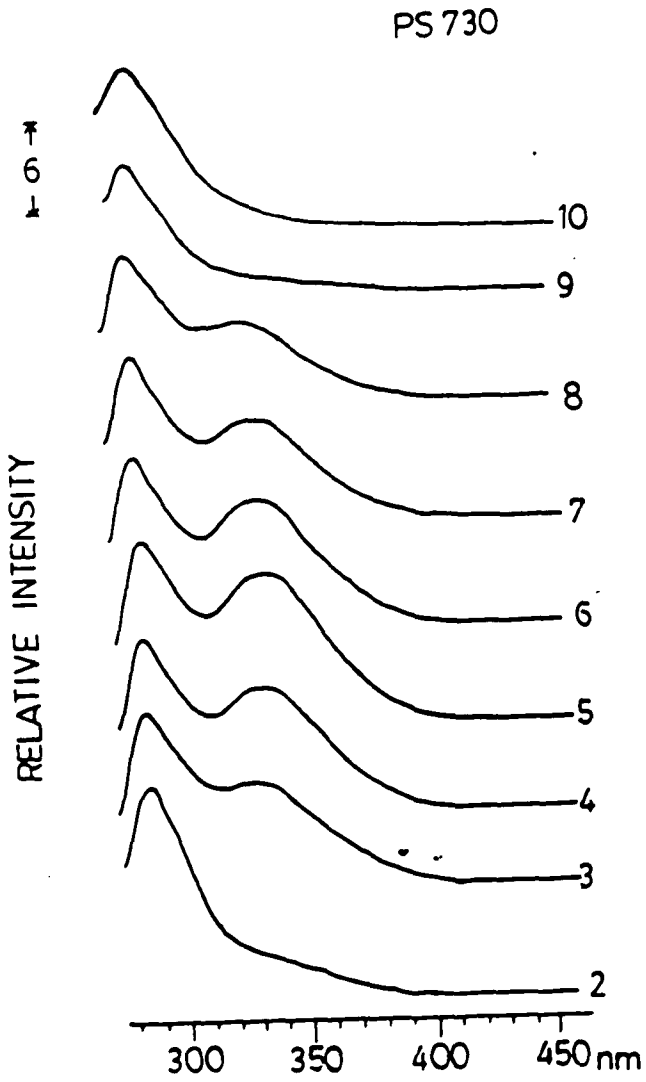

Figure 8.

Stopped Flow Fluorescence Spectra of Each Peak in the Chromatogram of PS730. Chromatographic conditions : same as Figure 4. Excitation wavelength, 260 nm.

(2) PAC Phases

Figures 9 and 10 are typical chromatograms of PS800 using PAC phases with UV detection at 254 nm and fluorescence detection, respectively. In Figure 9, the elution was 12:1 (v/v) isooctane-dichloromethane at 2 ml/min. In approximately 24 min about 12 peaks was separated on this PAC column.

(3) Alumina Absorbents

Figures 11 and 12 show chromatograms of PS800 using alumina absorbent column with UV detection and fluorescence detection, respectively. The eluent was pure isooctane at ambient temperature. In approximately 27 min, about 12 peaks were separated.

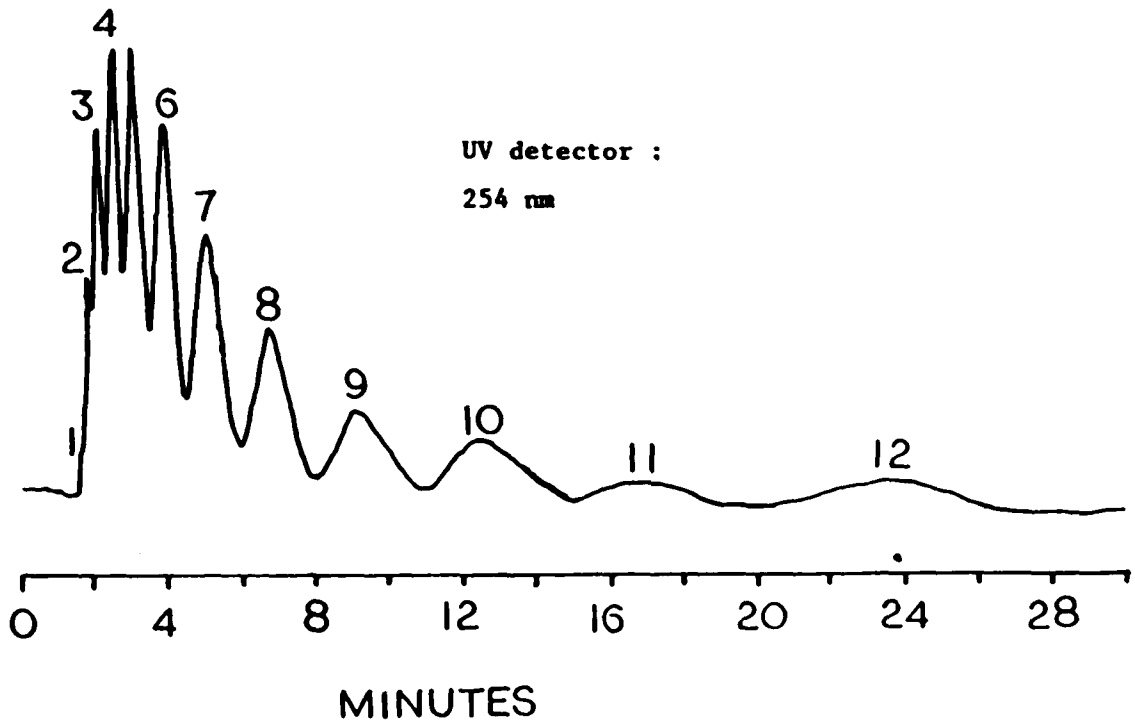

Figure 9. HPLC Separation of Polystyrene Standard PS800. Chromatographic conditions: PAC column (Whatman 25 cm x 4.6 mm i.d. Partisil PXS 10x25), 2 ml/min isooctane/CH_2Cl_2, ambient temperature.

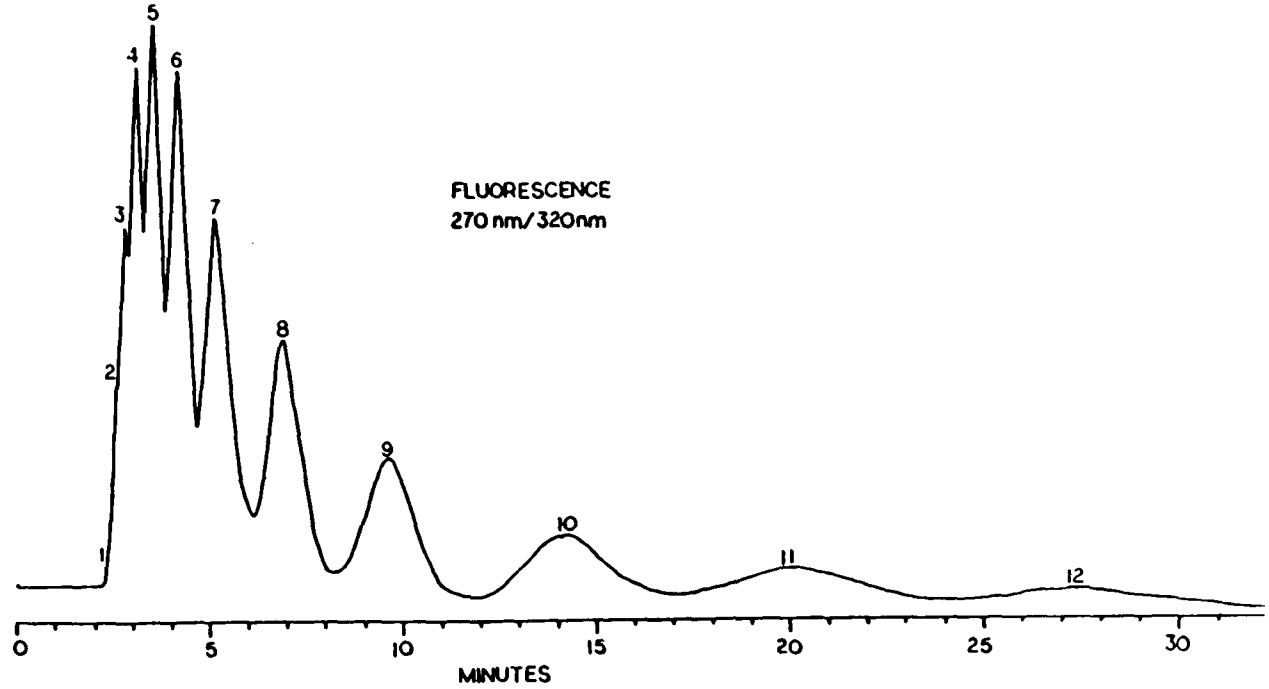

Figure 10. HPLC Separation of Components of PS800. Chromatographic conditions: same as Figure 9 except using a fluorescence detector, wavelength of excitation, 270 nm, and wavelength of emission 320 nm.

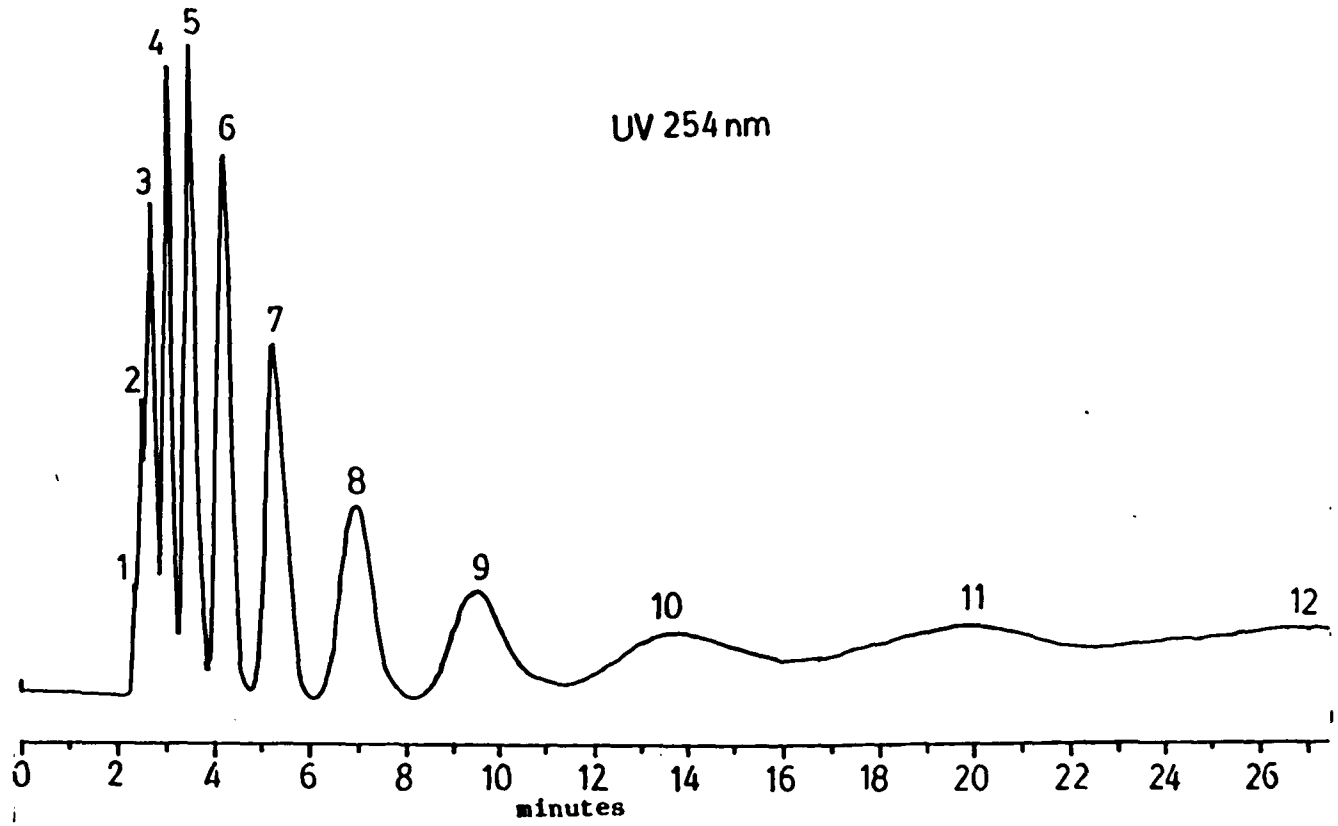

Figure 11. HPLC Separation of Components of PS800. Chromatographic conditions: Varian 25 cm x 2 mm i.d. Al-10-MicroPak column, 20 ml/h isooctane, ambient temperature, UV detector wavelength 254 nm.

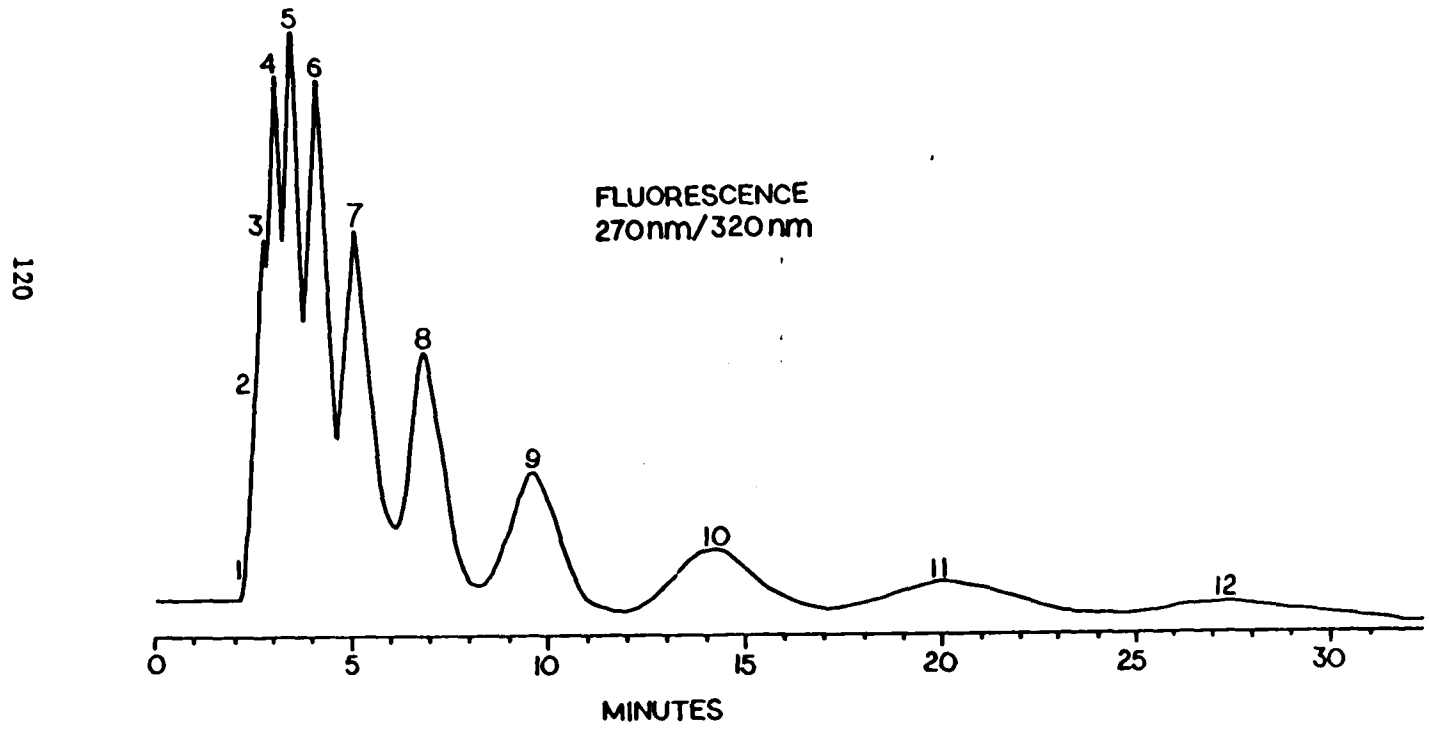

Figure 12. HPLC Separation of Components of PS800. Chromatographic conditions: same as Figure 11 except using fluorescence detection, excitation wavelength 270 nm, emission wavelength 320 nm.

IV. SUMMARY

The potential of normal bonded phase liquid chromatography (LC) has not been fully explored, probably because so much attention has been given to reversed-phase LC. This situation has been discussed by Abbott [9]. The ability of the nitrile phase to separate styrene oligomers has been demonstrated here. In addition we have shown that the nitrile phase acts in polar solvents such as dichloromethane as a size exclusion column. We also demonstrated here that both normal phase PAC and normal phase alumina columns are able to separate styrene oligomers. A potentially attractive aspect of these normal phase packings is with the use of LC-mass spectrometry (MS). With reversed-phase LC-MS, evaporation of the water-acetonitrile or water-methanol is a problem; with the more volatile organic solvents used with the nitrile phase, evaporation is easier. Fluorescence detection of polystyrene is far more sensitive than UV detection and should have wider applications in size exclusion chromatography of aromatic polymers.

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PART THREE

MULTI-MODE BEHAVIOUR OF CHEMICALLY BONDED STATIONARY PHASES IN LIQUID CHROMATOGRAPHY

I. INTRODUCTION

It has become almost axiomatic that there are exactly four modes of high performance liquid chromatography (HPLC), and that these are determined by the stationary phase: normal phase, reversed phase, size exclusion, and ion-exchange. Even such a variant as paired-ion chromatography is referred to as for example "reversed phase paired-ion". Thus all chromatography conducted using an alkyl bonded phase such as octyl or octadecyl is labelled and considered exclusively to be "reversed phase". Rarely would one use an octadecyl bonded phase with an eluent other than an aqueous solution of a polar organic solvent. An exception is the so-called NARP, nonaqueous reversed phase [1] in which mixtures such as acetonitrile (ACN) plus tetrahydrofuran or methylene chloride serve as the eluent. Normal phases are used virtually exclusively with a dilute solution of a polar modifier in a nonpolar solvent, e.g. 2% 2-propanol in hexane. Again there are exceptions although these are performed more for demonstration purposes than for practical application (e.g. 2).

The designation normal phase refers of course to the fact that the first LC column packings were polar adsorbents such as silica gel, or were used to support a polar, usually aqueous stationary liquid phase, to separate polar or moderately polar substances. The term "normal" came into being only to distinguish it from its supposed opposite, "reversed phase", i.e. one less polar than the

eluent and used for non-polar and moderately polar samples. In time, and especially in the past ten years, however, "normal" and "reversed phase" have come to be associated not with the relative polarities but with specific types of stationary phase.

Similarly, size exclusion and ion-exchange chromatography are identified in terms of particular types of stationary phase materials. In the latter case, however, it is worth remembering that some time ago Helfferich [3] pointed out that ion-exchange chromatography may have about as much to do with the exchange of ions as chromatography has to do with color. Crosslinked polystyrenes can be used not only in the size exclusion mode but also as adsorbents; Grieser and Pietrzyk [4] separated chloro- and nitro-phenols with a pH gradient. Mori and Yamakawa [5] and Robinson, et al. [6] used similar crosslinked polystyrene gels with a varity of mobile phases for separations based on adsorption rather than size exclusion.

Microporous silica particles function as size exclusion media as well as siliceous adsorbents [7]. Indeed, the latter property can confuse molecular weight distribution data derived from chromatograms obtained using porous silicas. These silicas are consequently often deactivated by methylating or otherwise treating the silanol groups, thus converting the materials to "reversed phase" [7,8].

For the past twenty years, the separation of macromolecules has been carried out using size exclusion chromatography with two

types of packings, cross-linked organic gels, and surface modified porous silica gels. The advantages of rigid siliceous packings over organic gels are (i) a wider range of solvents can be used, including highly polar organic solvents and aqueus mobile phases; (ii) the column equilibrate more rapidly with a new solvent system; (iii)silica particles can be used at high temperatures with polar solvent; (iv) the narrow pore size distribution of certain siliceous particles (e.g. 9-11) leads to high resolution; and (v) approximate molecular weight calibration curve can be predicted from size distribution data, which is not possible with organic gels.

The main advantage of rigid siliceous packing is the adsorption of polar solutes on surface silanol groups. Several workers have attempted to solve this problem by exhaustively modifying the surface with functional groups.

There are two ways to extend the linear size separation range of SEC. The usual method is to connect SEC columns of different pore sizes together to provide a wider molecular weight (MW) separation range. However, the chromatographic resolution of the combined column set(with an effectively broader pore size distribution) is less than that of a single column of a single size with the same length. In practice, this sacrifice in resolution is modest compared with the gain in convenience and versatility of a wider MW range column set. This is especially true for high performance SEC columns (< 10 um particles). Most

SEC laboratories prefer this system simply because the wider MW separation allows analysis of polymers of different molecular weight distributions without having to change and recalibrate the column set.

Recently, Yau et al. [12] proposed a new way to extend linear sizes separation range. They coupled SEC columns containing only discrete pore sizes having about one decade difference in pore size and approximately equal pore volumes. In the method described above, several packing materials of slightly different pore sizes and pore volumes are connected together. Yau. et al. [12] also demonstrated that a single packed column with a special new 10-um bimodal pore-size silica particles could provide a wide linear size separation range. This would reduce column inventory and improve convenience, while maintaining high resolution and accurate MW measurment.

Amstrong et al. [13] demonstrated that high MW polymers could be separated on a C18 reversed-phase column with gradient elution. This is a very useful discovery, because the separation of polymers is not restricted by both the pore size distribution and available pore volumes. Larmann et al. [14] recently confirmed that pore size has little effect on the reversed-phase separation of polymers.

We seek to demonstrate here that the association of normal and reversed phase LC with particular types of stationary phase is not always meaningful, and indeed restricts one's thinking about

potential application of HPLC. In view of the evident incipient interest in polar bonded phases, it seems timely to draw attention to this situation.

II. EXPERIMENTAL SECTION

A Varian 8500 LC was used with either a 25 cm X 2 mm i.d. Varian CN-Micropak column or a 25 cm X 2 mm i.d. Varian CH-10 Micropak C-18 column at ambient temperature. The Varian Varichrom UV detector was set at 254 nm. A flowrate of 10 ml/hr was used with all solvents except where noted. Solutes were dissolved in a solvent of the same composition as the eluent at an approximate concentration of 2 ug/ml; 1.0 ul aliquots were injected.

Samples were obtained from Aldrich, K&K, or J. T. Baker; the polystyrenes were from the Alfa polystyrene standard kit. Solvents were Distilled-in-Glass or equivalent quality and were degassed with a stream of helium.

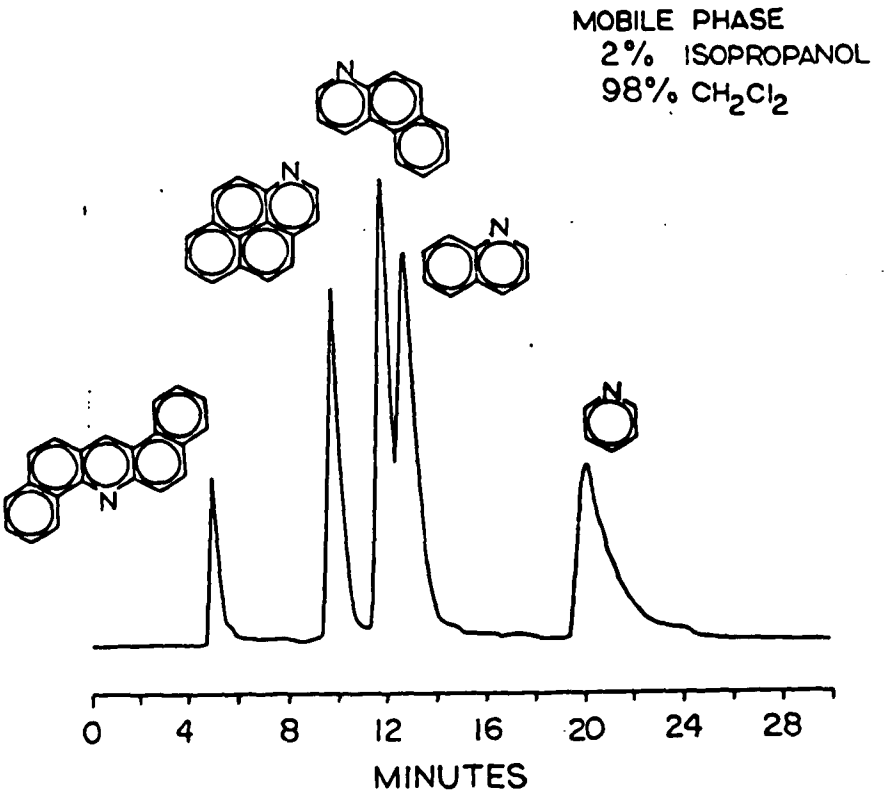

Figure 1. Separation of azaarenes. Chromatographic conditions: 25 cm x 2 mm i.d. Varian CN-micropak column, 10 ml/hr of mobile phase indicated, UV detector at 254 nm.

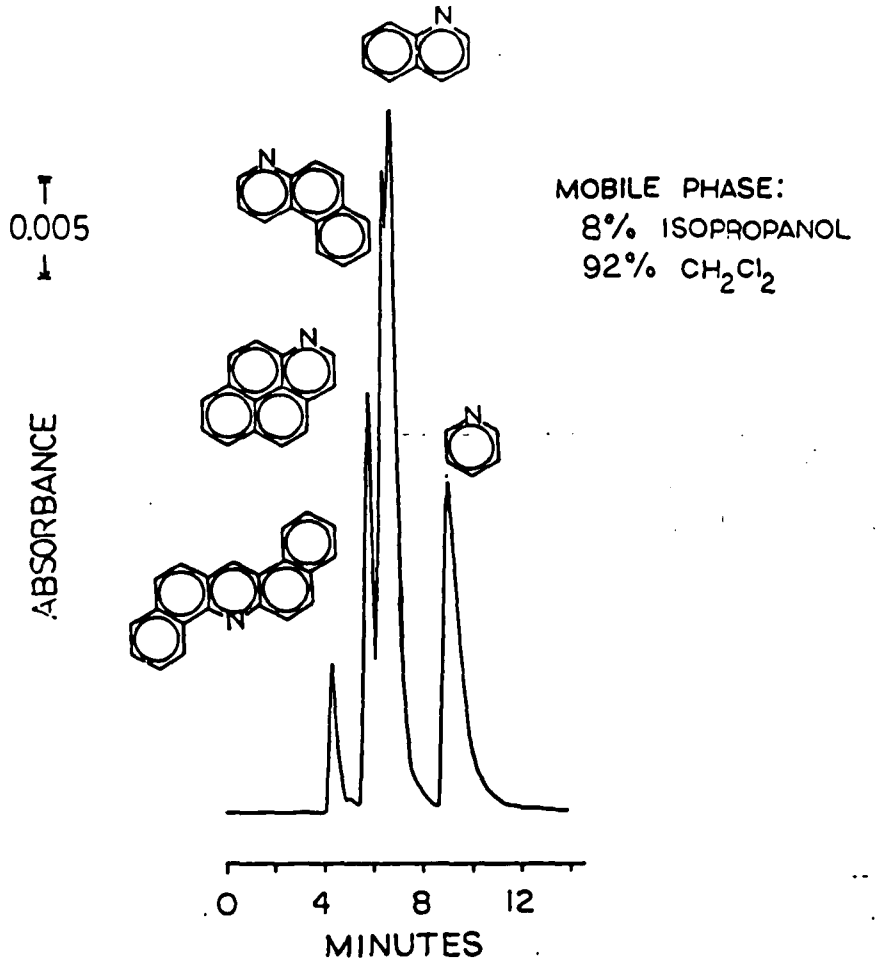

Figure 2. Separation of azaarenes. Chromatographic conditions : same as Figure 1 except mobile phase composition indicated.

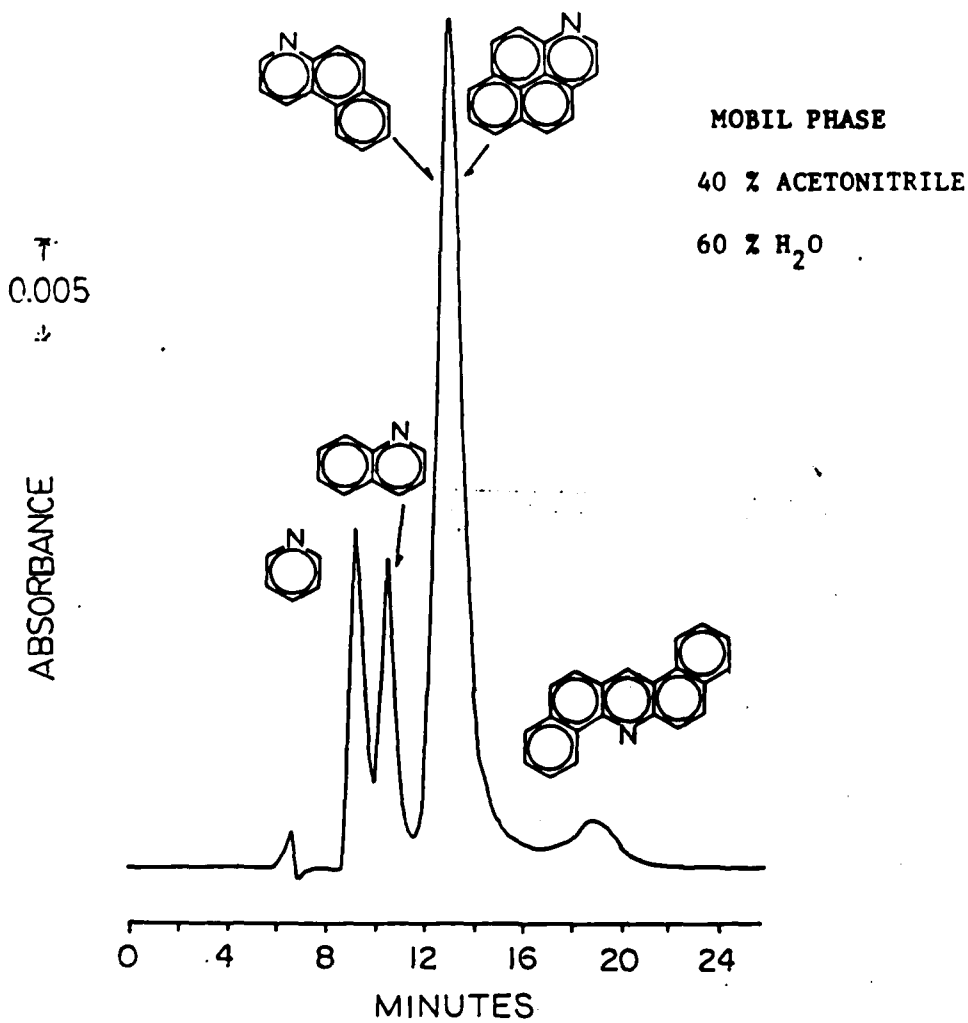

Figure 3. Separation of azaarenes. Chromatographic conditions: same as Figure 1 except mobile phase composition indicated.

III. RESULTS AND DISCUSSION

(1) AZAARENES

A typical normal bonded phase separation is presented in Figure 1. The elution order in the typical normal mode eluent, 2% 2-propanol in methylene chloride, is that of increasing basicity of the ring nitrogen. The result is quite similar to that reported earlier [15] on a microPorasil column with 1% 2-propanol in hexane; the more basic the compound the stronger the interaction with the bonded nitrile group, and the longer the retention. As is clear in Figure 2, increasing the alcohol modifier concentration simply reduces retention by more effectively displacing the polar solutes from the active nitrile sites.

The chromatogram in Figure 3 looks like a typical reversed phase separation. The elution order is the reverse of that in Figures 1 and 2 . Now retention increases with ring number, i.e. decreasing solubility in the aqueous mobile phase [16]. Increasing the % water increases the retention times but has no effect on relative retention. The elution order and relative retention times are quite similar to those reported for a microBondapak-C18 column [15]. The difference here is that the stationary phase used in Figure 3 is the same nitrile bonded column used in Figures 1 and 2.

This clearly emphasizes the importance of the eluent in bonded phase LC. One has been led to believe that use of a polar eluent with a polar stationary phase would always eliminate retention. Instead, the stationary phase is turned into a non-selective but nontheless retentive materials when water-acetonitrile is the mobile phase. To expand on what was stated earlier [16], for similar solutes the selectivity lies in the aqueous eluent, for polar as well as nonpolar bonded phases.

(2) PHENOLS AND ANILINES

To compare further typical polar and nonpolar bonded phases, a series of phenols and anilines was chromatographed on both the nitrile and C-18 phases using pure dichloromethane in both cases. The k' values are listed in Table . On the nitrile column, the acidic phenol can interact with the electron-rich nitrile group, and thus elutes after aniline which interacts less strongly via hydrogen bonding. That this acid-base type interaction is governing retention is clear from the k' values of the substituted phenols. As the ring is substituted with electron-donating or -withdrawing groups, which respectively decrease and increase phenol acidity, retention decreases or increases relative to phenol itself. As the hydroxyl group is increasing shielded by a tert-butyl group, retention decreases relative to phenol, as expected.

Compared with the nitrile column, on the C-18 column with pure dichloromethane eluent the elution order of phenol and aniline reverses. Clearly this means the ostensibly nonpolar C-18 packing contains acidic sites, i.e. the residual silanol groups which interact strongly with the basic aniline. Phenols are now retained via hydrogen bonding to the residual silanol groups. The elution orders of the substituted phenols are the same on the C-18 as on the nitrile phase, although they are retained less, and the resolution is poorer on the C-18 column because of tailing. But on both column as the phenolic group becomes shielded or provided with electrons, retention decreases relative to phenol, as expected.

The same two stationary phase-solute interactions, acid-base and hydrogen bonding, are operative with the anilines, although the roles of the stationary phase and solute are now reversed. The $-NH_2$ group can hydrogen bond to the nitrile groups and undergo acid-base interactions with the residual silanols on the C-18 column. Thus as shown in Table 1, electron-withdrawing groups decrease retention of the substituted phenols; electron-donating groups do the opposite. The elution order of the 4-substituted anilines is the same on the C-18 phase as on the nitrile phase. For the dimethyl anilines, a combination of shielding and electron-donation effects are evident, and again demonstrate a strong interaction between the basic $-NH_2$ groups and the exposed residual acidic silanols on the bonded phase.

Use of dichloromethane eluent with basic and/or hydrogen bonding solutes might in fact serve as a useful indicator of residual silanol groups on the C-18 phases. The well-demonstrated [17] discrepancies among C-18 phases of different manufacturers in terms of relative retentions is probably largely traceable to residual silanols; little has been done in devising simple quantitative chromatographic indicators to test for their presence.

TABLE 1

k' Values for Phenols and Anilines

on C-18 and Nitrile Phases Using CH_2Cl_2 Eluent

Compound	Nitrile	C-18
phenol	1.55	0.68
4-phenylphenol	1.28	0.47
4-nitrophenol	3.70	2.73
3-nitrophenol	3.17	2.27
2-nitrophenol	0.13	0.10
3,4-dimethylphenol	1.43	0.47
2,4-dimethylphenol	0.80	0.27
2,6-dimethylphenol	0.23	0.07
4-t-butylphenol	1.25	0.27
3-t-butylphenol	0.93	0.10
2-t-butylphenol	0.20	0.00
aniline	1.10	1,30
4-methylaniline	1.80	2.53
4-chloroaniline	1.00	0.86
4-nitroaniline	0.80	0.40
2,4-dimethylaniline	1.53	1.67
2,3-dimethylaniline	1.15	1.07
2,6-dimethylaniline	0.55	0.33

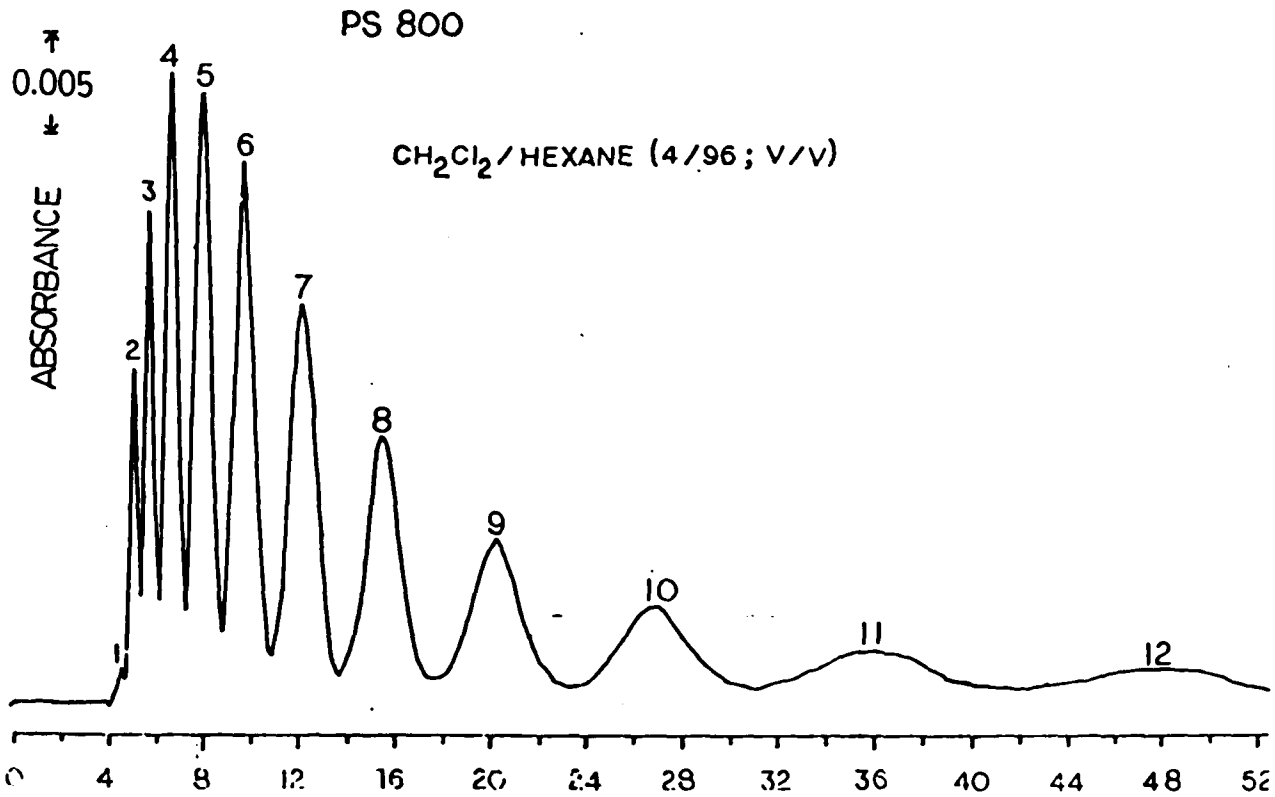

Figure 4. Separation of styrene oligomers in polystyrene standard PS800. Chromatographic conditions: same as Figure 1 except mobile phase indicated. Numbers above peaks correspond to the degree of polymerization.

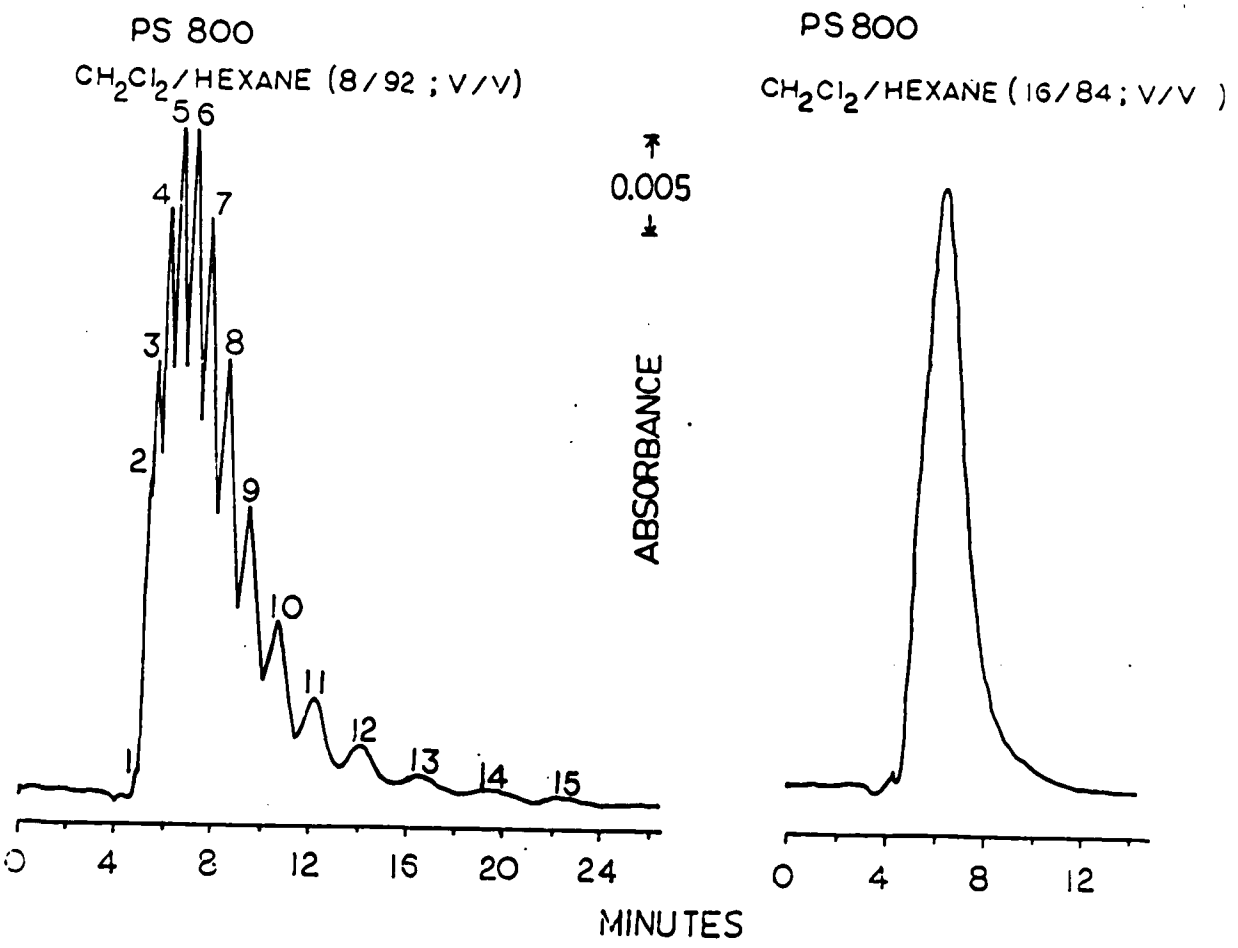

Figure 5. a. Separation of styrene oligomers in PS800. Chromatographic conditions : same as Figure 4 except mobile phase composition indicated. b. Chromatogram of PS800. Chromatographic conditiond : same as Figure 5a except mobile phase indicated.

(3) SIZE EXCLUSION CHROMATOGRAPHY

The silica base for the bonded groups is a microporous material of 60A average pore size; these silicas have been used for size exclusion chromatography (e.g. 7). We have made the interesting observation that for polystyrenes, the nitrile bonded column can act as a pure adsorbent, a mixed adsorbent-size exclusion medium, and a pure molecular sieve, depending on the composition of the mobile phase. The elution order on the nitrile column for the PS800 oligomers is that of increasing degree of polymerization, i.e. the usual reversed phase and normal phase order, for hexane-rich dichloromethane/hexane eluents, is shown in Figures 4 and 5. The collapse of the oligomer peaks into a single peak at a dichloromethane/hexane ratio of 1/4 shown in Figure 5b suggests that one might separate diverse molecular weight polystyrenes on the basis of solubility, i.e. typical reversed phase order. In Figure 6a such a separation is observed at a 40/60 ratio of dichloromethane/hexane; retention time increases rapidly with molecular weight. At a 50/50 ratio, however, the elution order is seen to reverse (Figure 6b); the higher molecular weight polystyrene elute before the lower, i.e. the size exclusion order. At a 90/10 ratio, styrene itself elutes at the interstitial volume, after the higher molecular weight polymers (Figure 6c). This suggests that there should be some solvent composition at which the two mechanisms -- adsorption and size

exclusion -- are operating simultaneously, giving no net separation. In fact we observe this at a 45/55 solvent ratio, as shown in Figure 7.

This remarkable result could have practical applications, for example in the prefractionation of polymeric materials or cleanup of complex samples. One would not need silicas of diverse pore sizes but could effect selective separations simply by varying the eluent composition.

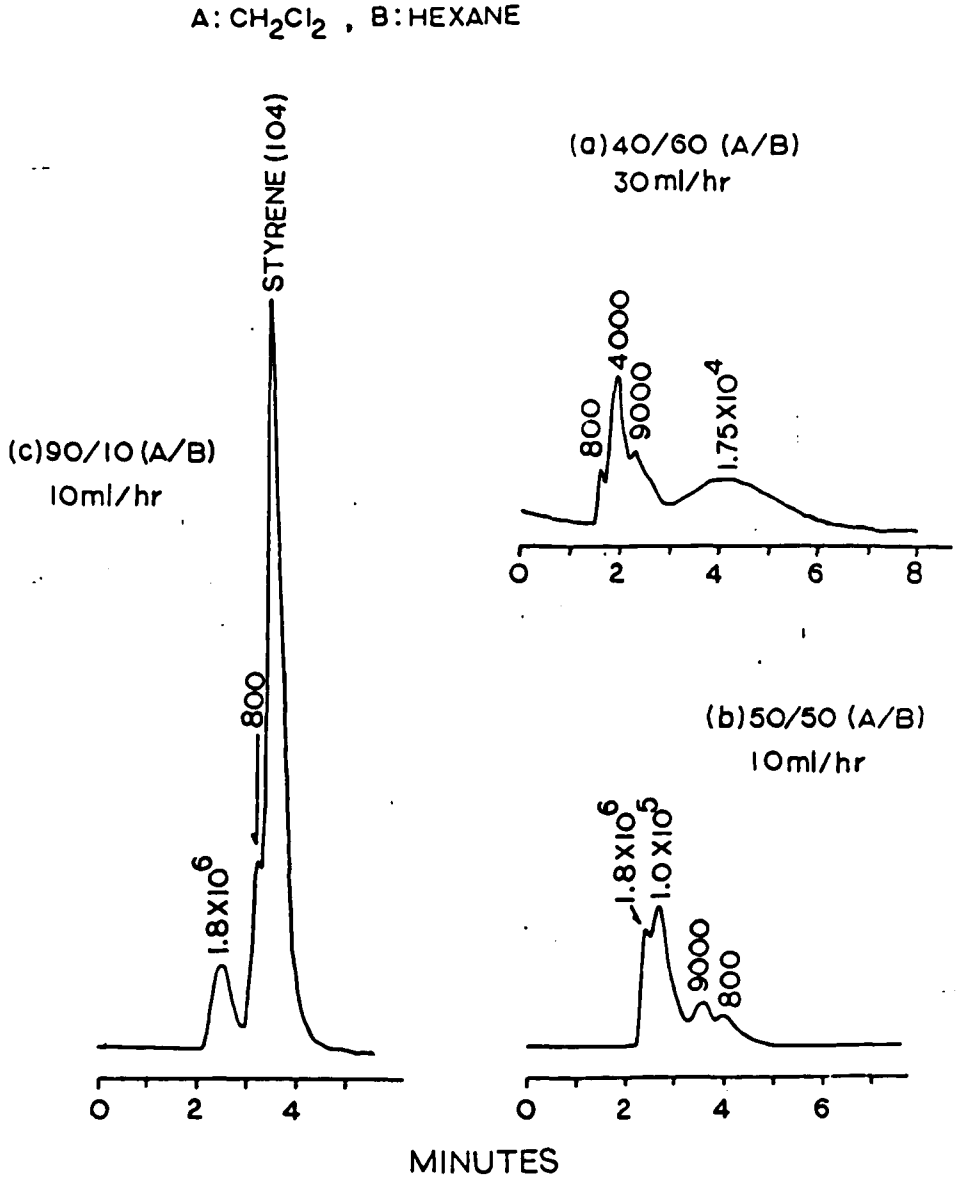

Figure 6. a. Adsorption-mode separation of polystyrenes. Chromatographic conditions: same as Figure 4 except mobile phase composition and flow rate indicated.

b. Mixed adsorption-size exclusion mode separation of polystyrenes. Chromatographic conditions : same as Figure 4 except mobile phase composition indicated.

c. Size exclusion separation of polystyrenes. Chromatographic conditions: same as Figure 4 except mobile phase composition indicated.

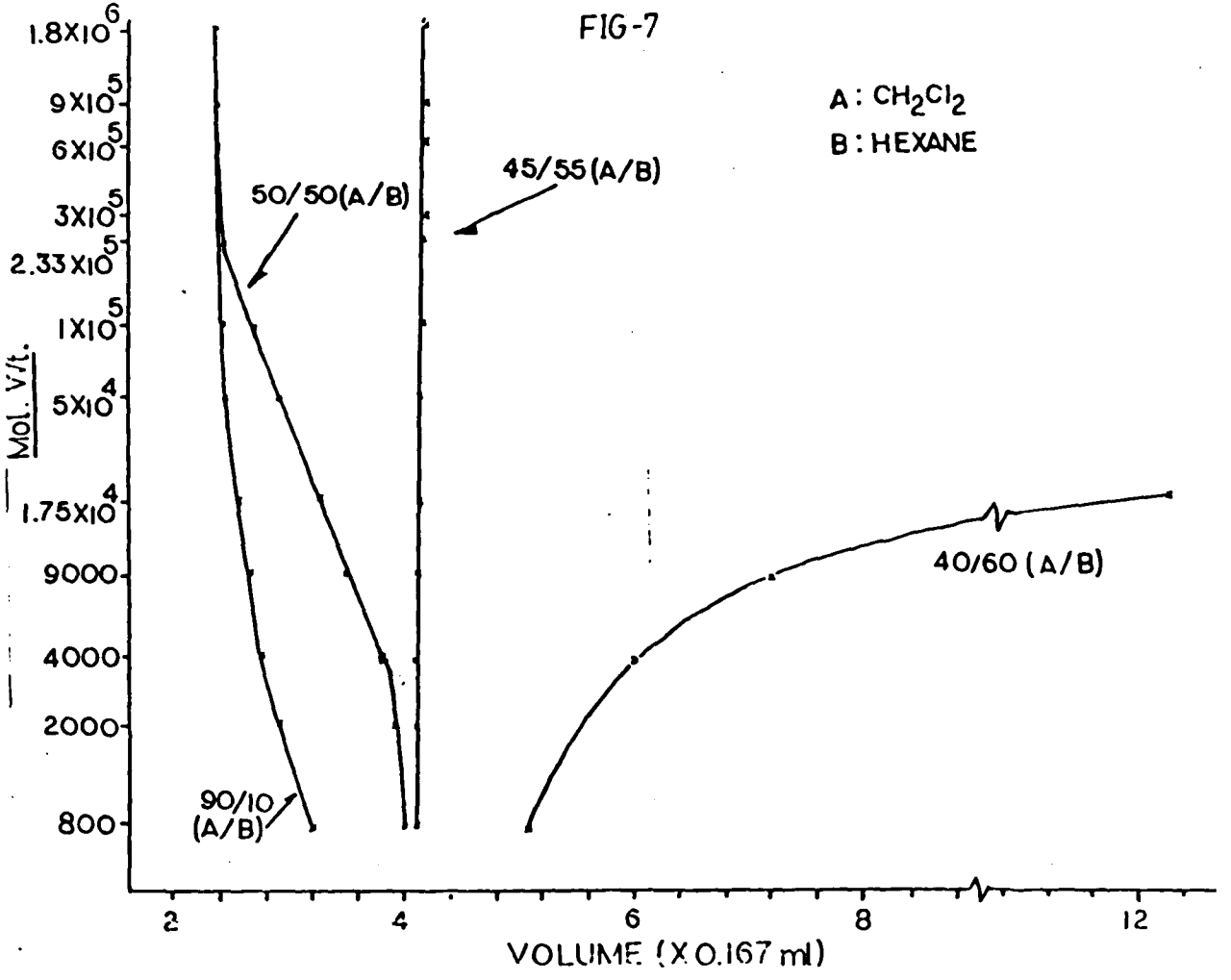

Figure 7. Effect of mobile phase composition on the log molecular weight-retention volume relationships for polystyrenes on the same nitrile-bonded phase column.

IV. SUMMARY

Reversed phase and normal phase will no doubt continue to be used. We suggest however that it may be advantageous to change the basis for these designation from the present definition in terms of the stationary alone, to one based on the primary source of the selectivity, in whichever phase it may be. Thus "normal" phase could be used to designate those combination of solute, stationary phase, and eluent in which the selectivity is determined primarily by the solute-stationary phase interactions. "Reversed" phase would then pertain to those in which the mobile phase controlled selectivity, i.e. solubility. Thus any given stationary phase may not function in the same mode with different solvents, and vice versa. As with all labels, it is of course the product that is most important; i.e. here, the chromatographic separation counts more than what the system producing it is called. But to match the appellation to the actual system would be far more descriptive than the present way.

In addition, it may encourage the more adventurous use of solvents; the full potential of HPLC will never be realized if only the common, and comfortable, combinations are used. This may be timely realization in view of the growing popularity of microbore columns. With their minimal solvent consumption requirements, and their compatibility with less conventional detectors, wider experimentation with solvents should result.

Another encouraging factor is the development of the optimization scheme of Glajch and Kirkland [18], which also emphasizes the importance of the solvent in determining LC selectivity.

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