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NOTE

The Determination of Residual Styrene in Copolymers by a Fast Gel Permeation Chromatography Procedure Using Microstyragel Columns

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Abstract

A fast and sensitive gel permeation chromatography procedure is described for the determination of residual styrene. Demonstrated precision levels are about the same (±5%) as those found in the gas chromatography procedure.

INTRODUCTION

Residual styrene in polymers has been traditionally determined by gas chromatography (GC) (*1*, *2*). In the GC procedure, polymers are generally dissolved in a good solvent, precipitated by a nonsolvent, and the dissolved styrene then injected into the column and quantitated. In most cases, however, a small amount of the polymer remains dissolved after precipitation, and extra precautions must be taken to avoid plugging the GC column.

The speed and resolving power of gel permeation chromatography (GPC) has been greatly increased by the introduction of Microstyragel column packing material. The high resolving power enables one to separate small molecules rapidly from a polymer matrix (*3*). The method is particularly suited for the separation and quantitative determination of styrene because of the very high sensitivity of detection using 254 nm wavelength in a UV detector.

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EXPERIMENTAL

A model 520 ALC/GPC high-speed liquid chromatograph (Waters Associates, Inc., Milford, Massachusetts) equipped with a model 6000 solvent delivery system, a UV detector fixed at 254 nm, and a model U6K valve injector were used for this study. The column set consisted of 2 × 500 Å and 3 × 100 Å μ-styragel columns also obtained from Waters Associates. Sample injections were made using Precision Sampling series C syringes both at 10 and 100 μl capacity.

A standard solution was prepared containing 1 μl styrene monomer (Eastman Kodak Reagent Grade 1465) per 250 ml of Spectrograde chloroform (Eastman Kodak) providing 0.036 μg styrene per ml. The Spectrograde chloroform was also used as the mobile phase.

Calibration Procedure

Replicate injections of 5, 10, 15, 20, and 25 μl containing various known levels of styrene were made. The mobile phase flow rate was set at a constant value of 0.8 ml/min. A Texas Instruments recorder, operating at 12 in./hr chart speed, was utilized to monitor the UV response at 254 nm. A calibration curve for the 5 to 25 μl injections was prepared. Figure 1 illustrates the relationship for multiple injections at five different concentration levels. Detector response is linear throughout the entire range of interest. The peaks are symmetrical and narrow, and the peak heights can be related directly to concentration. Table 1 contains replicate peak height values of the five concentration levels studied.

With calibration curves established, the procedure was tested with polymer samples containing different amounts of residual styrene. These samples were analyzed via the conventional gas chromatography technique as well.

Gas Chromatographic Procedure

One gram of the copolymer was placed in a 15-ml serum vial. To this, 10 ml of methylene chloride, containing 10 μl toluene internal standard, was added. A 1-μl injection of this solution was used for the determination A 6 ft × 1/8 in. column packed with 10% W-982 on 80–100 mesh chromosorb P (Applied Science) was used. Helium flow was kept at 15 ml/min. The injection port sleeve was packed with glass wool to trap resins. The injector port temperature was kept at 150°C and the detector

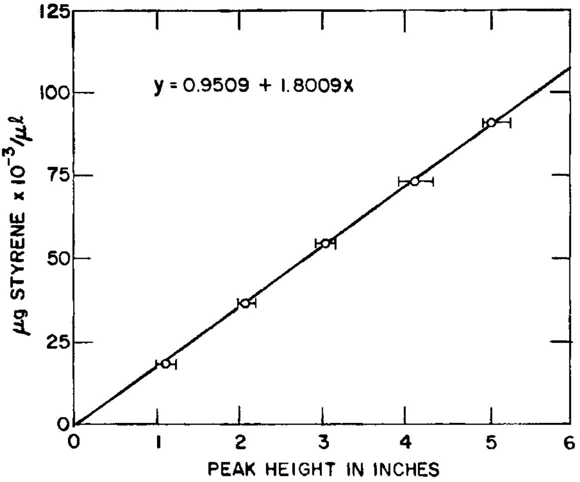

FIG. 1. Calibration curve for the amount of styrene in 5 to 25 μl samples containing 0.036×10^{-3} μg/μl styrene. Each point is an average of at least four analyses. Error bars represent the highest and lowest values obtained.

TABLE 1

Peak Height Results of Replicate Injections for Calibration (Concentration = 0.036×10^{-3} μg/μl)

	Peak height (in.)				
	5	10	15	20	25
Run no.	Microliters injected				
1	1.2	2.1	2.9	4.2	5.3
2	1.2	2.0	3.1	4.0	5.0
3	1.1	2.1	3.1	3.9	5.0
4	1.0	2.1	3.0	4.0	5.0
5			3.2	4.4	
Average	1.12	2.07	3.06	4.10	5.07
σ	0.096	0.0500	0.114	0.200	0.150
$\%\sigma$	8.5	2.4	3.7	4.9	2.9

temperature at 250°C. The oven was set to hold at 70°C for 8 min, then programmed to rise 160°C/min to 130°C. The upper limit temperature was held for 4 min.

Fast GPC Procedure

Samples of styrene copolymers were dissolved in chloroform (0.5% by weight) and 20 μl of each solution injected. The major copolymer portion, having a large molecular weight value (M_w = 70,000 to 200,000), emerged at the interstitial volume. The monomeric styrene eluted later as indicated in a typical chromatogram in Fig. 2. Peaks in between represent different oligomeric species. The entire separation takes place in about

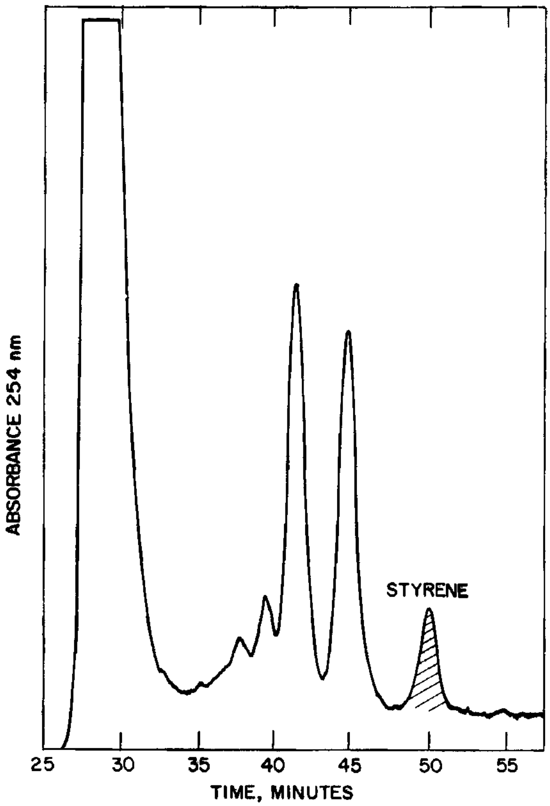

FIG. 2. Typical GPC chromatogram of a styrene copolymer.

TABLE 2
Percent Styrene in Copolymers by Microstyragel GPC and Gas Chromatographic Techniques

Sample	Percent styrene	
	Microstyragel GPC[a]	GC[a]
Copolymer I[b] (bulk polymerized) $M_w \approx 100{,}000$	0.0514	0.0500
Copolymer II[b] (bead polymerized) $M_w \approx 70{,}000$	0.0028	Not detected
Copolymer III[b] $M_w \approx 200{,}000$	0.0528	0.0530
Copolymer IV[b] $M_w \approx 200{,}000$	0.0490	0.0520

[a] Average of four determinations.

[b] Copolymer I, II, III, and IV are styrene-acrylate polymers. I and II contain 65% styrene, whereas III and IV contain 15% styrene.

50 min. Results obtained on GC and Microstyragel GPC determinations are presented in Table 2. It is interesting to note that the residual styrene content of the bead polymerized Copolymer II can only be detected by the GPC procedure. This is because the UV detector is more sensitive than the flame ionization detector used in GC.

Separation of Styrene, α-Methylstyrene, and Ethylbenzene

Styrene and α-methylstyrene are both principally prepared by the dehydration of alkylbenzenes such as ethylbenzene. An attempt was therefore made to separate the three on Microstyragel columns. Table 3 shows retention times of the three components injected individually. Ethyl-

TABLE 3
Retention Times for Styrene, α-Methylstyrene, and Ethylbenzene on Microstyragel columns

Compound	Molecular weight	Retention time (min)
Styrene	104.15	51.0
Ethylbenzene	106.00	50.8
α-Methylstyrene	118.18	53.05

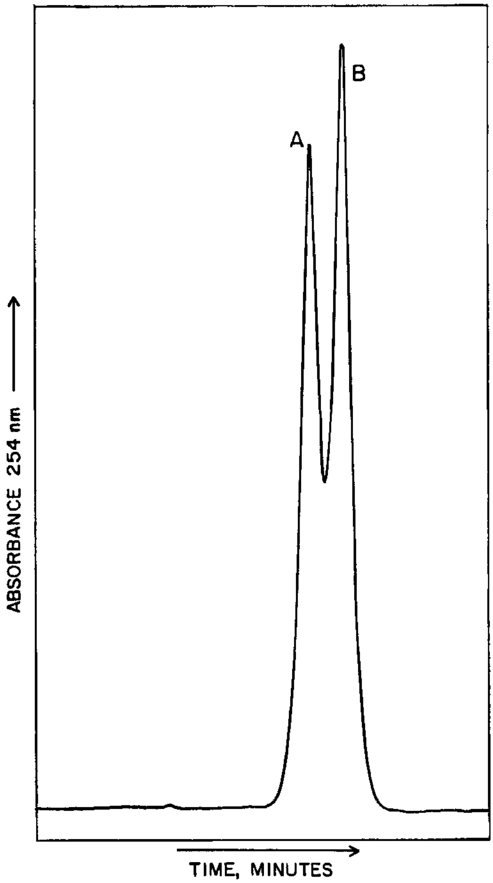

FIG. 3. GPC chromatogram of styrene, α-methylstyrene and ethylbenzene mixture. Peak A: styrene + ethylbenzene. Peak B: α-methylstyrene.

benzene and styrene cannot be separated in a mixture under the conditions described under the fast GPC procedure. They can, however, be separated from α-methylstyrene although the peaks do not show baseline separation. Figure 3 shows the separation of styrene, ethylbenzene, and α-methylstyrene. Peak A corresponds to the first two components while Peak B represents α-methylstyrene.

DISCUSSION

The proposed method offers a simple and more sensitive approach to quantitating residual styrene in styrene copolymers. Precision levels (±5%) are about equivalent to the GC method (*1*, *2*). The longer analysis time of the GPC technique is offset by the minimum sample preparation and methods development time. Since the separations are based on molecular size rather than chemical interaction with the column material, exhaustive trial and error determination of the column/eluent system for GC is eliminated in the proposed procedure. The sensitivity of the fast GPC method is evident by the fact that residual styrene in the 0.003% range was detected but remained undetected by the GC method. A combination GPC/LC procedure is being devised whereby the small molecules are initially separated by a fast GPC procedure and then subjected to LC separation. This should enable us to separate molecules of nearly identical size (viz. ethylbenzene and styrene).

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