NOTES

Problems Associated with the Gel Permeation Chromatography of Sulfur-Containing Polymers

The determination of meaningful molecular weights of sulfur-containing polymers such as polysulfones is difficult because of their poor solubility in the common organic solvents. Endgroup analyses, viscosity studies, and cryoscopic measurements on these polymers have provided unsatisfactory and unreliable molecular weight data.[1-3]

Recently we investigated the use of gel permeation chromatography (GPC) to determine the molecular weights of butene polysulfones[4,5] and poly(alkyl thiomethacrylates),[6,7] since these polymers are soluble in tetrahydrofuran. The instrumental problems encountered during this work were unexpected and are reported here in order that others interested in similar polymers will be cognizant of these difficulties. The instrument was a modified Waters Model 200 gel permeation chromatograph equipped with five sample columns. The permeability limits of these columns (in descending order) are 1×10^6 Å, 5×10^4 Å, 1.5×10^4 Å, 1×10^4 Å, and 1×10^3 Å.

The problems evidenced themselves in two different ways. The polysulfones "hung up" in the GPC columns resulting in severe plugging and deterioration of the column system with a concomitant rapid pressure increase. The thiomethacrylates did not cause column damage or a pressure increase in the system; however, the noise level increased, as shown in Figure 1, rendering molcular weight distribution determinations untenable. The noise characteristics were different from those normally associated with air bubbles or particulate matter in the refractometer cell.

These two problems have been attributed to physiochemical reactions of the compounds with components of the GPC. The plugging of the Styragel column beads with the polysulfones necessitated complete column refurbishing. The thiomethacrylate polymer coated the refractometer cell, probably by a reaction between the thio compound and the hydrophilic sites of the cell wall.

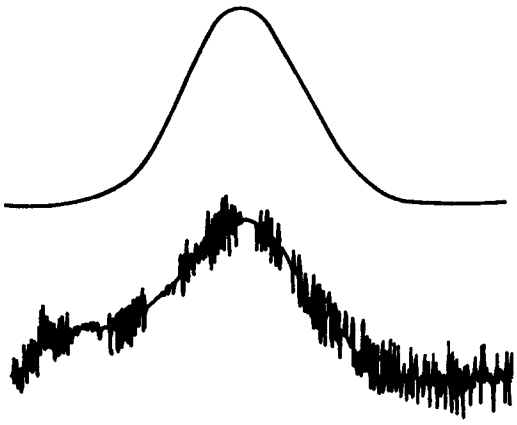

Fig 1. Comparison of a polystyrene and a characteristically noisy polyalkylthiomethacrylate chromatogram.

An experiment was performed to determine whether the plugging was caused by a reaction between the polymer and the Styragel beads, or was due to gel microparticles in the solutions. Samples of the butene polysulfones were passed through 5-micron, 1.2-micron, and 0.22-micron filters. A microscopic examination of these solutions in comparison to the original samples showed the complete absence of gel particles. This suggests that a reaction does take place on the column beads.

Several attempts to clean the cell using the standard acetone, water, and the 10% nitric acid treatment were unsuccessful, i.e., no improvement in the chromatogram noise level was observed. The following cleaning procedure was found to give satisfactory results. The refractometer cell was carefully removed, placed in a small beaker, and covered with concentrated nitric acid. Vacuum was applied to withdraw the air from the cell cavities. After 3 hr, small gas bubbles were observed on the internal surfaces of the cell, indicating that oxidation of the film coating was taking place. The soaking process was continued for 24 hr with several changes of the acid. Reinstallation of the cell in the GPC resulted in a very flat baseline, even at the higher sensitivity settings.

In conclusion, several suggestions are proposed to circumvent these problems. Substitution of passivated glass packing for the Styragel packing should prevent any reactions from occurring on the columns. The use of a sapphire cell should prevent the refractometer from becoming coated with polymer.

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