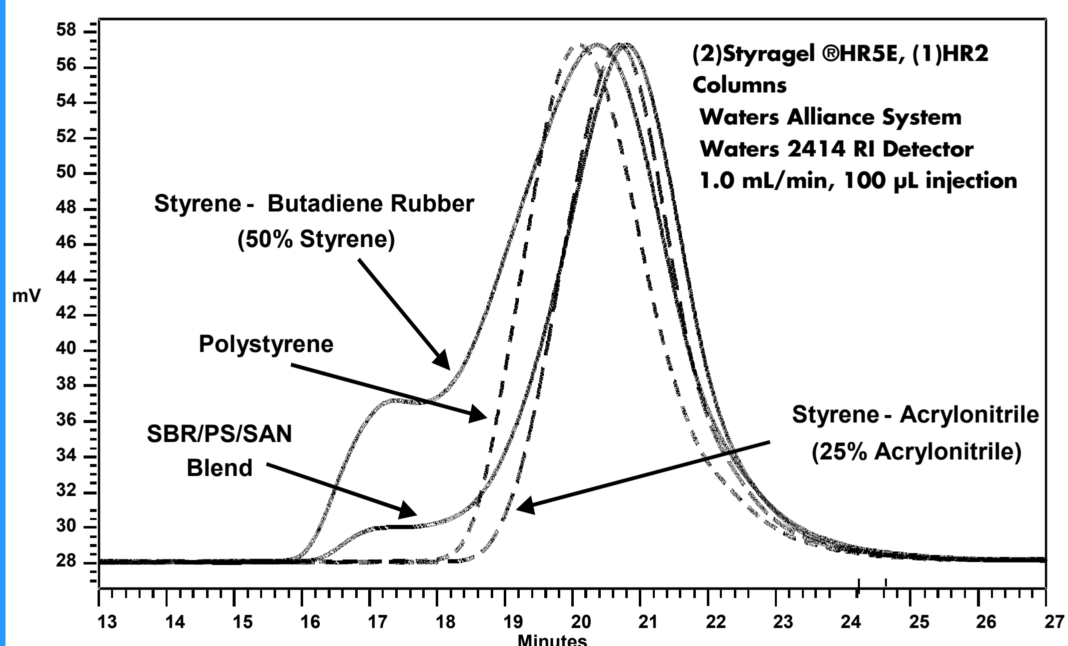
Performance PerSPECtives

Waters® Alliance® System:
Gradient Analysis of Polymer Blends

Introduction: Gel permeation chromatography (GPC) is a chromatographic technique that provides valuable information regarding the molecular weight distribution of a polymer. If the polymer is a true homopolymer, (not a copolymer or blend of polymers), the calculated molecular weight distribution will be accurate for that sample. However, GPC analysis provides no information about the actual composition of the material. Chemists must rely on other methods to determine the composition of the copolymer or polymer blend. This Performance PerSPECtive discusses use of a novel reversed-phase, gradient HPLC technique for polymer composition analysis.

GPC Analysis of a Polymer Blend: Manufacturers frequently blend two or more polymers in order to obtain specific physical properties for a final product. For example, an elastomer such as polybutadiene or polyisoprene may be blended with a more brittle polymer to impart flexibility to the finished material making it less susceptible to stress cracking. Many times polymers are blended to provide chemical resistance as when polyacrylonitrile is added to polystyrene. Chemists frequently need to determine both the molecular weight distribution as well as the percent composition of the individual components contained in blended polymer systems. Figure 1 illustrates overlays of several GPC chromatograms from the analyses of polystyrene, styrene-butadiene rubber (SBR), styrene-acrylonitrile (SAN), and a blend containing all three polymers. Molecular weight distribution information from these GPC analyses provide no information on composition.

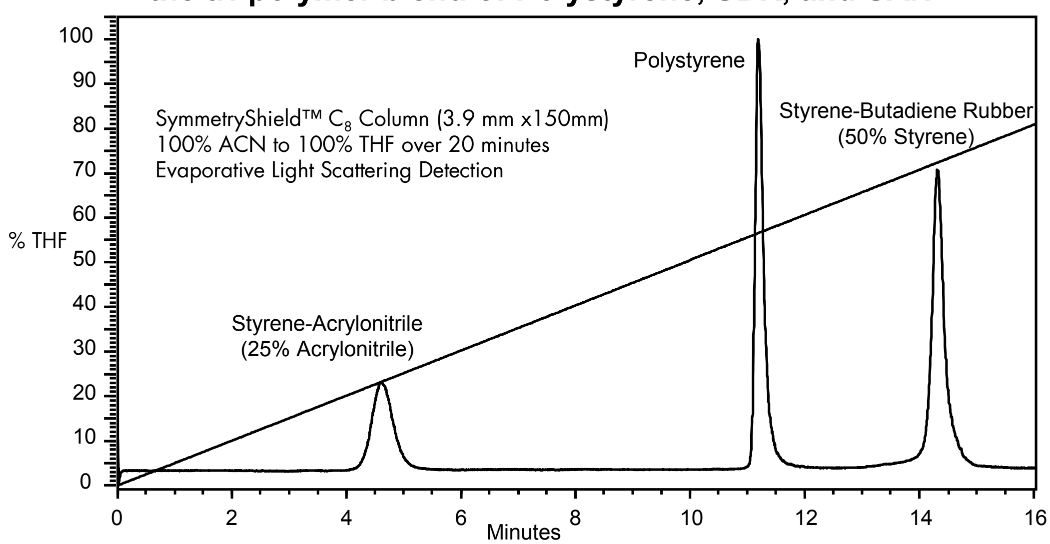
Figure 1: Overlay of GPC chromatograms of polystyrene, SBR, SAN, and an equal blend of the three polymers



Gradient Analysis of Polymers: Reversed-phase, gradient HPLC methods can help scientists obtain composition information on polymers. Compared to GPC, this HPLC separation mechanism relies primarily upon a precipitation / redissolution process. The polymer blend is dissolved in a suitable solvent such as tetrahydrofuran (THF) and injected onto the head of a reversed-phase C_8 or C_{18} column that has been equilibrated with 100% acetonitrile (ACN). The polymer blend precipitates as soon as it is exposed to the ACN at the head of the column. A gradient program, from 100% acetonitrile to 100% THF, is then run. During the solvent change, the three polymers in the blend begin to re-dissolve at different rates. In many cases, the column solely serves as a matrix to accommodate the separation and does not affect the separation. In other instances, the column actually plays a major role in the separation of the polymer blend, with selective adsorption being an important separation mechanism. Compound identification is made by comparing retention times between the eluted peaks from the polymer blend with the retention times obtained from the analysis of known polymer standards (with the same structure) under the same gradient conditions. Typically, a detector that is not affected by the gradient (UV, evaporative light scattering detector - ELSD) is required. In the example below, an ELSD was used.

Figure 2 shows the gradient HPLC separation of the same polymer blend that was separated by GPC in Figure 1. Note the baseline resolution of all three components. Using standards with known composition and concentration, both qualitative and quantitative information on the three components contained in the blend are readily obtained.

Figure 2: Reversed-Phase gradient HPLC separation of the tri-polymer blend of Polystyrene, SBR, and SAN



Summary: GPC analysis provides molecular weight distribution information on a polymer blend, but reverse-phase gradient HPLC analysis can be used to separate polymers in a blend based on composition.

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