Quantitative Analysis of Copolymers using a Pyroprobe

Application Note
General Interest

Author:

Karen Sam

Abstract

This application note demonstrates quantitative analysis of a poly (styrene-isoprene) copolymers including RSDs and a calibration curve.

Analytical pyrolysis is a powerful tool for the qualitative analysis of polymers. The analysis usually starts from a simple pyrogram match to an existing pyrolysis database to identify the polymer chemical structure. If multiple polymers are identified, a quantitative method is often adopted by comparing peak areas of the pyrolysis products to determine each polymer ratio. In this application, styrene-isoprene block copolymers, which are large volume, low priced commercial thermoplastic elastomers, are analyzed by following this approach.

Block copolymer standards styrene-isoprene at 14%, 17% and 22% (styrene to copolymer weight ratio) were obtained from Sigma Aldrich. Solutions of each copolymer standard were prepared in tetrahydrofuran to 1 mg/mL. A 5µL aliquot of each weight % copolymer solution was added to a Drop-In-Sample Chamber (DISC) tube, then pyrolyzed to a setpoint of 600°C using a CDS 6150 Pyroprobe.

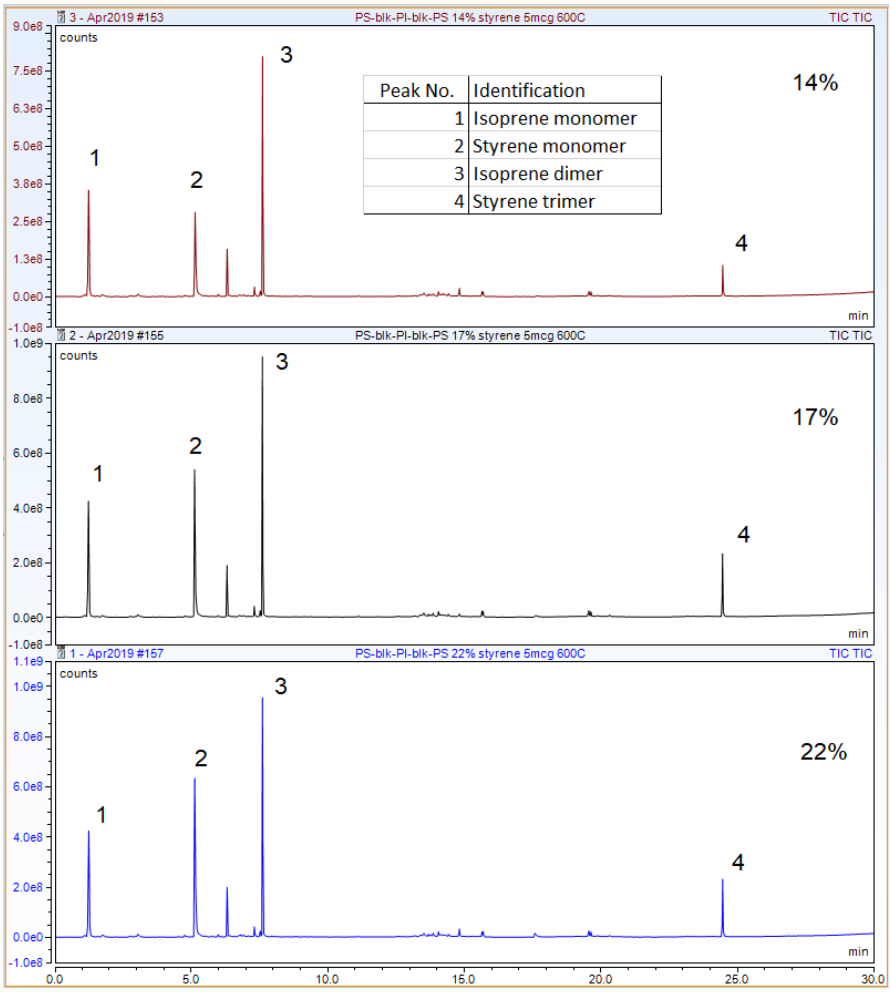

Figure 1. Poly(styrene-isoprene) copolymer pyrogram with 14% (top), 17% (middle), and 22%(bottom) styrene.

	Styrene:Isoprene Dimer Area Ratio	
Rep 1	0.85	
Rep 2	0.86	
Rep 3	0.87	
Rep 4	0.87	
Rep 5	0.86	
Rep 6	0.84	RSD
Rep 7	0.87	1.13%

Table 1. Styrene:Isoprene Dimer Area Ratio Replicate values for 17 wt% styrene poly(styrene-isoprene) copolymer.

Experimental Parameters

Samples were pyrolyzed in a DISC tube, using a CDS Model 6150 Pyroprobe.

DISC Chamber: 600°C 30seconds

Interface: 300°C
Transfer Line: 300°C
Valve Oven: 300°C

GC/MS
Column: 5% phenyl (30m x 0.25mm)
Carrier: Helium 1.25mL/min, 75:1 split
Injector: 300°C
Oven: 40°C for 2 minutes
10°C/min to 300°C
Ion Source: 230°C
Mass Range: 35-600amu

Figure 1 shows pyrograms of poly(styrene-isoprene) copolymers containing 14, 17, and 22 weight % styrene. When pyrolyzed, polystyrene is principally broken down to monomer (Peak 2 in Figure 1) and trimer (Peak 4 in Figure 1). As the styrene weight increases in the copolymer, so does the area of the peaks from polystyrene (Peaks 2 and 4) in relation to the peaks from poly-isoprene (Peaks 1 and 3).
Considering the signal to noise ratio and the simplicity of algorithm, the highest peaks from styrene monomer (Peak 2) and isoprene dimer (Peak 3) were chosen for quantitative analysis. Area ratios of these two peaks were plotted against the weight percent of styrene in each of the standards in Figure 2, which shows a linear calibration with a R2>0.99. The reproducibility study was also carried out from seven sample runs on the 17% styrene standard. An RSD of 1.13% is obtained in Table 1.

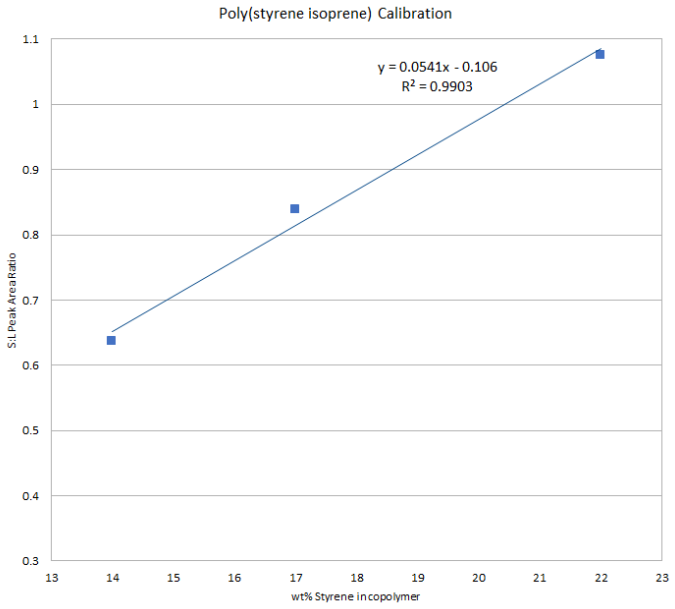

Figure 2. Styrene monomer to isoprene dimer ratio vs. styrene weight % in copolymer.

The linearity and RSDs demonstrate that the latest version of the Pyroprobe from CDS is adept at the quantitative analysis of copolymers.