Quantitative Analysis of Low Levels of Methyl Methacrylate in a Copolymer

Author:

Karen Sam

Application Note
General Interest

Abstract

Quantitative analysis of poly(methyl methacrylate) contamination with a calibration curve.

Introduction

When a material is made using several different monomers, like a styrene/butadiene rubber, ethylene/propylene copolymer or a latex paint, pyrolysis-GC/MS can be a valuable tool in identifying both monomers used and quantitatively determining the relative amounts of each. Whether mixtures, blends, laminates, random or block copolymers, compounds will be produced relating to each of the monomers present, which can be used study the molecular formula. This is frequently done using copolymers with just a few monomers, each of which represents a significant part of the copolymer. The same method can be used to determine small concentrations of monomers or even trace contaminants. In this application, a polystyrene copolymer with levels of methyl methacrylate contamination was analyzed.

Polystyrene copolymer, approximately 100µg, containing 0.1%, 0.2% and 0.3% and 0.4% poly(methyl methacrylate) contamination was pyrolyzed to a setpoint of 750°C using a CDS Pyroprobe to create a calibration curve.

Experimental Parameters

CDS Model 6150 Pyroprobe
Pyrolysis: 750°C 15seconds

Interface: 300°C
Transfer Line: 325°C
Valve Oven: 325°C

GC/MS
Column: 5% phenyl (30m x 0.25mm)
Carrier: Helium 1.00mL/min, 50:1 split
Injector: 300°C
Oven: 40°C for 2 minutes
                    10°C/min to 325°C
Ion Source: 230°C
Mass Range: 35-600amu

Results and Discussion

Figure 1 shows a pyrogram of product with 0.4% methyl methacrylate contamination. When pyrolyzed, polystyrene produces monomer, dimer, and trimer. This pyrogram shows styrene monomer, dimer and trimer as well as other peaks, including one for toluene, and a small, but still measurable peak for methyl methacrylate.
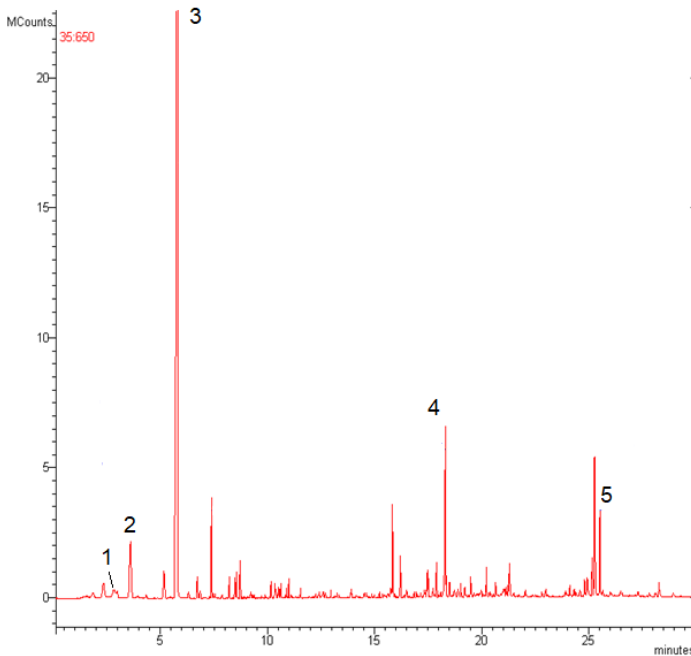
Figure 1. Polystyrene copolymer with 0.4% methyl methacrylate contamination. Peak 1: methyl methacrylate, Peak 2: toluene, Peak 3: styrene, Peak 4: styrene dimer, Peak 5: styrene trimer.

Figure 2 contrasts the 0.1% and 0.4% samples. As the relative amount of methyl methacrylate increases, its peak intensity increases. Considering the similarities in relative peak areas and retention times, the toluene peak was chosen to compare with methyl methacrylate for quantitative analysis.
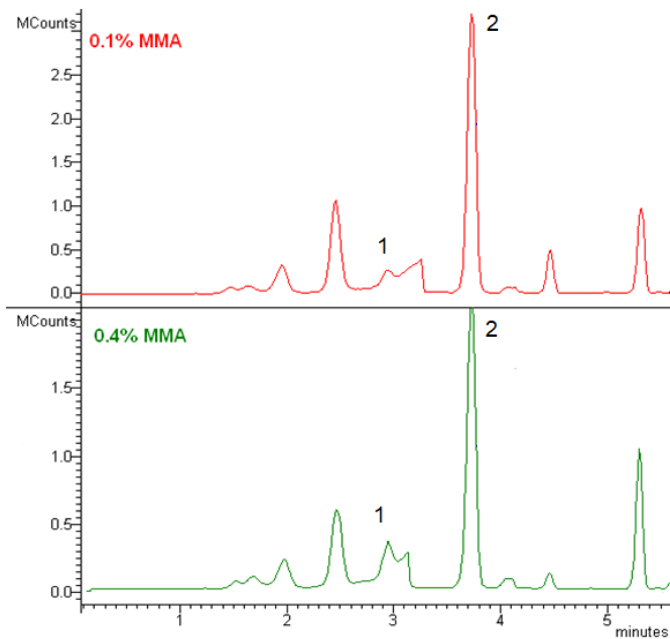
Area ratios of these two peaks were plotted against the weight percent of methyl methacrylate in each of the standards in Figure 3. This shows a linear calibration with an a R2>0.99. Using a peak area ratio of two peaks produced by pyrolysis of the sample makes the assay independent of the sample size, so it is not necessary to weigh each sample before pyrolysis. Producing a calibration curve from polymers of known content then makes it simple to determine the amount of methyl methacrylate contained in an unknown polymer.
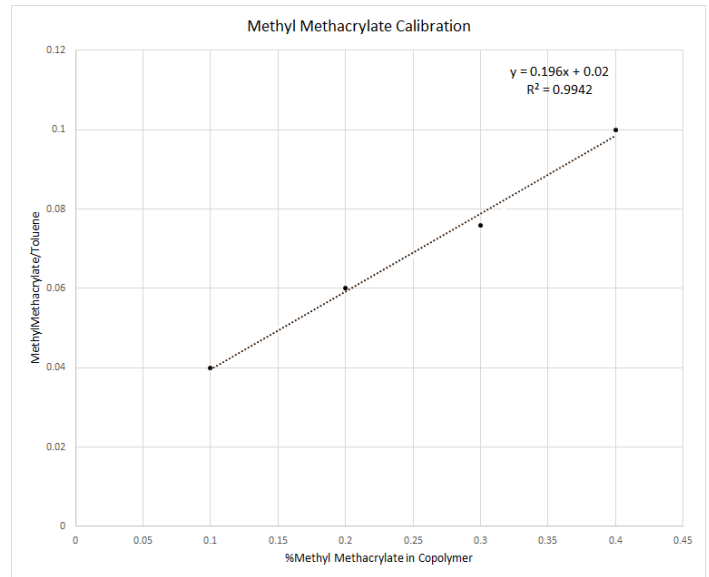

Figure 3. methyl methacrylate to toluene area ratio vs. methyl methacrylate % in copolymer.

Conclusion
The linearity demonstrates that the Pyroprobe from CDS is adept at the quantitative analysis of trace level copolymer contamination.

Figure 2. Polystyrene copolymer with 0.1% and 0.4% MMA in copolymer. Peak 1: MMA, Peak 2: toluene.