Quantification of Monomer Concentration without Calibration and Internal Standard using GC/Pyrolysis and the Polyarc® Reactor

Application Note

Acrylic Binders for Latex Paints

Author

Cidnie Hoang
BEHR Process Corporation
3400 W. Segerstrom Ave.
Santa Ana, CA 92704
chhoang@behr.com

Abstract

A Polyarc system was used, in conjunction with the traditional GC-Pyro/FID technique, for monomer concentration quantification. As with any chromatography method, monomer concentration quantification also requires multiple point calibration for each of the monomer of interest. With the Polyarc, the concentrations of BA and MMA monomers in an in-house prepared mixture were successfully quantified with relative errors of 3.6% and 3.2%, respectively. This was done with neither calibration nor the use of an internal standard. The results for BA and MMA in the 100% acrylic copolymer binder sample were also highly accurate, with relative errors of 0.9% and 1.5% for BA and 0.6% and 1.2% for MMA, with and without EGDE (internal standard), respectively. These show that no calibration or internal standard are required for monomer concentration quantification in a copolymer mixture.

Introduction

Acrylic binder is one of the major components in latex paints. There are several types of acrylic binders, such as 100% acrylics, vinyl acrylics, styrene acrylics, and much more. Generally speaking, the higher the acrylic content, the better the quality of the paint. One way to quantify the type and amount of acrylics in the binder is by the use of GC pyrolysis (GC-Py) with a flame ionization detector (FID). One major challenge with GC-Py is the formation of thermal decomposition byproducts of the original material since the sample is heated to a high temperature. It would be impossible to calibrate for each of the byproducts when standards are either not available, prohibitively expensive, or do not even exist. By converting all carbon-containing components to methane with the Polyarc system, prior to detection in the FID, the needs to calibrate can be eliminated since the area-per-mol of carbon is equivalent for all carbon-containing components after the conversion. The following work is done to show whether the method works and whether monomer concentration can also be quantified without the use of an internal standard.

Experimental

An Agilent 6890A GC equipped with a split/splitless inlet, a capillary optimized FID, mass spectrometer (Agilent 5975), CDS Pyroprobe 5000 series (Model 5200), and an ARC Polyarc reactor (PA-RRC-A02) were used for the analysis. Helium (99.999%, Airgas) was used as the carrier and FID makeup. Air (zero-grade, Airgas), and H_2 (99.99999+, Parker Balston H_2 generator) were supplied to the ARC electronic flow control module (PA-MFC-A09) and to the FID. The effluent of the GC column was sent to both the FID and MS detectors simultaneously through an Agilent 3-way CFT splitter (G3183-60500). The MS was connected to the splitter via fused silica capillary restrictor (R1) (Agilent, 160-2635-5, 0.6 m, 0.1 mm ID). The inlet to the Polyarc was connected directly to the splitter (R2) while the outlet of the Polyarc was connected directly to the FID. The pressure of the splitter was controlled by an electronic pneumatic control (EPC) set to 3.2 psig. Figure 1 illustrates the configuration.

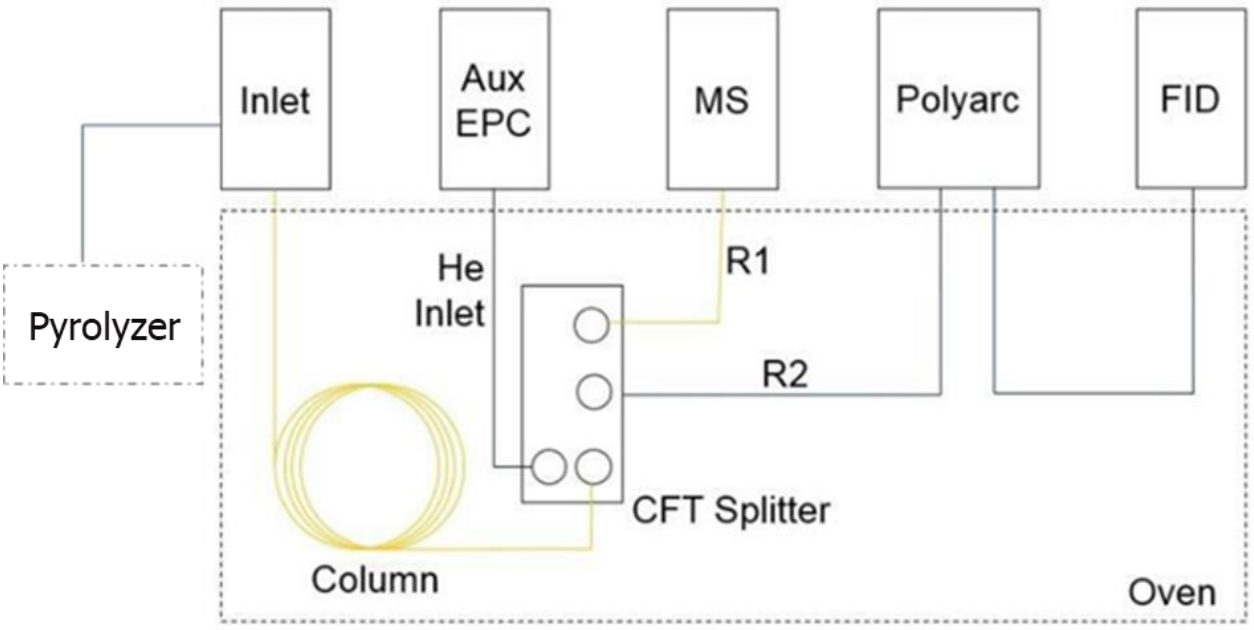

Figure 1: Configuration of GC-Polyarc®/FID and MS with the 3-way SFT splitter.

GC conditions

Front inlet	Split/Splitless
Inlet Liner	Agilent 5183-4647
Injection Mode	External Device (Pryolyzer)
Inlet temperature	260 °C
Inlet pressure	7.33 psi
Inlet Mode	50:1 Split
Column Flow	1 sccm, Constant Flow
Septum purge flow	3 sccm
Oven	40 °C (hold 2 min), 10 °C/min to 300 °C
Column	Restix Rxi624 Sil MS (30 m × 0.32 mm × 1.8 µm)
Syringe	10 µL
Injection volume	1 µL

Polyarc reactor conditions

Setpoint	293 °C
H_2	35 sccm
Air	2.5 sccm

sccm = standard cubic centimeter per minute

FID conditions

Temperature	270 °C
H_2	5 sccm
Air	150 sccm
Makeup	25 sccm (He)

Pyrolyzer conditions

Transfer Line Temperature	300 °C
Mode	Trap
Probe Temperature	50°C initial, 0°/min to 700°C final (15 sec)
Interface Temperature	50°C rest; 50°C initial, 20°/min to 325°C (1 min)
Trap Temperature	50°C rest; 300°C desorb (3 min)

Results and Discussion

An in-house prepared copolymer mixture of MMA and BA was analyzed with the Polyarc. This sample was first pyrolyzed, as-is without the addition of EGDE or further preparation, and the pyrolysates were analyzed after being detected by the FID (Figure 2). Each peak in the chromatograph was identified using the MS. The concentration of each monomer was calculated by first determining the relative mass response factors (RMRFs) using equation 1. Since no internal standard was added, one of the monomers was chosen to represent the "standard" and calculation was carried out as though there was one. In this case, BA was arbitrarily assigned as the "standard."

$$RMRF_A = \left(\frac{Mw_A}{Mw_S}\right)\left(\frac{\#C_S}{\#C_A}\right) \quad (1)$$

Where:

Mw_A = Molecular weight of monomer MMA
MW_S = Molecular weight of monomer BA
$\#C_S$ = Number of carbon atoms per molecule of BA
$\#C_A$ = Number of carbon atoms per molecule of MMA

Then the following equation was used to determine the mass percentage of each monomer by normalizing with the total peak areas of both BA and MMA:

$$X_A = \frac{(Area_A \cdot RMRF_A)}{\sum_{i=1}^{n}(Area_i \cdot RMRF_i)} * 100 \quad (2)$$

Where:

X_A = Mass fraction of a monomer of interest

(Refer to "Quantification with the Polyarc.pdf" at https://www.activatedresearch.com/documents/ for more information on the analysis procedure)

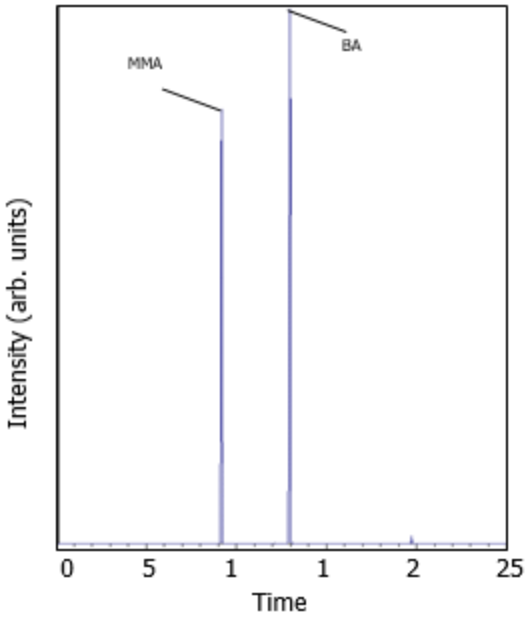

Figure 2: Polyarc/FID chromatogram of BA and MMA copolymer mixture without internal standard

As shown in Table 1, both monomers were quantified with relative errors of less than 4.0%. An 100% acrylic copolymer binder, with and without the addition of EGDE, was also analyzed. The results for BA and MMS in the binder sample were highly accurate, with relative errors of 0.9% and 1.5% for BA and 0.6% and 1.2% for MMA, with and without EGDE, respectively (Table 2).

Table 1: Concentrations of an in-house prepared BA and MMA mixture

Monomer	Concentration (wt%)		
	Gravimetric	Polyarc/FID	Relative %Error
BA	53.2	54.9	3.6
MMA	46.8	45.1	3.2

Table 2: Concentrations of BA and MMA in a commercial acrylic binder quantified with and without EGDE.

Monomer	Concentration (wt%)				
	Theoretical	Polyarc/FID w/EGDE	Rel. % Error (w/EGDE)	Polyarc/FID w/o EGDE	Rel. % Error (w/o EGDE)
BA	45.6	45.2	0.88	46.3	1.5
MMA	54.4	54.7	0.55	53.8	1.2

Conclusions

Monomer concentrations of copolymer samples were successfully quantified with high accuracy. This work also showed that data quantification can indeed be done without the need of calibration or an internal standard.

Contact Us

For more information or to purchase a Polyarc® system, please contact us at 612-787-2721 or contact@activatedresearch.com.

Please visit their website for details and additional technical literature.