

# An Improved Sample Preparation Method for Monomer Conversion Measurement Using Headspace Gas Chromatography in Emulsion Polymerization Research

Jin-Feng Zhong,<sup>1</sup> Xin-Sheng Chai,<sup>1</sup> Shi-Yu Fu,<sup>1</sup> Xiao-Li Qin<sup>2</sup>

<sup>1</sup>State Key Laboratory of Pulp and Paper Engineering, School of Light Industry and Food Science, South China University of Technology, Guangzhou 510640, China

<sup>2</sup>School of Light Industry and Food Science, South China University of Technology, Guangzhou 510640, China

Received 5 January 2011; accepted 13 August 2011

DOI 10.1002/app.35487

Published online 21 November 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** This article reports an improved headspace gas chromatographic (HS-GC) technique for the determination of monomers in polymer latex. The method is based on a HS-GC technique reported previously (Chai et al., *J Appl Polym Sci* 2006, 99, 392) but includes a major modification in the method of sample preparation. By using a weight-based sampling method, coupled with initial dissolution in dimethyl sulfoxide (DMSO), followed by water dilution,

the uncertainty in the sample preparation associated with previous method can be significantly reduced. The improved method is reliable, practical, and suitable for use in the kinetic study during emulsion polymerization. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3525–3528, 2012

**Key words:** monomer; headspace gas chromatographic; emulsion polymerization

## INTRODUCTION

In the previous article,<sup>1</sup> we have developed a headspace gas chromatographic (HS-GC) method for the determination of the methyl methacrylate (MMA) monomer in its polymer latex. The concept of this novel technique is to dissolve the latex sample from the polymerization process in a large volume of water. This dissolution reduces the formation of monomer droplets (in the less polymerized samples) and the adsorption of monomers on polymer particles (in the more highly polymerized samples) which can negatively affect the monomer vapor-liquid phase equilibrium in HS-GC measurement. As a result, the residual MMA in the samples can be more accurately quantified. However, it was noticed that the dissolution of monomer droplets in the less polymerized samples is a very slow process near room temperature. Also, the monomer droplets can easily float to the surface of the water solution and result in monomer loss during mixing. On the other hand, in the latex samples with a higher degree of polymerization, polymer agglomeration can easily take place in water and entrap monomers so they are not transferred to the headspace for detection. These sample preparation problems can adversely

affect the precision and accuracy of the monomer analysis, and thus limit the utility of the method.

In this work, we reported on an improved sample preparation procedure used for monomer(s) measurement based on the HS-GC technique reported previously. The method was successfully applied to the determination of monomer conversion during methyl methacrylate (MMA) and vinyl acetate (VAc) emulsion copolymerization.

## EXPERIMENTAL

### Instruments and operations

All measurements were carried out with an automatic headspace sampler (DANI HS 86.50, Italy) and a gas chromatograph (GC-2010, Shimadzu, Japan).

The GC employed a 30 m long 0.35 mm ID DB-5 capillary column operating at a temperature of 50°C with a nitrogen carrier gas flow of 3.8 mL/min. It was equipped with a flame ionization detector, with hydrogen and air flow rates of 35 and 400 mL/min, respectively. The headspace operating procedure consisted of 12 min of strong shaking at 60°C to enhance dissolution and achieve liquid-vapor phase equilibrium, a vial pressurization time of 0.2 min, a sample loop fill time of 1.0 min, and a loop equilibration time of 0.05 min.

### Preparation for MMA and VAc emulsion copolymerization samples

Typically, a solution was prepared by adding MMA (16.14 g, 1612 mmol), VAc (13.86 g, 1610 mmol), and

Correspondence to: X.-S. Chai (xschai@scut.edu.cn).

Contract grant sponsor: Natural Science Foundation of China; contract grant number: 21076091.

TABLE I  
The Weights of Sample at Different Sampling Interval

Total conversion, %	Sample weight <sup>a</sup> , g					RSD, %
0	0.1979	0.1969	0.1968	0.1930	0.1991	0.43
49.3	0.1320	0.1914	0.2123	0.1522	0.1235	3.7
71.3	0.1980	0.1381	0.1895	0.1735	0.1638	14.0
75.1	0.1651	0.1765	0.2059	0.2055	0.1987	12.5

<sup>a</sup> 0.20 mL emulsion sample was withdrawn.

sodium dodecyl sulfate (0.9 g, 3.12 mmol) to deionized water (70 mL) which was heated to 70°C in a three-neck flask equipped with a short-path graham condenser, while subjected to mechanical agitation at 200 r/min. The flask was flushed with pure N<sub>2</sub> gas over the liquid to avoid a direct contact between the solution and air during the process. The polymerization reaction was initiated by the addition of 1 mL of potassium persulfate solution (0.33 wt % of monomer).

#### Sample preparation for HS-GC measurement

About 0.2 g of the liquor in the emulsion copolymerization process was sampled by a micro-pipette (0.50 mL) at the desired time and added to 2 mL of DMSO, acting as a presolvent, placed in a 25-mL beaker. By weighing the difference before and after the addition of the sample, an accurate weight of the sample taken from the process was determined. The solution in the beaker was quantitatively transferred to a 1000-mL volumetric flask, diluted to the mark with distilled water, and mixed by repeated inversions. A 2-mL sample of the resulting solution was taken from the flask and added to a 20-mL headspace sample vial, which, after being sealed with a septum, was ready for the HS-GC analysis.

## RESULTS AND DISCUSSION

### The weight-based sampling

Emulsion polymerization is a dynamic process, and the viscosity of the latex varies during the process. As seen in Table I, to withdraw an accurate volume of the sample from the process (especially for the samples with higher monomer conversions) is very difficult, which produces a larger relative standard deviation (RSD) in five repeated weighting for these process samples. Therefore, the uncertainty in volume-based sampling, i.e., assuming that the weights from all process sampling are all identical<sup>1</sup> is significant, which affect the accuracy in monomer quantification. In this present work, although we still used the micro-pipette for rapid sampling, the sample was weighed in a small beaker (containing DMSO; see next section) in order to rapidly obtain a more accurate measure of

the sample size. The following equation is used for the calculation of monomer conversion based on sample weights and GC peak areas if the GC detector's response is linearly proportional to the content of the monomer in the tested sample solution,

$$R = \left( 1 - \frac{A_g^t/M^t}{A_g^0/M^0} \right) \times 100\% \quad (1)$$

where  $A_g^0$  and  $A_g^t$  are the GC peak areas for the analyte in the samples, and  $M^0$  and  $M^t$  are the total weight of the liquid sample at  $t = 0$  and  $t = t$ , respectively.

### Latex dissolution in DMSO

Because of the possible agglomeration of polymer particles that could occur during the sample preparation method used previously,<sup>1</sup> there was a distinct possibility that monomers might be entrapped by the polymers. This possibility could be minimized by various approaches, such as using ultrasound. However, for speed and simplicity, we used DMSO (an important polar aprotic solvent that dissolves both polar and nonpolar compounds and is miscible in a wide range of organic solvents, as well as water<sup>2</sup>) as a presolvent to dissolve or disperse the monomer and polymer particles. Even the highly viscous samples from the emulsion polymerization can be easily dispersed in DMSO.

In this work, we transferred the process sample to a small beaker containing 2 mL DMSO to obtain an accurate sample weight (see previous section) and to rapidly separate the residual monomers and polymer particles, as just described. To evaluate the present method, three parallel sample solutions, with and without DMSO addition, were prepared. The results from HS-GC testing showed that the RSD for the involved DMSO solutions was about 5%, which is much better than that of 20+% found in the solutions without DMSO as used by the previous method from a comparison study.

### Considerations in sample dilution

The polymer latex is a multiphase system consisting of aqueous, organic monomer, and polymer particle

**TABLE II**  
The Minimum Dilution Ratio Suggested For the Sample Preparation<sup>5</sup>

Monomer name	CAS no.	Solubility (wt %)	Dilution ratio
Methyl acrylate	96-33-3	5.53	150
Glycidyl methacrylate	106-91-2	2.67	200
Ethyl acrylate	140-88-5	2.13	200
Vinyl acetate	108-05-4	2.01	200
Methyl methacrylate	80-62-6	1.56	200
Butyl acrylate	141-32-2	0.14	700
Styrene	100-42-5	0.032	3000

phases. The monomer in the latex must be completely dissolved (i.e., below its solubility limit) in an aqueous phase, so that it can be quantified by HS-GC based on a well-defined vapor-liquid phase equilibrium. However, if the sample is diluted too much, it affects the sensitivity in the HS-GC measurement. Therefore, a proper ratio of dilution should be selected. In Table II, we list the recommended minimum dilution ratios for the typical monomers used in the synthesis of chemical additives employed in the papermaking process. These figures are based on the solubility data at a temperature of 60 °C reported previously.<sup>3</sup>

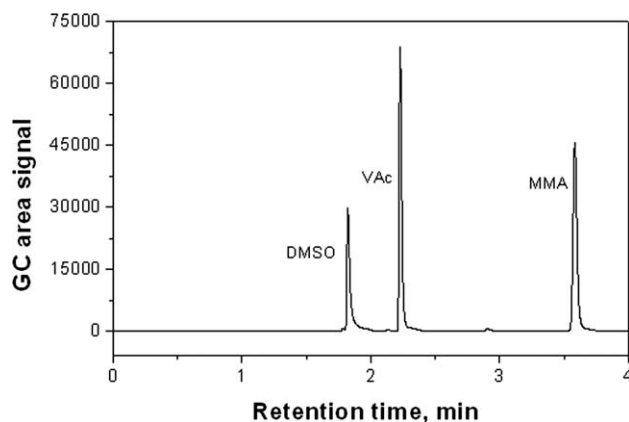
It should be pointed out that in the case of a monomer with a very low solubility, e.g., styrene, a larger volume of sample solution and/or a larger volume of headspace sample loop<sup>4</sup> should be used in order to introduce enough analyte to be detected by the GC, i.e., exceed the instrument's limit of quantitation.

#### Measurement precision and method accuracy

GC repeatability testing with this improved method was conducted, and the RSD from five replicas for VAc and MMA were 2.10% and 0.56%, respectively. Clearly, compared with the RSD of 2.6% in MMA testing obtained by the previous method,<sup>1</sup> the present method greatly improves the measurement precision due to the modification in the sample preparation. The measurement principle of the present method is identical to that reported previously,<sup>1</sup> in which the accuracy of the method was evaluated by a set of samples with known monomer contents. Thus, it is expected that the better measurement precision and the weight-based sampling mode in the present methods also improves the accuracy in the determination of monomer(s) conversion.

#### Application: Monomer conversion during MMA and VAc emulsion copolymerization

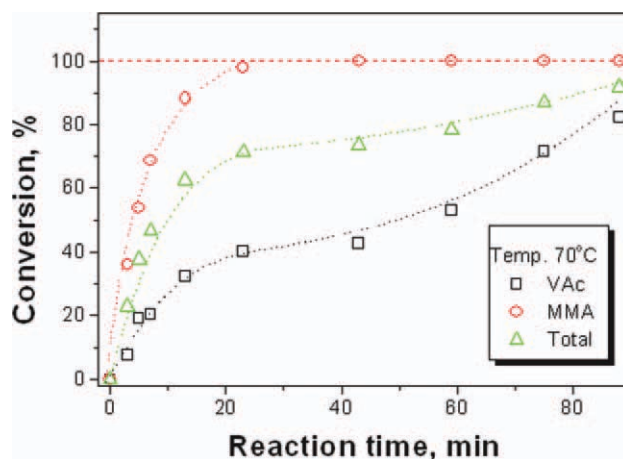
MMA and VAc emulsion copolymerization was performed at a temperature of 70°C with a total mono-



**Figure 1** Chromatogram from a diluted latex sample by HS-GC.

mer content of 30 wt % (the mole ratio of MMA:VAc = 1 : 1), in an aqueous solution (~ 100 mL). About 0.2-mL samples were withdrawn from the reaction mixture at various times during the emulsion polymerization process. The samples were prepared and analyzed as described above.

As observed in the Figure 1, two monomers (MMA and VAc) and DMSO are well-separated by the GC column at the given operation condition. Thus, the conversions of the monomers MMA and VAc were calculated by eqs. (1) based on the GC peak areas and sample weights. Figure 2 shows the time-dependent conversion profiles of MMA, VAc, and the total monomers, respectively, during the emulsion copolymerization. It can be seen that although a high conversion of MMA was achieved within a short time (~20 min), the conversion of VAc is slower under the given conditions. The conversion of VAc is the rate-determining step for the overall conversion of the monomers in this copolymerization process. This fact should be considered



**Figure 2** The relationship between the monomer conversions and process time. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

when attempting to synthesize MMA-VAc copolymers of a particular composition, by using different relative initial ratios of MMA and VAc and/or using a slower addition of MMA to the reaction mixture.

### CONCLUSIONS

An improved procedure of the sample preparation for monomer measurement using HS-GC has been developed. The present method can significantly reduce the uncertainty noticed in the previous method, and it thus makes the method more useful and reliable. The present method is practical and suitable for use in emulsion polymerization-related research.

The authors acknowledge helpful discussions with Dr. Donald G. Barnes of Peking University during the preparation of this article.

### References

1. Chai, X. S.; Hou, Q. X.; Schork, F.J. *J Appl Polym Sci* 2006, 99, 392.
2. David, H. R.; Zaffaroni, A. *Annals NY Acad Sci* 1967, 141, 13.
3. Chai, X. S.; Schork, F. J.; Anthony, D.; Wilson, K. *Ind Eng Chem Res* 2005, 44, 5256.
4. Chai, X. S.; Schork, F. J.; Anthony, D. *J Chromatogr A* 2005, 1070, 225.
5. Lide, D. R. *CRC Handbook of Chemistry and Physics*, 80th ed.; CRC: Boca Raton, FL, 1999.