

# Determination of the Methyl Methacrylate Monomer in Its Polymer Latex by Headspace Gas Chromatography

X.-S. Chai,<sup>1,2</sup> Q. X. Hou,<sup>1</sup> F. J. Schork<sup>3</sup>

<sup>1</sup>School of Light Industrial and Food Engineering, Guangxi University, Nanning, 530004, China

<sup>2</sup>Institute of Paper Science and Technology, Georgia Institute of Technology, 500 10th Street, Atlanta, Georgia 30332

<sup>3</sup>School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, 500 10th Street, Atlanta, Georgia 30332

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**ABSTRACT:** This article reports a headspace gas chromatography (GC) method for the determination of the residual monomer in a methyl methacrylate polymer latex or emulsion. Because of the multiphase nature of a polymer latex, the level of the residual monomer cannot be quantified by headspace GC on the basis of its vapor–liquid equilibrium (VLE) without significant thermodynamic assumptions. With a significant dilution of a polymer latex sample followed by vapor–liquid equilibration at an elevated temperature, the monomer droplets are completely dissolved in the aqueous phase, and monomer absorption in the polymer particles can be minimized. Thus, VLE is established in the

diluted latex, and a linear relationship between the monomer concentration in the vapor and aqueous phases can be obtained. This technique eliminates sample pretreatment procedures such as solvent extraction in the conventional GC method, and it avoids the risk of polymer deposition on the GC column caused by a direct injection of a monomer-containing solvent. It also eliminates the possibility of solvent interference in the conventional GC monomer analysis. This method is simple, accurate, and automated. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 392–397, 2006

**Key words:** latices; monomers

## INTRODUCTION

Emulsion polymerization involves carrying out free-radical polymerization in submicrometer polymer particles dispersed in a continuous aqueous phase to produce a polymer latex with applications in synthetic rubber, paints and coatings, and adhesives. Obviously, the monomer conversion rate is one of the most important parameters in emulsion polymerization, and the levels of the residual monomer must be tightly controlled for health and safety reasons. Monomer conversion can be obtained by a traditional method, typically gravimetry. By the evaporation of the water, residual monomer, and any other volatile components and by the weighing of the remaining polymer solid, the residual monomer can be calculated from a knowledge of the recipe. Other methods, such as densitometry,<sup>1</sup> ultrasound velocity,<sup>2</sup> and calorimetry,<sup>3</sup> have been used for conversion measurements. Recently, advanced analytical techniques such as Fourier transform infrared<sup>4</sup> and Raman<sup>5</sup> spectroscopy have been developed for online or inline monitoring of the

compositions in emulsion polymerization processes. However, the calibrations in these methods are based on other reference methods, typically gravimetry and gas chromatography (GC). GC has been classified as a direct technique and is widely used for monomer quantification because most monomers are highly volatile.<sup>6</sup> In contrast to gravimetry, the GC method determines the monomer conversion directly from the residual monomer remaining in the polymer latex. Polymer latex is a multiphase system in which the residual monomer is distributed between the aqueous phase and the solid polymer particle phase. Therefore, sample pretreatment is required before the GC analysis. Solvent extraction or direct sample dilution with a water-soluble organic solvent such as tetrahydrofuran are common techniques used in such a sample pretreatment. However, there are several problems in the practical application, mainly because the nonvolatile dissolved polymer species in the resulting solution are deposited on the GC column and not only deteriorate the column separation performance for monomer species but also eventually damage the column. To overcome the weakness of the solvent extraction method, a thermal desorption technique for GC sample preparation has been reported.<sup>7</sup> In this method, the polymer is heated to 100°C and purged with helium to a monomer trap for 20 min, after which the trap is thermally desorbed (at 300°C for 4 min) to a gas chromatograph for analysis. The method is limited to the quantifica-

Correspondence to: X.-S. Chai (xin-sheng.chai@ipst.gatech.edu).

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tion of the residual monomer in solid samples. A full evaporation (FE) headspace GC technique was initially reported by Markelov and Guzowski,<sup>8</sup> and it is particularly suitable for liquid sample analysis. This method uses a very small sample size to achieve a nearly complete transfer of solutes from a condensed matrix or solids into a vapor phase in a very short period of time. Therefore, it not only has no need for sample pretreatment but also eliminates the unknown extraction efficiency problem. In a previous work,<sup>9</sup> we applied the FE headspace GC method for quantifying organic sulfur compounds in kraft black liquor. Recently, we successfully demonstrated an FE headspace GC technique for quantifying the residual methyl methacrylate (MMA) concentration in a polymer latex at very high conversions.<sup>10</sup> The major advantage of the method is that the polymer latex sample can be directly measured by headspace GC without any sample pretreatment. However, it is not as applicable to samples with lower monomer conversions in which there is a significant amount of the monomer in the polymer latex. This is because the monomer vapor pressure, compared with the total headspace pressure, is relative large and the headspace total vapor is no longer constant. As a result, a much smaller sample size must be used, and this will cause a larger error in sampling.

In this work, we applied a conventional headspace method for quantifying the monomer in the polymer latex. By significantly diluting the sample and conducting the sample equilibration at an elevated temperature, we minimized the negative effect of a high monomer concentration on the monomer quantification.

## EXPERIMENTAL

### Chemicals

All chemicals used were from commercial sources. A standard MMA emulsion (30.0 wt % monomer dispersed in water) was obtained by ultrasonic agitation for 30 s at room temperature.

### Emulsion polymerization samples

An MMA latex was produced by the miniemulsion polymerization process. The latex was a 30% solid stable emulsion of submicrometer poly(methyl methacrylate) (PMMA) particles in water. A set of polymer latexes with monomer conversions of 20, 40, 60, and 80% were prepared by the mixing of the PMMA latex with the standard, unpolymerized MMA emulsion (30.0%) at different ratios.

### Apparatus and operations

The GC conditions were as follows. The HP-5 capillary column was 30 m long with an inner diameter of 0.35

mm. The column operating temperature was 30°C; the carrier gas helium flow was 3.8 mL/min. A flame ionization detector was employed with hydrogen and air flows of 35 and 400 mL/min, respectively. The headspace operating conditions were 12 min of strong shaking for the equilibration of the sample at the desired temperature, 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.

A 0.250-mL sample was diluted with water to a total volume of 250 mL. A 2-mL diluted solution was taken by pipette and added to the headspace sample vial for vapor-liquid equilibrium (VLE), and then the vapor phase was withdrawn from the vial for GC analysis. The standard solution used in the one-point calibration method was prepared in the same way on the basis of the standard MMA emulsion (30%). An average value was obtained from three headspace GC measurements on the standard solution.

## RESULTS AND DISCUSSION

### Monomer distribution in the polymer latex and its vapor-liquid phase equilibrium

A polymer latex is a multiphase system; the monomer is dissolved in the aqueous phase, contained in monomer droplets, and dissolved in the polymer particles. If monomer droplets are present, the concentration of the monomer in the aqueous phase is constant at its solubility limit. On the basis of a three-phase partition model reported by Anderson,<sup>11</sup> the total concentration of the monomer in the liquid system ( $C_l$ ) can be expressed as follows:

$$C_l = C_{aq} + D + SX \quad (1)$$

All symbols are defined in Table I.

The distribution of the monomer between aqueous polymer solid phases can be described by

$$S = K_1 C_{aq} \quad (2)$$

According to eqs. (1) and (2), the total monomer in this liquid system can be written as

$$C_l = C_{aq}(1 + K_1 X) + D \quad (3)$$

where  $D > 0$ ,  $C_{aq}$  is the saturation concentration, that is, the solubility at the given temperature.

For a volatile monomer, the vapor-liquid partition coefficient can be written as

$$H_c = C_g / C_{aq} \quad (4)$$

TABLE I  
Symbols and Definitions

$D$	Content of monomer droplets in the total liquid sample (mg/L)
$X$	Content of polymer particles in the total liquid sample (g/L)
$S$	Amount of the dissolved monomer adsorbed per unit mass of polymer solid (mg/g)
$C_{aq}$	Concentration of the monomer in the water phase (mg/L)
$K_1$	Aqueous–solid monomer partition coefficient (L/g)
$H_c$	Vapor–liquid partition coefficient
$M_l$	Total monomer mass in the system (mg)
$C_g$	Monomer concentration in the vapor phase (mg/l)
$V_g$	Volume of the vapor phase
$V_l$	Volume of polymer latex (L)
$V_w$	Volume of the diluent (water) (L)
$R$	Dilution ratio
$k$	Ratio of droplets to dissolved monomer
$A$	GC peak area
$k_{GC}$	GC response factor to vapor monomer content
$K$	Coefficient

When a given volume ( $V_l$ ) of a polymer latex is added to a closed headspace sample vial, the total monomer in the system can be expressed as

$$M_l = C_g V_g + C_l V_l \quad (5)$$

By the combination of eq. (3) with eqs. (4) and (5), the total monomer mass in the vial can be written as

$$M_l = C_g \{V_g + [(1 + K_1 X) V_l / H_c]\} + D V_l \quad (6)$$

Equation (6) shows that conventional headspace GC cannot be directly applied to the polymer latex for monomer quantification because the content of the monomer droplets is unknown. The partition coefficients,  $K_1$  and  $H_c$ , are constant at a given temperature, and they are independent of the monomer concentration in a very diluted solution system.

#### To eliminate monomer droplets by a significant sample dilution

Because of the solubility limit, excess monomer in the sample is in a droplet form. However, through significant sample dilution, the droplets can be completely dissolved into the water. Thus, on the basis of the mass balance of the dilution sample in the headspace sample vial, eq. (6) can be further written as

$$M_l = C_g \{V_g + [(k + 1 + K_1 X) V_w / R H_c]\} \quad (7)$$

with

$$R = V_w / V_l \quad (8)$$

and

$$k = D / C_{aq} \quad (9)$$

If the monomer droplet content is much greater than that absorbed in the polymer particles in the original sample, that is,  $k + 1 \gg K_1 X$ , the polymer solid absorption effect is neglected. Thus, the total monomer content in the sample can be quantified by the headspace GC method.

#### Polymer solid absorption effect

An organic solvent that is sparingly soluble in water (e.g., toluene) can be absorbed by the polymer particles in a latex. As a result, the corresponding equilibrium vapor solute concentration decreases, and this reflects the amount of the organic solute in the aqueous phase. Figure 1 shows the relationship between the vapor toluene GC signal (normalized) and the amount of the polymer (from a commercial polyacrylate latex) added in a set of aqueous dispersions with the same amount of toluene (170 ppb) at two temperatures and in a set of solutions with the same amount of ethanol (100 ppm) at a temperature. Toluene is absorbed by the hydrophobic polymer, and the amount of toluene absorbed is proportional to the polymer added. However, the same polymer does not adsorb ethanol. Figure 2 shows the relationship between the equilibrated monomer vapor concentration and its liquid content in a set of diluted solutions ( $R = 0\text{--}20$ , i.e., polymer solid concentration = 2–30%) based on a highly converted PMMA latex sample (~30% solids). Although there are no monomer droplets remaining in the solution (i.e.,  $D = 0$ ) and both the monomer and polymer contents are equally reduced by the dilution, a nonlinear response in MMA can be observed. However, for a coexisting water-soluble species, ethanol, the vapor concentration is linearly proportional to the concentration in the solution. The

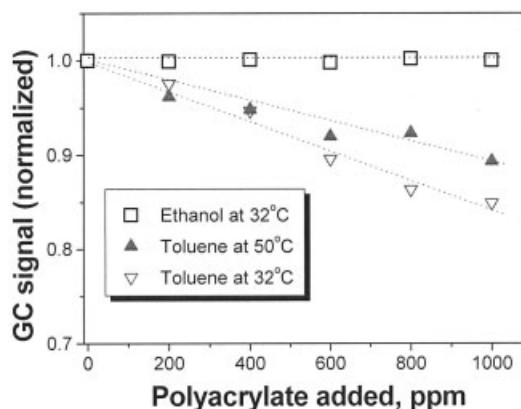
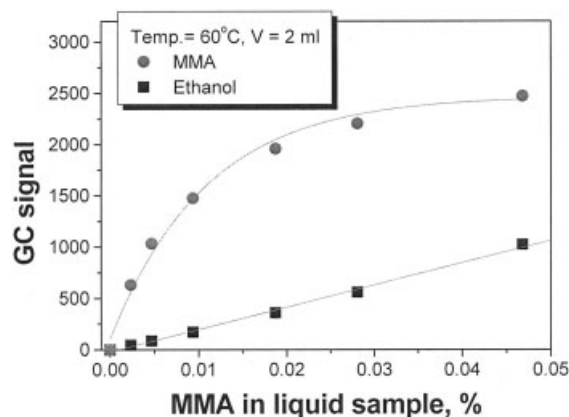


Figure 1 Polymer absorption effects with toluene.



**Figure 2** Polymer absorption effects in a set of less diluted samples.

information presented in these two figures indicates that a hydrophobic polymer can absorb a hydrophobic organic solute. Thus, a headspace GC technique for the quantification of a monomer based on VLE has to take such an absorption effect into account.

As mentioned previously, the monomer and polymer contents are equally reduced by the sample dilution. According to eqs. (1) and (2), the amount of the monomer absorbed by the polymer particles ( $C_{ad}$ ) can be expressed as

$$C_{ad} = K_1 C_{aq} X \quad (10)$$

Obviously, the amount of the monomer absorbed by the polymer particles is proportional to the product of the monomer concentration in the aqueous solution and the polymer solid content. Thus, with sample dilution, the absorbed monomer decreases extensively. Therefore, significant sample dilution can eventually minimize the polymer absorption effect to an accepted level. Figure 3 shows headspace GC measurements for a set of solutions with significant dilution. When the polymer solid content is less than ~1.2% (i.e., <1200 ppm), a linear relationship between the GC response and MMA concentration is obtained. This indicates that the effect of the polymer solid on the residual monomer measurement is negligible. Thus, eq. (7) can be further simplified as

$$M_l = C_g(V_g + kV_w/RH_c) = KA \quad (11)$$

where  $K$  is equal to  $k_{GC}(V_g + kV_w/RH_c)$  with  $k_{GC} = C_g/A$ .

Therefore, the residual monomer quantification can be simply performed on the basis of this headspace GC technique with external calibration or a standard addition method.

With the assistance of the superb sensitivity of a GC flame ionization detector, a very small level of residual monomer in the highly diluted sample can still be detected, as shown in Figure 3.

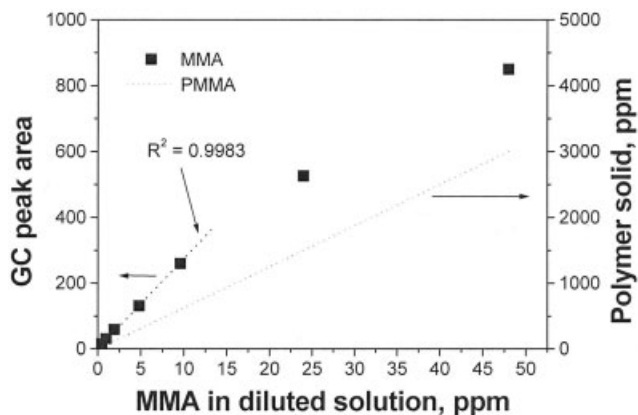
### Equilibration time

In this method, it is important to achieve a nearly complete release of the residual monomer from the polymer solid phase. MMA monomer droplets dissolve in water relatively quickly. In the presence of polymer solids, the migration rate for the monomer from inside the polymer solids to the diluent (water) is slow. Therefore, a longer equilibration time is helpful to remove this portion of the monomer from the solid phase to the water phase. In this work, a diluted sample solution was prepared and magnetically stirred at room temperature for a period of time. Then, 2 mL of the solution was added to a closed vial, which was placed in a 60°C oven in a headspace sampler with strong shaking for further equilibration. According to our previous study,<sup>12</sup> a 12-min equilibration time is sufficient to achieve a VLE for a volatile solute under the given conditions. We conducted a comparison study using our previous technique<sup>10</sup> and the current technique on a given latex sample, and the data from these two techniques match very well. Therefore, the equilibration time chosen for this work is justifiable.

A very long equilibration time might be required only in the case in which the sample contains an extremely low amount of the residual monomer. However, we do not recommend this method for such an application because our method is based on significant sample dilution that affects the detecting sensitivity for such a sample.

### Temperature effect

Because the VLE partition coefficient of the monomer is proportional to the temperature, a higher equilibration temperature can lead to more monomer in the vapor phase, which improves the measurement sensitivity of the headspace GC method. Thus, the linear response range shown in Figure 3 is expected to be



**Figure 3** Polymer absorption effects in a set of significant diluted samples.

**TABLE II**  
**Repeatability Test on an Emulsion Polymer**  
**Latex Sample**

Sample No	Sample size (mL)	GC peak area
1	2.00	4078.1
2	2.00	3809.4
3	2.00	3938.5
4	2.00	3867.4
5	2.00	3899.1
		RSD = 2.6%

The sample dilution ratio was 1000. Conversion rate = 40%.

extended. Figure 1 also shows that the polymer absorption effect at a higher temperature (50°C) is less significant than that at a lower temperature (32°C). Therefore, it is expected that the polymer absorption effect can be further minimized when a higher equilibration temperature is chosen. However, a higher temperature leads to a higher MMA content in the headspace. Because of limits due to the capillary column separation capacity and GC detecting linear response range, headspace sample dilution or GC inlet splitting is mandatory, and this is an inconvenience for an application in which the MMA content covers a range of 0–30% in the process samples. On the other hand, we noticed a fouling/corrosion problem in the headspace-sampling conduit (which caused flow channel clogging) when we operated the system at a temperature above 70°C for a long period. We think that the higher water vapor pressure and trace amounts of acidic gas such as CO<sub>2</sub> might be the causes of such problems.

In this work, a moderate temperature (60°C) was chosen, and the monomer GC measurement optimization was performed through the variation of the polymer latex sample dilution ratio and liquid sample size in headspace GC testing.

### Measurement precision

GC repeatability testing with this method was conducted, and the results are shown in Table II. A relative standard deviation (RSD) of 2.6% was obtained according to the recorded GC peak area for MMA from five measurements of a polymer latex sample, which included the uncertainty from both sampling and GC detecting.

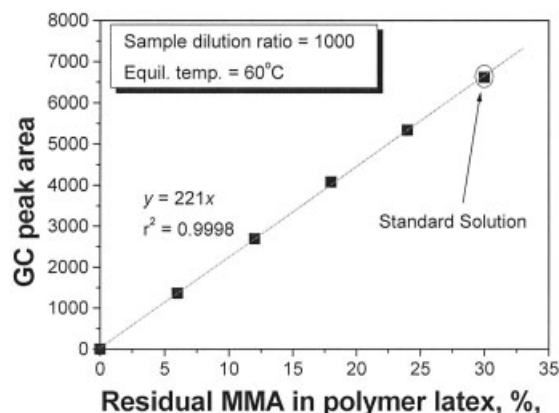
### Method validation and calibration

A set of synthetic polymer latexes with known residual monomer contents of 6, 12, 18, and 24% were prepared. These solutions were diluted 1000 times before headspace GC measurements. Figure 4 shows

a response curve of the vapor-phase GC signal to the corresponding diluted sample solution. The last solution was prepared from a pure 30% MMA emulsion solution (without PMMA). After such a dilution (1000 times), the MMA droplets were completely dissolved in the aqueous water because the MMA concentration in the diluted solution was 0.030%, which is much lower than its solubility (~1.56%) at room temperature.<sup>13</sup> Because all points from GC measurements for those samples at their desired contents are perfectly located in a straight response line ( $y = 221x$ ,  $R^2 = 0.9998$ ) that goes through the point of the standard sample solution (which is called one-point calibration), this method is valid for the quantification of the MMA content in polymer latex samples with a polymer solid range of ~0–30%. On the basis of an excellent performance of the commercial headspace for the MMA measurements, as shown in Figures 3 and 4, the one-point calibration method applied for this study is justifiable. On the other hand, a simple and practical calibration method is highly desired for process-related analysis and quality control during the MMA emulsion polymerization.

## CONCLUSIONS

We have successfully demonstrated a headspace GC technique for the determination of the monomer content in a polymer latex. With significant sample dilution, the droplets in the sample can be completely dissolved in the aqueous phase, and the polymer absorption effect on the dissolved monomer in the aqueous solution can be neglected. This method is simple, accurate, and automated. It eliminates the use of hazardous organic solvents in the sample pretreatment and, therefore, is environmentally sound.



**Figure 4** Response curve of headspace GC measurements to MMA in diluted solutions of the polymer latex with different conversion rates.

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