Determination of residual monomer in polymer latex by full evaporation headspace gas chromatography

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Abstract

This study demonstrated a full evaporation (FE) headspace gas chromatographic technique for the determination of residual monomer in methyl methacrylate (MMA) polymer latex. A very small amount ($\sim$10–30 mg) of latex was added to a sealed headspace sample vial (20 ml). A near-complete monomer mass transfer from both liquid (aqueous phase) and solid phase (polymer particles) to the vapor phase (headspace) is achieved within 5 min at a temperature of 110 °C. The method eliminates sample pretreatment procedures such as the solvent extraction. Thus, it avoids the risk of polymer deposition on the GC system caused by a directly injection of extraction solvent in the conventional GC monomer analysis. The present method is simple, rapid, and accurate.
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1. Introduction

Emulsion polymerization is an important industrial process. High conversion of monomer to polymer in such a process is desired because it not only improves the efficient production of the polymers but also reduces to the amount of residual monomers, which are generally regarded as toxic to the human health. Current regulations require residual monomer concentrations in the parts-per-million range. Therefore, the method that able to quantify the residual monomer can provide the important information that is very helpful for the process control, modification and optimization. Monomer conversion rate is one of the parameters used for evaluating the emulsion polymerization process. It can be obtained by the traditional method, typically, gravimetry. The residual monomer can be calculated from a knowledge of the recipe by evaporating water, residual monomer and any other volatile components, and weighing the remaining polymer solid. Many other methods, such as densitometry [1], ultrasound velocity [2], and calorimetry

[3] have been used for conversion measurement. Recently, the advanced analytical techniques such as Fourier transform inferred [4] and Raman [5] spectroscopy have been developed for on-line or in-line monitoring the compositions in emulsion polymerization process. However, all these methods provide a relative poor accuracy in monomer quantification for the samples with very high conversion. Therefore, a method for accurately determination of the residual monomer is highly needed. Historically, gas chromatography (GC) has been classified as a direct technique and widely used for monomer quantification since most of monomer compounds are highly volatile [6]. Aided by the superb sensitivity of flame ionization detector, GC can accurately determine very small levels of residual monomer in liquid samples. In polymer latex, the residual monomer is distributed between the aqueous phase and the solid, polymer particle phase. Therefore, a sample pretreatment is required before the GC analysis. Solvent extraction is a common technique used in such a sample pretreatment. However, it has several problems in the practical application. First, the solvent can partly or completely dissolve the polymer, which is introduced into GC system together with the solvent. As a result, these non-volatile polymer species are deposited on the GC system, which will deteriorate the GC separation

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performance for monomer species. Secondly, the traces of compounds of interest might be masked by the direct solvent injection due to a very large solvent peak in GC chromatogram. Moreover, multiple solvent extraction steps may be required for the monomer with a relative large solubility in water, which makes the sample pretreatment more complicated, tedious, and time-consuming. To overcome the weakness of the solvent extraction method, a thermal desorption technique for GC sample preparation has been reported [7]. In this method, the polymer was heated to 100 °C and purged with helium to a monomer trap for 20 min, after which the trap was thermally desorbed (at 300 °C for 4 min) to a gas chromatograph for analysis. The method is limited to quantification of the residual monomer in solid samples.

A full evaporation (FE) headspace GC technique was initially reported by Markelov and Guzowski [8], and it is particularly suitable for liquid sample analysis. This method uses a very small sample size to achieve a near-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, we have successfully applied the FE headspace GC method for quantifying organic sulfur compounds in kraft black liquor [9]. We believe FE headspace GC method can be also used for the determination of residual monomer in emulsion polymerization sample.

The objective of the presented study is to demonstrate a simple, rapid and accurate FE headspace GC method for determination of residual methyl methacrylate (MMA) in emulsion polymerization process liquid sample based on a commercial headspace GC system.

2. Experimental

2.1. Chemicals

All chemicals used in the experiment were from commercial sources. A standard MMA solution was prepared by adding 100 μL pure MMA in 20 mL water. The MMA concentration is 4750 mg/L.

2.2. Emulsion polymerization sample

A MMA emulsion polymerization product sample was obtained from a miniemulsion polymerization process. The latex was a 30% solids stable emulsion of submicron poly-MMA particles in water. Samples were withdrawn from the reactor and inhibited with hydroquinone, then cooled in ice water to below room temperature. This freezes the monomer conversion. This process takes less than two minutes.

Six synthetical samples was prepared by adding 40 μL MMA into solutions with a poly-MMA content range from 0 to 25%.

2.3. Apparatus and operations

All measurements were carried out using an HP-7694 Automatic Headspace Sampler and Model HP-6890 capillary gas chromatograph (Hewlett-Packard, Palo Alto, CA, USA). GC conditions were: HP-5 capillary column at 30 °C, carrier gas helium flow rate of 1.1 mL/min. A flame ionization detector was employed with hydrogen and air flow rates of 40 and 400 mL/min, respectively. Headspace operating conditions were: 5 min strong shaking for sample equilibration at a temperature of 110 °C, vial pressurization time of 0.2 min, sample loop fill time of 0.2 min, and loop equilibration time of 0.05 min.

The sample preparation and measurement procedures were as follows: inject 10–30 μL (or weigh equivalent amount) of sample solution into a closed 21.6 mL vial by micro syringe and place it in the headspace sample tray for headspace GC measurements. Directly add the sample on a piece of filter paper placed in the vial is helpful for improving liquid evaporation.

3. Results and discussion

3.1. Methodology

In a high conversion (>95%) polymer latex sample, it can be assumed that the monomer species are distributed in both aqueous and solid polymer particle phases. When the latex is introduced to the closed vial with a headspace, it can be regarded as a three-phase (i.e., liquid, solid and vapor) partitioning system. Garbarini and Lion [10] have suggested a model for a three-phase system. It was first assumed that the distribution of solute between aqueous and solid phases can be described by:

$$S = K_1 C_{aq} \tag{1}$$

where S is the amount of the solute partitioned to unit mass of solid and K_1 the linear solute–solid partitioning coefficient. C_{aq} is the concentration of solute in water phase. Although there is a significant effect of particle size on K_1 for submicron particles, this is insignificant for low monomer concentration.

The total liquid-phase concentration of solute is expressed as:

$$C_1 = C_{aq} + SX \tag{2}$$

where X is the content (mg/L) of solid.

For the volatile solute, the vapour–liquid partitioning coefficient, K, can be written as:

$$K = \frac{C_g}{C_{aq}}, \tag{3}$$

where C_g are solute concentration in the vapour phase.

The total solute in the headspace sample vial is:

$$M_t = C_g V_g + C_1 V_1 \tag{4}$$

According to Eqs. (1)–(4), the vapour solute concentration in the vial can be finally written as:

$$C_g = \frac{M_t}{V_g + [(1 + K_1 X)V_1/K]} \qquad (5)$$

It is known that the vapour–liquid partitioning coefficient (K) is proportional to the temperature, while the solute–solid partitioning coefficient, K_1, defined in Eq. (1) is disproportional to the temperature. Therefore, through performing the sample equilibration at a high temperature and using a small sample volume, the value in item, $[(1 + K_1 X)V_1/K]$, is decreased. If $V_g \gg [(1 + K_1 X)V_1/K]$, the total amount of solute is only a function of the vapour concentration in the headspace vial, i.e.,

$$M_t \approx C_g V_g \qquad (6)$$

Thus, we can quantify the total monomer in the emulsion polymerisation liquid by a full evaporation headspace GC technique.

3.2. Evaluation of the completeness of monomer mass transfer

To check for completeness of solute mass transfer from solid and condensed phases to the vapor phase and for the efficiency of FE headspace extraction, a sample solution (conversion rate >99%) from MMA emulsion polymerization process was used for the demonstration. The sample vial was purged with fresh helium after each run to remove the residual vapor from the previous headspace extraction. The GC peak areas, A_1 and A_2, represent the vapor concentration of MMA from the first and second headspace extraction, respectively. The ratio (R), i.e., A_2/A_1, can be regarded as a parameter for indicating the completeness of the headspace extraction. The smaller value of R, the more complete the solute mass transfer dose.

3.2.1. Effect of temperature

Solute mass transfer has two paths in the headspace extraction, one is the dissolved monomer transported from the aqueous phase to the vapor phase, and another is that the monomer desorbed from polymer particle surface into the aqueous phase. Temperature plays an important role in both processes. It was reported that a complete residual styrene desorption from a polystyrene foam sample can be achieved within 30 min at a temperature of 120 °C and a longer time was needed if the process was performed at a lower temperature [11]. In our work, we have investigated the temperature effect on MMA solute mass transfer, which is shown in Fig. 1. It can be seen that increasing temperature can promote the MMA mass transfer to the vapor phase and a near-completion of mass transfer can be achieved within 5 min for a 15 mg sample at a temperature of 110 °C. It should be pointed out that the polymer decomposition might take place if the operating temperature is too high. The
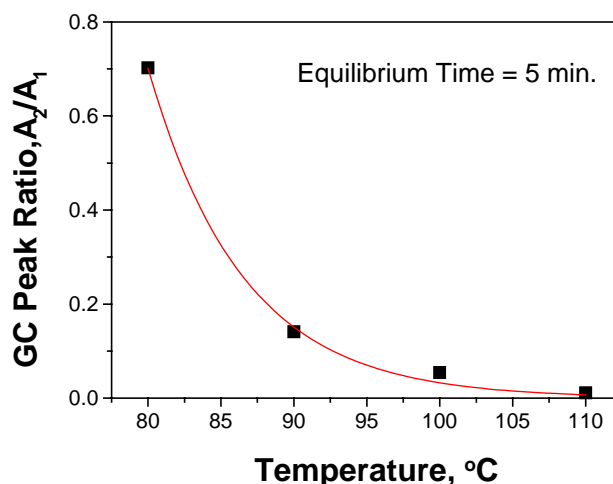

Fig. 1. Effect of temperature on FE headspace extraction.

latex used in this analysis was inhibited with ppm quantities of hydroquinone to prevent further polymerization. In addition, the post-added monomer was inhibited to prevent thermal polymerization. When carrying out this type of analysis on polymer latex samples, the sample should be inhibited to prevent further polymerization, especially on heating.

3.2.2. Effect of equilibration time

The literature data [11] showed that the equilibration time plays a more important role on the monomer desorption from a dry solid sample when compared an aqueous polymer sample. In our previous work [12], it was observed that a rapid vapor–liquid equilibrium in a two-phase system can be achieved by reducing the sample size. For an efficient sample analysis, rapid and near-complete mass transfer is highly desired. As mentioned, there are two (or more) mass transfer processes are involved in the headspace extraction vial containing polymer latex. Fig. 2 shows the time effect
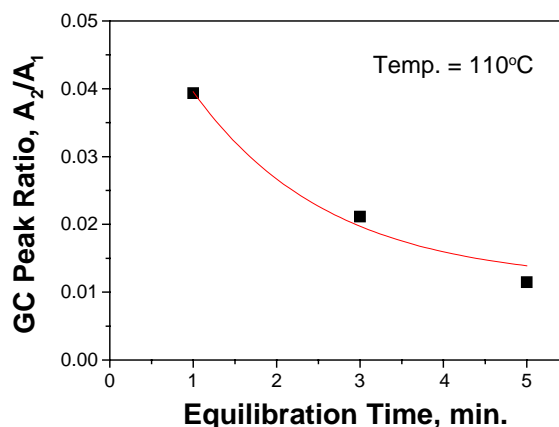

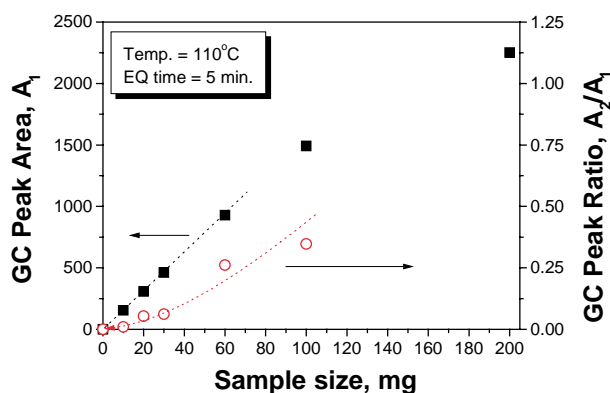Fig. 2. Effect of equilibration time on FE headspace extraction.

Fig. 3. Effect of sample size (symbols: (■) GC response; (○) peak ratio).

on the MMA mass transfer in a three-phase system. Results show that a near-complete mass transfer in headspace vial can be achieved within a very short period of time at the given temperature and sample size. Since the sample drying process gradually takes place for the polymer latex, in the headspace extraction process, the monomer desorption in liquid system is expected to be much easier than that from a dried solid sample.

3.2.3. Effect of sample size

Because the headspace extraction is performed at a closed vial, it is not possible to achieve a truly full evaporation. With a very small sample size, a near-complete evaporation can be achieved and it satisfies the measurement precision requirement in the GC method. Fig. 3 shows both a GC response to the vapor solute concentration and the ratio from two adjacent headspace extraction runs versus the emulsion polymerization sample size. It can be seen that although a linear GC response was covering a wider range of the sample size, an acceptable headspace extraction efficiency (>94%) can be obtained if the sample size less than 30 mg as shown in Fig. 3. It is obvious that more water is included in the closed vial when a larger sample size used, part of which remains in a condensed form. Thus, it limits the solute mass transfer to the vapor phase and cannot meet the near-completion mass transfer requirement for the monomer quantification.

In the present work, the full evaporation technique (FET) conditions [8] have been further proved. A set of synthetical samples containing same amount of MMA and different amount of poly-MMA from 0 to 25% were prepared and 20 mg of each sample was used in the testing. It was found that GC signal counts is constant (a relative standard deviation of 3.8% from six measurements), i.e., independent of the liquid sample or poly-MMA solid content at the given experiment conditions. Since the GC responses on these measurements are identical, the FET conditions must exist.

3.3. Method precision

The repeatability testing with the present method was conducted and the results shows that the relative standard deviation of 1.5% was obtained according to the recorded GC peak area for MMA from five measurements on an emulsion polymerization sample, which includes the uncertainty from both sampling and GC detecting. The sample size in the testing is 10 mg.

3.4. Method calibration and validation

A calibration curve was obtained based on injecting different volumes of a standard MMA solution (1–10 µL) for FE headspace GC runs. A linear relationship between the GC signals record and mass of MMA in the solution added in the headspace sample vials was found, and it is expressed as:

$$A = -7.1 + 46.9 \times C \tag{7}$$

with $R^2 = 0.9992$.

A standard addition method was used for quantifying the amount of MMA in an emulsion polymerization product sample. In this method, different amounts of pure MMA were added to the sample and then FE headspace GC measurement was performed. The linear relationship in the standard addition method can be expressed as:

$$A = 313.2 + 2200 \times C_s \tag{8}$$

with $R^2 = 0.9999$; where C_s represents the amount (%) of MMA added in the tested sample.

When $A = 0$ C_s equals to the amount of monomer the original sample. According to Eq. (8), we can obtain that there is 0.142% of residual MMA remaining in the latex, i.e., the amount of MMA that cannot be converted to the polymer.

According to the calibration Eq. (7), the amount of residual MMA in the sample is 0.16%, which well matches the data obtained by the standard addition method. Thus, we can conclude that the present technique is justifiable for quantification of residual monomer in the emulsion polymerization sample.

We also added the different amounts of pure MMA into a polymer latex to prepare a set of samples with a different amounts of residual MMA covering the range from 0 to 6% (w/w). Twenty milligrams of each of samples was taken for FE headspace GC testing. The results showed that the GC response is linearly proportional to the amount of residual MMA in the samples, indicating that the present method is applicable for the residual MMA analysis in the typical emulsion product samples. Further study will be pursued for monomer quantification in the process sample with the lower polymer conversion.

4. Conclusions

We successfully demonstrated the full evaporation headspace gas chromatographic technique for the determination of residual MMA in the high conversion emulsion polymerization. By choosing a very small sample size and high temperature, a near-completion of residual MMA mass transfer can be achieved by the full evaporation headspace technique. The present method is simple, rapid, and accurate. It eliminates the use of hazardous organic solvents for extraction, and therefore is also environmentally sound.

Acknowledgements

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