

## Short communication

## A full evaporation headspace gas chromatographic method for determination of monomer conversion in cellulose graft poly-methyl methacrylate

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## ABSTRACT

This paper reports on a full evaporation headspace gas chromatographic method for rapid determination of monomeric methyl methacrylate (MMA) in the cellulose graft poly-methyl methacrylate (PMMA) via an atom transfer radical polymerization process. The data show that a near-complete mass transfer of MMA from the very small liquid sample size (<30 mg) to the vapor phase (headspace) was achieved within 5 min at 105 °C. The present method has excellent precision (RSD < 0.3%) and accuracy (recovery = 97%) for the quantification of the residual MMA in cellulose graft PMMA liquid samples.

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## 1. Introduction

Atom transfer radical polymerization (ATRP) is an advanced technique that has the ability to design graft, linear, block, star or dendritic forms in a predictable manner (Matyjaszewski & Xia, 2001). Due to its biodegradability and biocompatibility (Klemm, Heublein, Fink, & Bohn, 2005), cellulose graft polymer is receiving more attention in many specific applications, e.g., as a carrier for drug delivery (Marie, Arne, & Martin, 2000; Nishio, 2006). As a practical matter, it is important to determine the extent of monomer conversion when evaluating such polymerization processes.

Unfortunately, it is difficult to employ many available methods, e.g., the conventional gravimetry, to accurately determine the degree of conversion in samples from a cellulose-based ATRP process. For instance, such a determination in a commonly used reaction medium involving non-volatile solvents (Chang, Yamabuki, Onimura, & Oishi, 2008; Lin, Zhan, Liu, Fu, & Zhang, 2009; Meng et al., 2009) is difficult. High performance liquid chromatography (Pekka, Varpu, & Pekka, 1995) and gas chromatography (GC) (Schoenfeld, Conard, & Lautenschlager, 1979) are the typical techniques for quantification of residual monomer in process samples from an aqueous reaction medium, thus the monomer conversion can be calculated from a knowledge of the recipe. In order to minimize the polymer effect on the sample testing, pretreatment such

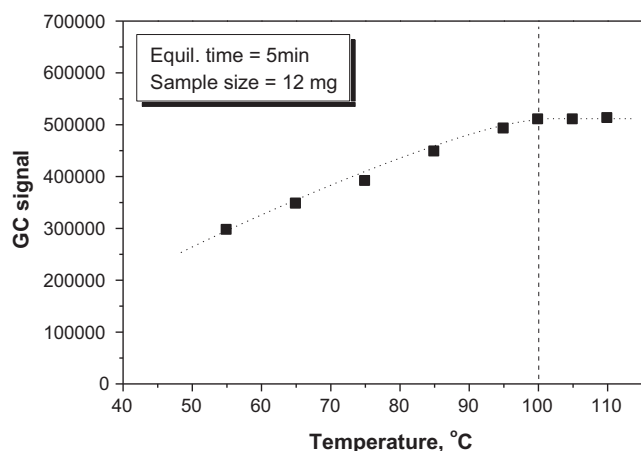
as solvent extraction, is usually required. However, such a solvent extraction is not suited for samples from a cellulose-based ATRP process that uses organic solvents or ionic liquids as a reaction medium. Recently, an advanced nuclear magnetic resonance (NMR) technique has been applied to determine the conversion of vinyl monomers grafted on cellulose via ATRP processes (Lin et al., 2009; Meng et al., 2009; Sui et al., 2008). However, Chang et al. (2008) found that it was difficult to accurately determine the monomer conversion by NMR due to an incomplete dissolution of cellulose-grafted PMMA in the conventional deuterated solvents. Moreover, even if NMR method can be used to determine conversion of the monomer in some instances, the pretreatment steps required for sample purification before the analysis makes the method complicated, time-consuming, and subject to large errors.

Full evaporation headspace gas chromatography (FE HS-GC) has been found to be an analytical technique particularly suitable for samples with complex matrices, including solids (Ioffe & Vitenberg, 1984; Richard, 1976). The major advantage of FE HS-GC is that there is no need or less need to pre-treat the sample prior to analysis. Based on FE HS-GC, we have successfully developed several methods for quantifying organic compounds in many difficult samples (Chai, Liu, & Zhu, 2000; Chai, Hou, & Schork, 2004; Li, Zhan, Fu, Liu, & Chai, 2007; Li, Chai, Deng, Zhan, & Fu, 2009).

In this paper we present a FE HS-GC method for the determination of residual monomer in cellulose-based ATRP process samples. The effect of the HS-GC operating conditions, i.e., the equilibration temperature, time, and sample size, were also investigated.

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**Fig. 1.** Effect of equilibration temperatures on the amount of MMA detected in the vapor phase.

## 2. Experimental

### 2.1. Materials, instruments and operations

All chemicals were purchased from the commercial sources.

HS-GC measurements were carried out with an automatic headspace sampler (DANI HS 86.50, Italy) and a GC system (2010, Shimadzu, Japan) that equipped with a flame ionization detector and employed a DB-5 capillary column operating at a temperature of 50 °C with a nitrogen carrier gas flow rate of 3.8 mL/min. Headspace operating conditions were as follows: 5 min with strong shaking for the sample equilibration at 105 °C, vial pressurization time of 0.2 min, and sample loop fill time of 0.2 min.

### 2.2. Cellulose graft PMMA via ATRP

Cellulose chloroacetyl chloride (Cell-ClAc) was used as a macro-initiator for the polymerization of MMA by ATRP using CuBr<sub>2</sub>/tetramethyl ethylenediamine (TEMED)/ascorbic acid (AsAc) as a catalyst. 0.3 g of Cell-ClAc was added to a flask containing a reaction mixture of dimethylacetamide (20 mL) and MMA (0.128 mol), which was stirred under N<sub>2</sub> atmosphere for 15 min. When the initiator was completely dissolved, equal molar amount (0.128 mmol) of CuBr<sub>2</sub>, TEMED, and AsAc were added to the flask, then the solution was immersed in an oil bath maintained at 50 °C.

### 2.3. Process sampling and HS-GC measurement

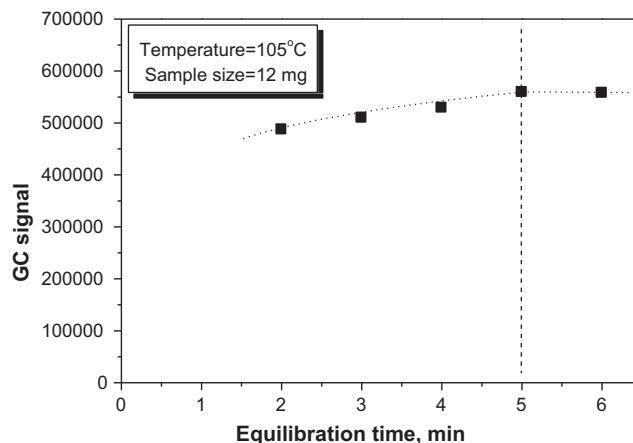
About 0.2 mL of the liquid mixture in the ATRP process was sampled by a micro-pipette at the desired time and added to a 1 mL centrifuge tube. The sample was quickly cooled to 0 °C, and then centrifuged at 4000 r/min in order to precipitate the suspended Cell-PMMA product. About 12 mg of the supernatant was withdrawn from the tube and transferred to a pre-weighed 20 mL headspace sample vial. After receiving the sample, the vial was weighed again to obtain an accurate weight of the sample by difference. The sample was then analysed by HS-GC.

## 3. Results and discussion

### 3.1. Evaluation of the completeness of MMA mass transfer

#### 3.1.1. Equilibration temperature

In Fig. 1, it can be seen that the transfer to the vapor phase is maximized at temperatures above 100 °C after 5 min for a sample size of 12 mg. To verify a near-complete interphase transfer under



**Fig. 2.** Effect of equilibration time on the amount of MMA detected in the vapor phase.

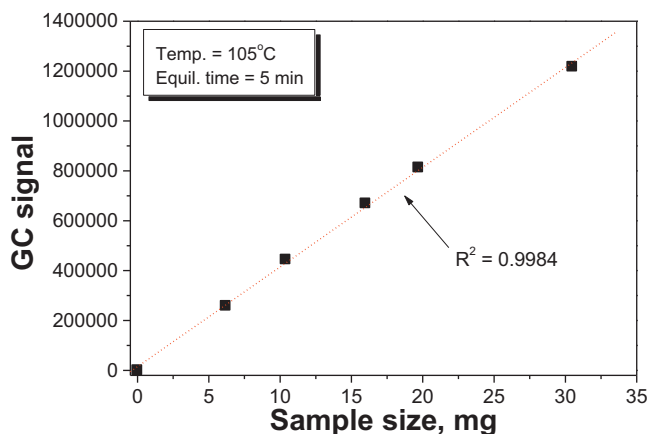
these conditions, a 12 mg sample solution was put on a small piece of filter paper that was placed in a headspace vial. After the first measurement by HS-GC at 105 °C for 5 min, the filter paper was transferred to another headspace vial for a second measurement at same conditions. The results showed that the ratio of the GC signal area ( $A$ ) of these two measurements (i.e.,  $A_2/A_1$ ) was less than 0.6%, indicating that a near-complete monomer mass transfer was achieved in the first headspace equilibration. Therefore, we chose a temperature of 105 °C for the rest of the study.

#### 3.1.2. Equilibration time

As shown in Fig. 2, the vapor–liquid equilibrium of MMA from a cellulose graft PMMA process liquid sample can be achieved after 5 min at 105 °C, which is similar to that observed in our previous studies (Chai et al., 2004; Li et al., 2007; Li et al., 2009) using different analytes. In the present work, a time of 5 min was chosen as the exposure (headspace equilibration) time at this temperature.

#### 3.1.3. Sample size

In the previous studies (Chai et al., 2004; Li et al., 2007; Li et al., 2009), it was found that a small sample size, i.e., less than 30 mg, is suitable for use in FE HS-GC analysis. In Fig. 3, it is shown that the GC signals of the headspace measurement is linearly related to the size of the process sample used in the range of 0–30 mg, indicating that a near-complete MMA mass transfer was achieved at the given conditions. Considering a relative low monomer conversion in the present processes, a sample size of ~12 mg was chosen in this work



**Fig. 3.** Effect of sample size on the amount of MMA detected in the vapor phase.

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