Carbohydrate Polymers 86 (2011) 367–370

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Short communication

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

Jin-Feng Zhong [a], Xin-Sheng Chai [a,*], Xiao-Li Qin [b], Shi-Yu Fu [a]

[a] State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China
[b] School of Light Chemistry and Food Science, South China University of Technology, Guangzhou, China

ARTICLE INFO

Article history:
Received 2 November 2010
Received in revised form 6 April 2011
Accepted 20 April 2011
Available online 28 April 2011

Keywords:
Methyl methacrylate
Headspace gas chromatography
Full evaporation

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.

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-violate 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.

* Corresponding author. Tel.: +86 13 416390033; fax: +86 20 22236078.
E-mail addresses: xschai@scut.edu.cn, xschai@gmail.com (X.-S. Chai).

0144-8617/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2011.04.050

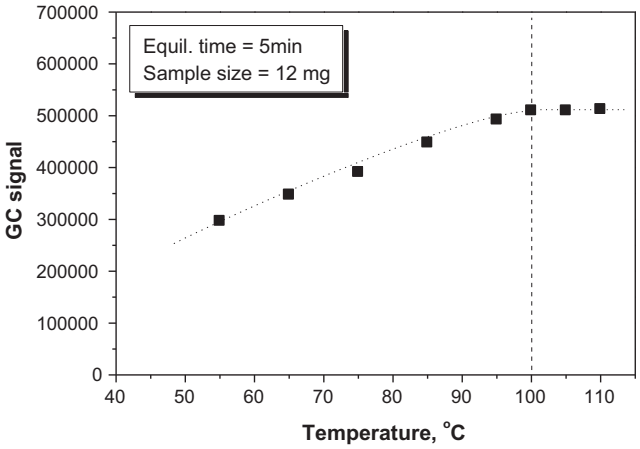

Fig. 1. Effect of equilibration temperatures on the amount of MMA detected in the vapor phase.

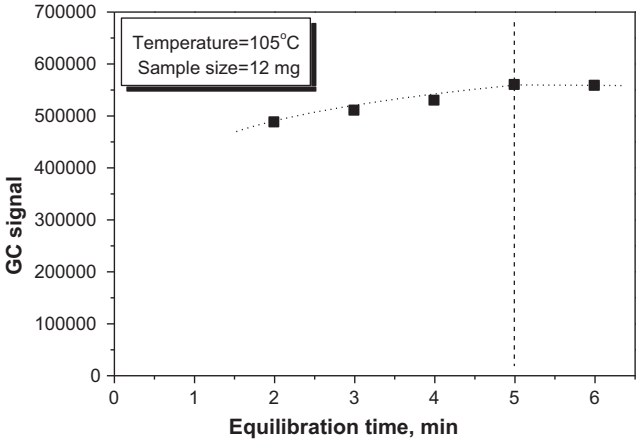

Fig. 2. Effect of equilibration time on the amount of MMA detected in the vapor phase.

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 $CuBr_2$/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_2 atmosphere for 15 min. When the initiator was completely dissolved, equal molar amount (0.128 mmol) of $CuBr_2$, 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 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%, indicting 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

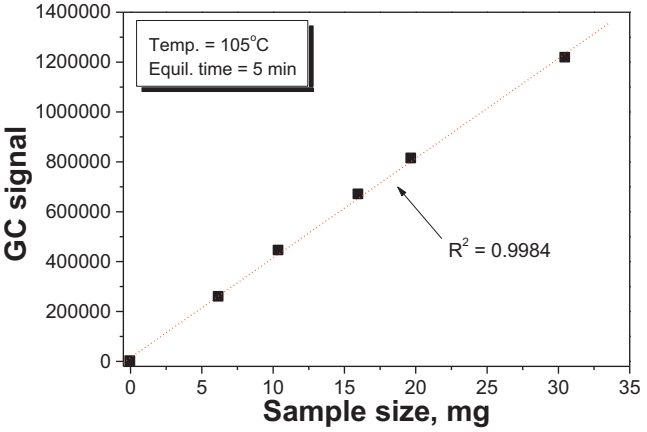

Fig. 3. Effect of sample size on the amount of MMA detected in the vapor phase.

Table 1
Recovery of the method[a].

Sample no.	MMA, mg		Recovery, %
	Added	Measured	
1	3.4	3.3	97
2	5.7	5.8	101
3	10.7	10.4	97

[a] 5 mg of sample was used.

in order to obtain a GC signal in a measurable range with the instrument used and also to minimize the possible MMA condensation due to its high vapor concentration in the sample vial.

3.2. Method calibration, precision and validation

A calibration curve was obtained by injecting different volumes of a standard MMA solution (0–12 mg) in the headspace sample vials and treated at the given full evaporation conditions for the HS-GC runs. A linear relationship was found between the GC signal and mass of MMA added in the headspace sample vials,

$$A = -14679(\pm 11839) + 120294(\pm 1823) \times C \quad (n = 6, \quad R^2 = 0.9991) \quad (1)$$

where A is the GC peak area of MMA in the vapor phase and C is the amount (in mg) of MMA added in the headspace sample vial.

The precision of the present method was also studied. The relative standard deviation (RSD) of five replicates was less than 0.30%.

To verify the present method, we prepared a set of samples by accurately adding different amount of pure MMA to a 5 mg Cell-graft-PMMA liquid sample, in which the content of MMA covers the range found in the process samples. The original sample (i.e., without added pure MMA) was measured as a reference. The additional contribution to GC peak area by the MMA in the spiked samples could then be determined.

Table 1 shows the comparison of the amount of MMA added and the amount detected by FE HS-GC. The good recoveries shown in the table indicate that the present method is suitable for the determination of the residual MMA in the samples from the Cell-graft-PMMA process.

3.3. Determination of monomer conversion during cellulose graft PMMA polymerization

3.3.1. Calculation of monomer conversion

By definition, the monomer conversion (R) at time t can be expressed as

$$R = \frac{M_0 - M_t}{M_0} \times 100\% \quad (2)$$

where M_0 and M_t are the initial mass of the monomer in the start solution ($t = 0$), and the residual monomer at the reaction time t, respectively.

Because the monomer mass (M) added in the vial is fully evaporated, it can be written as $M \approx C_g V_g$ (Chai et al., 2004). Also, the vapor concentration (C_g) of monomer is linearly proportional to GC peak area (A), i.e., $C_g = kA$, thus Eq. (2) can be written as,

$$R = \frac{C_0 - C_t}{C_0} \times 100\% = \frac{A_0 - A_t}{A_0} \times 100\% \quad (3)$$

Due to the high viscosity of the process samples, it is difficult to obtain an identical sample size in each FE HS-GC measurement. Thus, the monomer conversion was calculated according to a weight-based equation derived from Eq. (3), i.e.,

$$R = \left(1 - \frac{A_t/M_t}{A_0/M_0}\right) \times 100\% \quad (4)$$

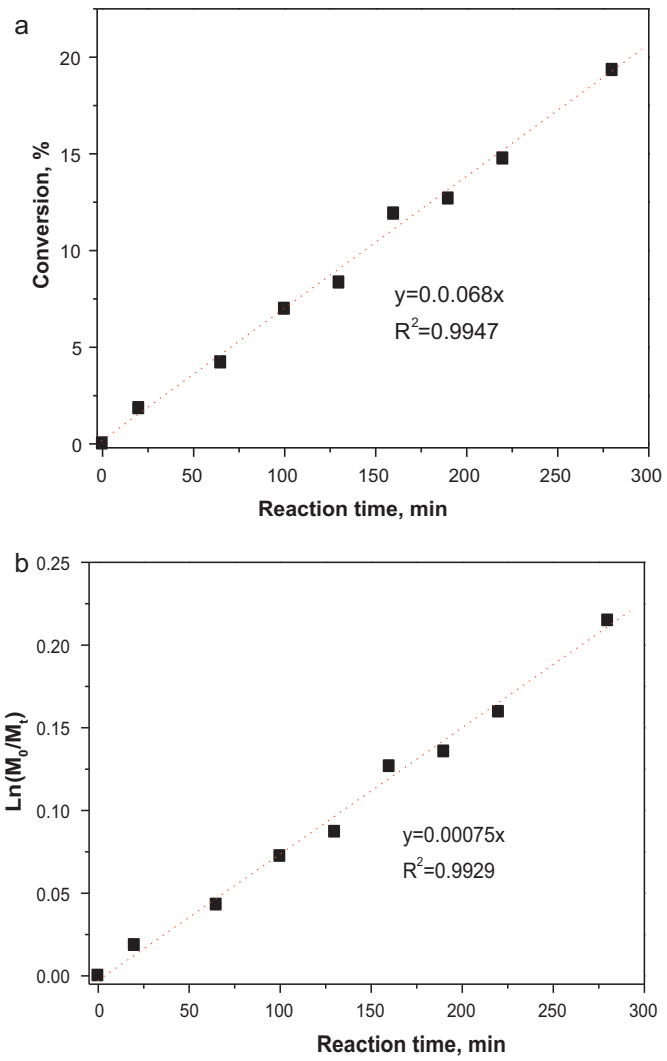

Fig. 4. Relationship between (a) MMA conversion; (b) $Ln[M]_0/[M]_t$ and reaction time.

3.3.2. MMA conversion during cellulose graft PMMA via ATRP process

Fig. 4(a) shows the time-dependent profile of MMA conversion during cellulose graft PMMA via ATRP process. It can be seen that there is a linear relationship between the MMA conversion and the reaction time in the process at the given conditions.

The linear relationship between $Ln(M_0/M_t)$ and reaction time is used to verify that if the reaction system is a controllable ATRP process (Matyjaszewski & Davis, 2002). According to Eq. (2), we can easily calculate the value of $Ln(M_0/M_t)$ when the monomer conversion data are available, i.e.,

$$Ln\left(\frac{M_0}{M_t}\right) = Ln\left(\frac{1}{1-R}\right) \quad (5)$$

The linear relationship shown in Fig. 4(b) confirms that the reaction is a controllable ATRP process at the given conditions.

4. Conclusions

A FE HS-GC technique for determining the conversion of MMA in the cellulose graft PMMA via ATRP has been developed. The present method is simple, rapid, and accurate, and suitable for the appli-

cation in the investigations monomer conversion in cellulose graft vinyl monomer polymerization research.

Acknowledgements

The authors acknowledge the Natural Science Foundation of China (No. 21076091) for sponsoring the research and Dr. Donald G. Barnes for the helpful discussions during the preparation of this paper.

References

Chai, X. S., Liu, P. H., & Zhu, J. Y. (2000). Analysis of volatile organic sulphur compounds in kraft liquors by full evaporation headspace gas chromatography. *Journal of Pulp and Paper Science*, *26*(5), 167–173.

Chai, X. S., Hou, Q. X., & Schork, F. J. (2004). Determination of residual monomer in polymer latex by full evaporation headspace gas chromatography. *Journal of Chromatography A*, *1040*, 163–167.

Chang, F. X., Yamabuki, K., Onimura, K., & Oishi, T. (2008). Modification of cellulose by using atom transfer radical polymerization and ring opening polymerization. *Polymer Journal*, *40*(12), 1170–1179.

Ioffe, B. V., & Vitenberg, A. G. (1984). *Head-space analysis and related methods in gas chromatography*. New York: John Wiley & Sons Inc.

Klemm, D., Heublein, B., Fink, H. P., & Bohn, A. (2005). Cellulose: Fascinating biopolymer and sustainable raw material. *Angewandte Chemie International Edition*, *44*, 3358–3393.

Li, H. L., Zhan, H. Y., Fu, S. Y., Liu, M. R., & Chai, X. S. (2007). Rapid determination of methanol in black liquors by full evaporation headspace gas chromatography. *Journal of Chromatography A*, *1175*, 33–136.

Li, H. L., Chai, X. S., Deng, Y. L., Zhan, H. Y., & Fu, S. Y. (2009). Rapid determination of ethanol in fermentation liquors by full evaporation headspace gas chromatography. *Journal of Chromatography A*, *1216*, 169–172.

Lin, C. X., Zhan, H. Y., Liu, M. H., Fu, S. Y., & Zhang, J. J. (2009). Preparation of cellulose graft poly (methyl methacrylate) copolymers by atom transfer radical polymerization. *Carbohydrate Polymers*, *78*(3), 432–438.

Marie, S., Arne, B., & Martin, M. (2000). Nonionic cellulose ethers as potential drug delivery systems for periodontal anesthesia. *Journal of Colloid and Interface Science*, *229*, 365–374.

Matyjaszewski, K., & Davis, T. P. (2002). *Handbook of radical polymerization*. New York: John Wiley & Sons, Inc.

Matyjaszewski, K., & Xia, J. H. (2001). Atom transfer radical polymerization. *Chemical Review*, *101*(9), 2921–2990.

Meng, T., Gao, X., Zhang, J., Yuan, J. Y., Zhang, Y. Z., & He, J. S. (2009). Graft copolymer prepared by atom transfer radical polymerization (ATRP) from cellulose. *Polymer*, *50*, 447–454.

Nishio, Y. (2006). Material functionalization of cellulose and related polysaccharides via microcompositions. *Advances in Polymer Science*, *205*, 97–151.

Pekka, K. V., Varpu, M., & Pekka, A. (1995). Residual monomer content and its release into water from denture base materials. *Dental Materials*, *11*(5–6), 338–342.

Richard, J. S. (1976). Modification solution approach for the gas chromatographic determination of residual monomers by head-space analysis. *Analytical Chemistry*, *48*(9), 1398–1403.

Schoenfeld, C. M., Conard, G. J., & Lautenschlager, E. P. (1979). Monomer release from methacrylate bone cements during simulated in vivo polymerization. *Journal of Biomedical Materials Research*, *13*(1), 135–147.

Sui, X. F., Yuan, J. Y., Zhou, M., Zhang, J., Yang, H. J., Yuan, W. Z., et al. (2008). Synthesis of cellulose-graft-poly(N,N-dimethylamino-2-ethylmethacrylate) copolymer via homogeneous ATRP and their aggregates in aqueous media. *Biomacromolecules*, *9*(10), 2615–2620.