Polymer Testing 28 (2009) 730–736

Contents lists available at ScienceDirect

Polymer Testing

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

Analysis Method

Spectral and chemical determination of copolymer composition of poly (butyl acrylate-*co*-glycidyl methacrylate) from emulsion polymerization

H. Bakhshi, M.J. Zohuriaan-Mehr*, H. Bouhendi, K. Kabiri

Iran Polymer and Petrochemical Institute (IPPI), P.O. Box 14965-115, Tehran, Iran

A R T I C L E I N F O

Article history:
Received 3 May 2009
Accepted 16 June 2009

Keywords:
Copolymer composition
Glycidyl methacrylate
Butyl acrylate
Spectroscopy
Elemental analysis
Titration

A B S T R A C T

Batch emulsion polymerization was used for preparing poly(butyl acrylate-*co*-glycidyl methacrylate) with different copolymer compositions at 75 °C with potassium persulfate as an initiator. Solubility and gel content of the prepared copolymers were studied. Four different spectral (^{1}H-NMR and FTIR) and chemical (elemental analysis and titration) methods were used to determine the copolymer composition. The epoxy was used as a key functional group, particularly in FTIR and titration methods of quantification. Results obtained from the chemical methods showed good agreement with those of the spectral methods. Effects of some probable phenomena occurring during copolymerization were investigated to account for differences of data obtained from the different analytical methods. Finally, the methods were compared and ^{1}H-NMR and elemental analysis were recognized as preferred approaches for the copolymer composition determination.

1. Introduction

Emulsion polymerization is a preferred process for industrial preparation of polymer lattices, because it produces high molecular weight polymers and no or negligible volatile organic compounds (VOC) [1,2]. Acrylic emulsions used frequently for surface coating formulations are generally based on methyl methacrylate (MMA) and butyl acrylate (BA). Recently, we have focused on the functional emulsions having glycidyl methacrylate (GMA).

GMA is one of the interesting monomers because of the presence of an epoxy group, which permits a large number of chemical reactions [3–7], offering the opportunity for chemical modification [8–14].

Copolymers of GMA present various industrial applications such as coatings [15–21], leather adhesives [22–25], biomaterials [14,26,27], pressure sensitive adhesives [28,29], dental composites [30], super-absorbents [26,31], in situ compatibilization [32–34] and surface modification [35–37].

Determination of copolymer composition is obviously necessary because it has direct effects on the final copolymer properties [38–41]. For this purpose, in the past few decades, ^{1}H-NMR spectroscopic analysis has been established to be a powerful tool for the estimation of copolymer composition due to its simplicity, rapidity and sensitivity. It has also been employed for determining tacticity and sequence distribution [42–50].

Infrared (IR) spectroscopy is a very conventional means for characterization of polymers. Canto and Pessan [51] developed an infrared method to estimate the copolymer composition of copolymers of GMA and (meth)acrylates based on measurements of absorbance of chemical groups. This method utilizes monomeric mixtures as standards instead of blends or copolymers, which represents a more practical solution to obtain a calibration curve.

A titration method based on HCl-dioxane regent has been proffered by Kline [52] for epoxy content measuring in resins which was modified by Kling and Ploehn [53] for GMA containing copolymers. Kling and coworkers also

---

* Corresponding author.
E-mail addresses: mjzohuriaan@yahoo.com, m.zohuriaan@ippi.ac.ir (M.J. Zohuriaan-Mehr).

0142-9418/$ – see front matter © 2009 Published by Elsevier Ltd.
doi:10.1016/j.polymertesting.2009.06.003

tendered another titration method based on epoxy group reaction with a soluble alkylamine with the advantage of not needing to use 1,4-dioxane and sample drying [53].

Elemental analysis, a useful method for quantitative analysis, can also be employed for copolymer composition determination [47–50,54–61].

The GMA-copolymer composition has been determined by several methods such as ^{1}H-NMR [22,23,25,62–68], quantitative ^{13}C NMR analysis [33,34,69], infrared spectrometry [14,51,67], elemental analysis [14,55] and titration [14,20,51,53,68,70–72]. Various comonomers such as MMA [21,63], ethyl methacrylate [63], butyl methacrylate [63,68], methyl acrylate [63], ethyl acrylate [20,21,63,67], 2-hydroxyethyl acrylate [72], styrene [14,21,33,51,53,66,71] and methyl styrene [66] have been copolymerized with GMA mainly via bulk and solution techniques.

However, to the best of our knowledge based on a comprehensive survey of the literature, no report has been published on determining composition of GMA-BA copolymer prepared by emulsion polymerization. In the present work, we focused on the comparative analysis of the copolymer composition by both spectral (^{1}H-NMR and FTIR) and chemical (elemental analysis and titration) methods.

2. Experimental

2.1. Materials

Butyl acrylate (BA, Fluka) and glycidyl methacrylate (GMA, Merck) as monomers were purified by vacuum distillation and kept at −4 °C prior to the polymerization reactions and the preparation of monomeric mixture for determining the FTIR calibration curve. Potassium persulfate (KPS, Merck) as initiator, sodium dodecylbenzene sulfonate (SDBS, reagent grade, Merck) as emulsifier, sodium bicarbonate as buffer and hydroquinone as inhibitor were used without further purification. Distilled water (DW) was employed as the continuous phase. Acetone, chloroform, dimethylsulfoxide (DMSO), ethyl acetate, ethyl methyl ketone (EMK), tetrahydrofuran (THF) and toluene (all from Merck) were used as solvents and methanol (Merck) was used as non-solvent for the produced polymers.

2.2. Polymerization

Batch emulsion polymerization were carried out at 75 ± 1 °C in a 500-mL 4-necked laboratory glass reactor fitted with a reflux condenser, 3-bladed stainless steel impeller, nitrogen inlet and inlet tube for initiator and inhibitor injection. The reaction components are given in Table 1. Monomers, water, emulsifier and buffer were added to the reactor. The reactor contents were brought to 75 °C and purged with nitrogen for 30 min to remove any dissolved oxygen prior to the start of the reaction. The desired amount of initiator dissolved in 2.5 mL distilled water was added to the reactor. To keep monomer conversion below 12%, the polymerization was inhibited by hydroquinone (10% aqueous solution, 10 mL) after 30–60 s.

The latex product was dried at room temperature and then adequate methanol was added to it to remove residual monomers, initiator, emulsifier and inhibitor. The remaining polymer was swollen in acetone for 24 h and then maintained in methanol for 24 h to extract the remaining impurities. This procedure was repeated twice, continuing with keeping the polymer at methanol for 72 h. To ensure complete removal of all trace impurities, the latter stage was repeated again. The final polymer samples were dried in a vacuum oven at room temperatures to reach constant weight.

Table 1
Recipes[a] for preparing the BA-GMA copolymers.

Sample code	Monomers in feed		Gel content in product (%)
	BA (wt%)	GMA (wt%)	
S1	90	10	29.8
S2	80	20	33.4
S3	70	30	35.5
S4	60	40	38.2
S5	40	60	41.5
S6	20	80	75.4

[a] Total monomers 48 g, water 150 g, SDBS 1.440 g, $NaHCO_3$ 1.200 g, KPS 0.300 g.

2.3. Characterization

Monomer conversion (X), was defined as the weight ratio of the polymer formed to initial monomers. After inhibitor addition, samples (∼1 mL) were directly taken from the reactor and dried in a vacuum oven and the conversion calculated as follows:

$$X = \frac{Weight\ of\ dried\ sample - Weight\ of\ inhibitor}{Weight\ of\ sample \times Solid\ content}. \tag{1}$$

2.3.1. Solubility studies

Solubility of the samples was tested in various polar and non-polar solvents (dimethylsulfoxide, ethyl acetate, toluene, chloroform, tetrahydrofuran, methyl ethyl ketone and acetone). About 50–100 mg of the polymer was added to about 50 mL of different solvents and kept stirred. The solubility of the polymers was recorded after 48 h.

2.3.2. Gel content

The gel content of samples was determined using chloroform as an extraction solvent. A known weight (50–100 mg) of the polymer was added to about 50 mL of chloroform and kept under stirring for 48 h. Then, the mixture was filtered using 2-μm filter paper and dried at room temperature to reach constant weight. The gel content was calculated as follows:

$$Gel\ Content = \frac{W_2}{W_1} \times 100. \tag{2}$$

where W_1 and W_2 are the weight of initial and dried sample, respectively.

2.3.3. Measurements

^{1}H-NMR spectra were obtained on a 400 MHz FT-NMR spectrometer (Bruker Instruments, model Avance 400, Germany) at room temperature using $CDCl_3$ as a solvent and TMS as an internal standard.