

## Research Article

# Facile Synthesis of Magnetic Copolymer Microspheres Based on Poly(glycidyl methacrylate-co-*N*-isopropylacrylamide)/Fe<sub>3</sub>O<sub>4</sub> by Suspension Photopolymerization

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Magnetic copolymer based on poly(glycidyl methacrylate-co-*N*-isopropylacrylamide) microspheres was prepared by 2,2-dimethoxy-2-phenylacetophenone- (DMPP-) photo initiated and poly(vinyl alcohol)- (PVA-) stabilized single step suspension photopolymerization. The effect of chemical interaction, morphology, and thermal properties by adding 0.1% w/v Fe<sub>3</sub>O<sub>4</sub> in the copolymer was investigated. Infrared analysis (FTIR) showed that (C=C) band disappeared after copolymerization, indicating that the magnetic copolymer microspheres were successfully synthesized and two important bands at 908 cm<sup>-1</sup> and 1550 cm<sup>-1</sup> appear. These are associated with the epoxy group stretching of GMA and secondary amide (N-H/C-H) deformation vibration of NIPAAm in magnetic microspheres. The X-ray diffraction (XRD) result proved the incorporation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles with copolymer microspheres as peak of Fe<sub>3</sub>O<sub>4</sub> was observed. Morphology study revealed that magnetic copolymer exhibited uniform spheres and smoother appearance when entrapped with Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The lowest percentage of Fe<sub>3</sub>O<sub>4</sub> nanoparticles leached from the copolymer microspheres was obtained at pH 7. Finally, thermal property of the copolymer microspheres was improved by adding a small amount of Fe<sub>3</sub>O<sub>4</sub> nanoparticles that has been shown from the thermogram.

## 1. Introduction

Magnetic polymer microspheres with core-shell morphology combining a polymer material and inorganic nanoparticles give unique properties of both materials which have been investigated extensively in various fields, such as isolation biological compound, drug delivery, and protein purification, particularly in sorbent to remove metal ions and enzyme immobilization [1–4]. This is due to their multifunctional properties such as small and uniform size, various functional groups on the surface, and large surface area [5, 6]. Moreover, considering their magnetic properties, this magnetic polymer

can easily separate and provide not only better physical and chemical stability, but also superior biological compatibility as reported [6]. The presence of polymer material provides the magnetic nanoparticle with high abundance of functional group through copolymerization and chemical modification step. These magnetic polymer microspheres capable to ensure a strong magnetic response and polymeric material can provide favourable functional groups and ability to protect nanoparticles aggregation [5]. Therefore, many polymer materials such as poly(styrene-glycidyl methacrylate) magnetic have been prepared in which Fe<sub>3</sub>O<sub>4</sub> was modified with polyethylene glycol (PEG) and oleic acid (OA) [7]. The

results reveal that the polymer is porous with high magnetic contents. Lan et al. 2013 [8] synthesized hyaluronic acid-supported magnetic microspheres utilized as adsorbent for heavy metal removal. The resultant microspheres showed superparamagnetic behavior, which made these adsorbents magnetically separable after the adsorption performance.

Glycidyl methacrylate (GMA) based copolymers have benefit because of the presence of reactive epoxy group. Epoxy groups have unique capability because they can be easily modified to a variety of functional groups such as aldehyde, aliphatic primary amino, and diazotizable primary aromatic groups [6]. Furthermore, polymers with epoxide groups offer numerous functionalization possibilities in mild reaction conditions [9]. It is suitable for prospective immobilization of enzymes and other proteins and nucleic acids [10]. *N*-isopropylacrylamide (NIPAAm) acts as a second monomer in this system. It is one of the most well-known temperature-sensitive polymers, exhibiting a low critical solution temperature (LCST) at 32°C which provides hydrogel with the possibility to have high swelling degrees at low temperatures and shrink at high temperatures [11]. Thermoresponsive swelling behaviour can be designed and utilized in several advanced applications as reported by Kali et al. 2013 using novel amphiphilic conetworks (APCN) consisting of thermoresponsive poly(*N*-isopropylacrylamide) cross-linked by hydrophobic methacrylate-telechelic polyisobutylene. This study revealed the LCST of these conetworks decreases to the range of 25–28°C in comparison with 34.1°C for the homopolymer network of poly(NIPAAm). As a consequence, significant decreases of swelling degree in water between 20 and 35°C are observed [12]. In addition, hydrophilic/hydrophobic balance in the NIPAAm unit results from hydrophilic (amide group) and hydrophobic (isopropyl group) regions of poly(NIPAAm). Below the LCST, hydrogen bonding between hydrophilic segments and water molecules is dominant which can lead to enhancing dissolution or swelling in water. As the temperature increases, hydrophobic interactions among the hydrophobic segments become stronger, while hydrogen bonding becomes weaker, resulting in shrinking of the hydrogels [13].

Thus far, several conventional procedures have been proposed for the encapsulation of iron oxide nanoparticles in polymer shells including solvent evaporation and heterogeneous polymerizations such as suspension, emulsion, and dispersion/precipitation polymerization [14–17]. Upon completion of polymerization, iron oxide nanoparticles are evenly distributed or could be within the pores of the polymer [18]. Recently, researchers had prepared magnetic poly(vinyl acetate-divinylbenzene) microspheres using modified suspension polymerization. As a result, they can control beads size within 10 µm, but the size distribution was still wide and a part of the microspheres sphericity was altered. In the case of products that were prepared by emulsion polymerization, there are still some drawbacks such as weak magnetic responsiveness, low particle yield, and severe flocculation of microspheres. Therefore, suspension radical polymerization can be considered to be the most favorable approach in the preparation of magnetic monodisperse microspheres [1, 17]. Furthermore, suspension photopolymerization technique

was carried out either without or with a low amount of cross-linking agent [19].

In view of these problems, this work proposes a new method of suspension photopolymerization that offers a rapid and straightforward technique of copolymerization. The effects of incorporating iron oxide (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles into the copolymer microspheres also were investigated using several physical analyses. The analyses include phase transition of the resultant magnetic copolymer that was measured by differential scanning calorimetry (DSC), morphology property using scanning electron microscopy (SEM), and iron oxide (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles leached from the copolymer microspheres and was also determined by atomic absorption spectroscopy (AAS).

## 2. Experimental

**2.1. Materials.** Glycidyl methacrylate, GMA (Sigma-Aldrich), *N*-isopropylacrylamide, and NIPAAm (Sigma-Aldrich) were stored in a refrigerator and at room temperature until use, respectively. Iron oxide, Fe<sub>3</sub>O<sub>4</sub>, 20–50 nm (Sigma-Aldrich), 2,2-dimethoxy-2-phenylacetophenone, DMPP (Sigma-Aldrich), poly(vinyl alcohol), and PVA (Sigma-Aldrich) were selected as the photo initiator and stabilizer, respectively. The cross-linker, ethylene glycol dimethacrylate (EGDMA), was obtained from Sigma-Aldrich. Deionised water was used for making the aqueous solution during the experiment. All chemicals were used without purification.

**2.2. Synthesis of Magnetic Copolymer.** The magnetic copolymer GN73 was prepared via suspension photopolymerization as described below. A mixture was comprising 70% v/v GMA, 30% w/v NIPAAm, 0.1% w/v Fe<sub>3</sub>O<sub>4</sub>, and 600 µL of EDGMA in a sample bottle followed by 5 mL of 1% w/v PVA and 1.6% w/v DMPP added to a sample bottle. This mixture was sonicated at 37°C for 10 min to assure adequate dispersion [20]. The photo curing of the final mixture was performed under ultraviolet (UV) radiation in a UV box (RS Ltd.) containing four units of 60 watt UV lamps. The irradiation was carried out for 10 min under a nitrogen atmosphere [21]. After completion of polymerization, the copolymer microspheres were centrifuged at 5000 rpm for 10 min to remove the suspended medium. The polymerization reaction led to the formation of milky magnetic copolymer (GMA-NIPAAm) microspheres which were resuspended in 10 mL of ethanol and centrifuged again under similar conditions. The ethanol wash step was repeated three times to complete removal of unreacted monomers. Finally, magnetic copolymer GN73 microspheres were resuspended in 10 mL of deionised water and stored at room temperature until use [22]. All the steps were repeated to obtain the copolymer without magnetic particles (GN73).

**2.3. Characterization Techniques.** Functional groups in the magnetic copolymer GN73 were determined using Fourier transform infrared (FTIR, Perkin-Elmer Spectrum BX) at normal transmission mode and wavelength from 4000 to 370 cm<sup>-1</sup> at 2 cm<sup>-1</sup> resolution. Each sample (powder form)

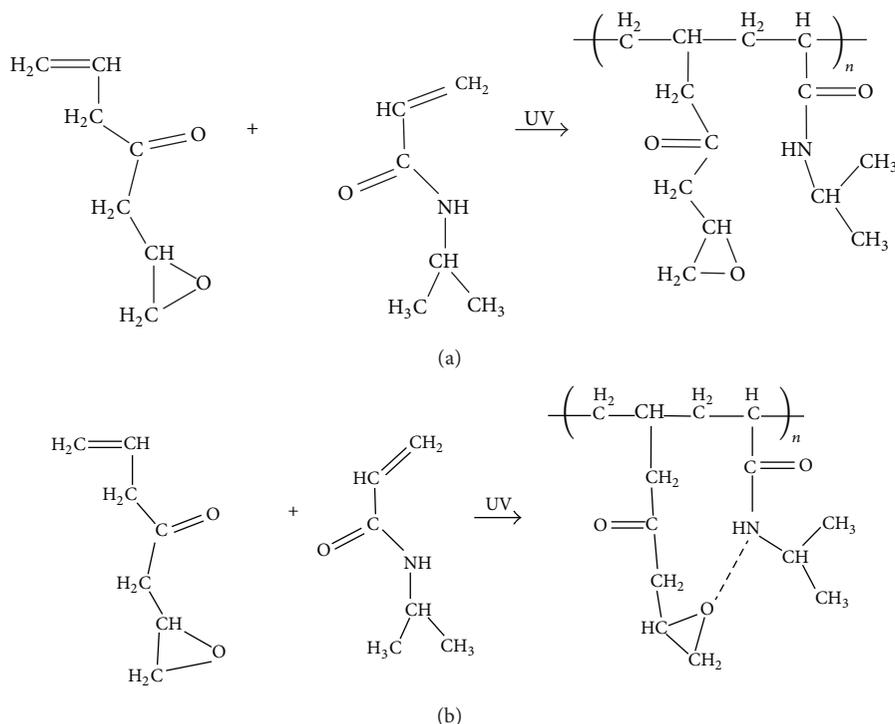


FIGURE 1: (a) The proposed mechanism of glycidyl methacrylate and *N*-isopropylacrylamide using suspension photopolymerization. (b) The possible intermolecular interaction in poly(glycidyl methacrylate-co-*N*-isopropylacrylamide).

was analyzed in a form of KBr disc. The phase composition and structure of the magnetic copolymer GN73 were determined by X-ray powder diffraction (XRD) using a D8-Advance Bruker AXS (monochromated Cu  $K\alpha$  radiation = 1.5418 Å). Typically, the diffractogram was recorded in a  $2\theta$  range of 3–80°. The phase transition behaviour of magnetic copolymer GN73 was determined by using DSC (Perkin Elmer model DSC-7). About 4 mg of magnetic copolymer GN73 microspheres was placed in an aluminium pan and sealed tightly using aluminium lid. Thermal analysis was performed from 0 to 220°C under dry nitrogen atmosphere with a flow rate of 5 mL/min at heating rate of 10°C/minutes. Morphology and size of the magnetic copolymer GN73 microspheres were studied using SEM (Zeiss Supra 55VP, Germany). Magnetic copolymer GN73 microspheres were dried at room temperature, coated with a thin layer of platinum (about 100 Å) in vacuum, and observed at 10,000x magnification. In this study, three types of leaching medium were used: 50% acetic acid solution (pH 3.0), 50 mM phosphate buffer solution (pH 7.0), and 50 mM sodium citrate/NaOH buffer solution (pH 12.0). Approximately, 250 mg of the magnetic copolymer was placed in a test tube containing 10 mL of a leaching medium and shaken with a rotary shaker for 24 h. Then, the amount of iron oxide ( $\text{Fe}_3\text{O}_4$ ) nanoparticles that leached out into the medium was determined by an atomic absorption spectroscopy (AAS 5EA, Carl Zeiss Technology, Zeiss Analytical Systems, Germany).

### 3. Results and Discussion

**3.1. Preparation of Magnetic Microspheres.** The proposed reaction for the formation of magnetic polymer microspheres via suspension photopolymerization is displayed in Figures 1(a) and 1(b). Initially, iron oxide ( $\text{Fe}_3\text{O}_4$ ) nanoparticles and monomers (GMA and NIPAAM) were restricted in suspension droplet, which was stabilized by PVA and EGDMA. When the mixture was polymerized by the UV irradiation, the miscibility of monomer mixture and iron oxide ( $\text{Fe}_3\text{O}_4$ ) nanoparticles resulted in a phase separation. However, before the iron oxide ( $\text{Fe}_3\text{O}_4$ ) nanoparticles totally escaped from the polymer phase, the viscosity became high enough to prevent the phase separation. Hence, the magnetic microspheres were obtained after only 10 min of UV irradiation [23]. Miscibility monomer depends either on specific interactions or on intermolecular repulsion. Since there are epoxy ring in GMA chain and active hydrogen in the side chain of NIPAAM, they are leading to the formation of intermolecular interaction as shown in Figure 1(b).

**3.2. FTIR Analysis.** The chemical composition of the magnetic copolymer was assessed using FTIR spectroscopy. Figure 2(a) illustrates the FTIR spectra of the copolymer GN73 and magnetic copolymer GN73 is shown in Figure 2(b). Both spectra show important characteristic peak at 908  $\text{cm}^{-1}$ , indicating the presence of epoxy group

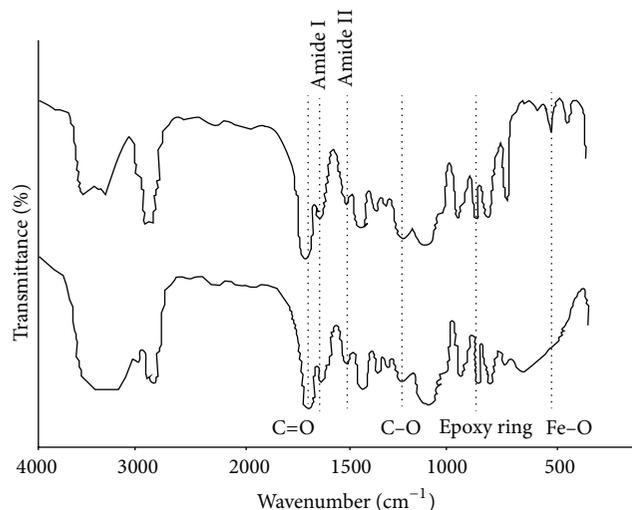


FIGURE 2: FTIR spectra of (a) magnetic copolymer GN73 and (b) copolymer GN73.

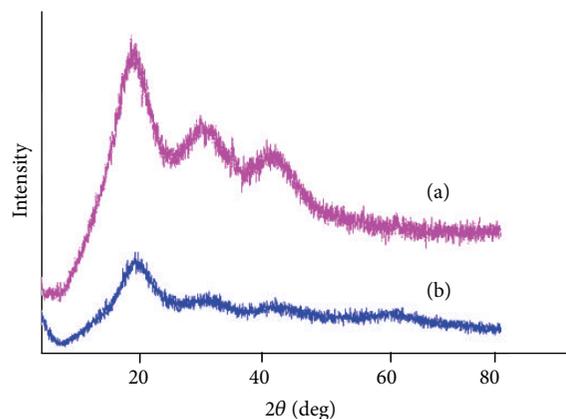


FIGURE 3: Comparison of peaks in X-ray diffraction for (a) magnetic copolymer GN73 and (b) copolymer GN73.

in copolymer. Besides, the spectra show absorption peaks at  $1733\text{ cm}^{-1}$  (C=O carbonyl vibration) and two peaks at  $1670\text{ cm}^{-1}$  and  $1550\text{ cm}^{-1}$  correspond to amide I (C=O/C-N) and amide II (N-H/C-H) vibration, respectively, representing the acrylamide vibration of NIPAAm unit. The peak at  $1258\text{ cm}^{-1}$  could be attributed to the stretching vibrations of C-O configuration of GMA. In addition, a new sharp peak was observed at  $594\text{ cm}^{-1}$ . It may be due to the Fe-O vibration band of bulk  $\text{Fe}_3\text{O}_4$  that is bound in tetrahedral geometry [24]. These results proved that magnetic nanoparticles were successfully entrapped onto the copolymer microspheres by suspension photopolymerization.

**3.3. XRD Analysis.** The structure of iron oxide in magnetic copolymer was analyzed using X-ray diffraction (XRD) [25]. Diffractogram (Figure 3) shows a diffraction pattern between copolymer GN73 and magnetic copolymer GN73. The XRD patterns of magnetic copolymer GN73 microspheres, as illustrated in Figure 3, did not change distinctly as the copolymer

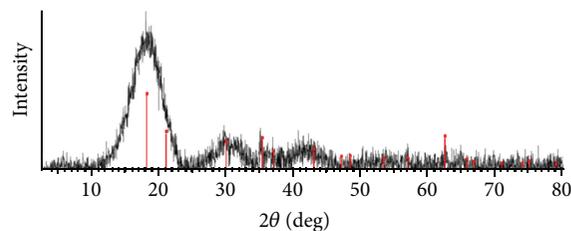


FIGURE 4: XRD analysis of magnetic copolymer GN73 peaks. Vertical bar is iron oxide standard.

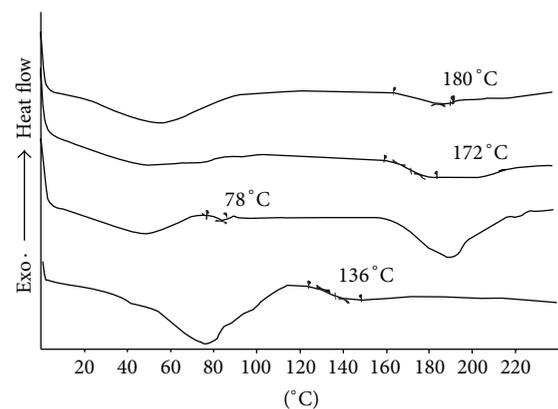


FIGURE 5: DSC thermogram of (a) magnetic copolymer GN73, (b) copolymer GN73, (c) poly(GMA), and (d) poly(NIPAAm).

GN73 (a peak at  $2\theta$  of about  $19.0^\circ$ ) only increases the peak strength. Therefore, it could be demonstrated that iron oxide ( $\text{Fe}_3\text{O}_4$ ) nanoparticles had been successfully incorporated into the copolymer microspheres and GN73 without being destroyed [23]. The XRD patterns of magnetic copolymer GN73 and pure iron oxide ( $\text{Fe}_3\text{O}_4$ ) nanoparticles are shown in Figure 4. The overlap between magnetic copolymer GN73 and iron oxide ( $\text{Fe}_3\text{O}_4$ ) nanoparticles peak proved the existence of iron oxide ( $\text{Fe}_3\text{O}_4$ ) nanoparticles in magnetic copolymer (the diffraction peaks at  $2\theta$  of about  $18.2^\circ$ ,  $21.1^\circ$ ,  $30.0^\circ$ ,  $37.0^\circ$ ,  $45.0^\circ$ , and  $62.5^\circ$ ). It is apparent that the diffraction pattern of the iron oxide ( $\text{Fe}_3\text{O}_4$ ) in copolymer is closed to the standard pattern for crystalline iron oxide [26]. The overlaps show the presence of iron oxide at the spinal structure [24].

**3.4. DSC Analysis.** Phase transition behaviour of each sample was analyzed using differential scanning calorimeter (DSC). The  $T_g$  of poly(GMA), poly(NIPAAm), copolymer GN73, and magnetic copolymer GN73 was shown in Figure 5. The  $T_g$  of poly(GMA) obtained via suspension photopolymerization was  $78^\circ\text{C}$  and comparable to the  $T_g$  of poly(GMA) by using precipitation polymerization that was  $83^\circ\text{C}$  [27]. The  $T_g$  value for cross-linked poly(GMA) has increased to  $78^\circ\text{C}$  compared to the reported finding,  $60^\circ\text{C}$  for poly(GMA) homopolymer without cross-linker. The increase of  $T_g$  may be due to cross-linking effect which significantly lowers the mobility of chains. Thus, a higher temperature is needed for promoting chain mobility [28]. In Figure 5(c), the endothermic peak refers to the melting point ( $T_m$ ) of poly(GMA) around  $190^\circ\text{C}$ .

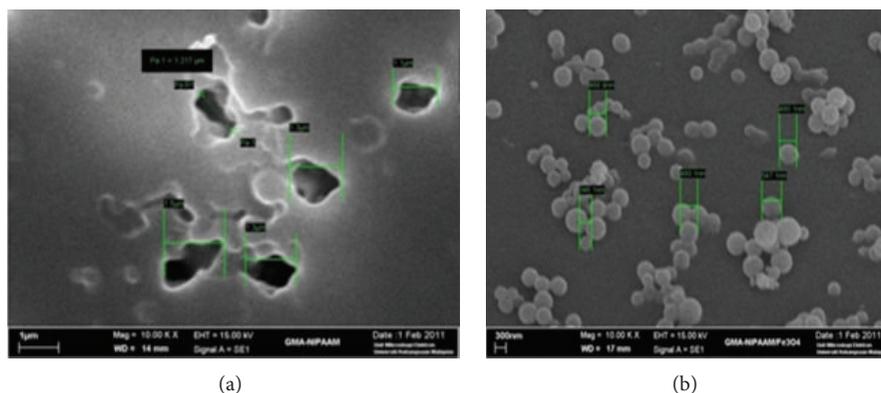


FIGURE 6: The micrographs for (a) copolymer beads surface without iron oxide nanoparticles and (b) distribution of beads for magnetic copolymer GN73.

Figure 5(d) indicates moisture removal from 60 to 85°C for poly(NIPAAm). The observation was also reported in the poly(NIPAAm) homopolymer that was obtained by radical polymerization [29]. On the other hand, the glass transition temperatures of poly(GMA) and poly(NIPAAm) were 78°C and 136°C, respectively; the  $T_g$  values of copolymer GN73 were higher than those of pure components which are 172°C. This is probably caused by higher extent of H-bonding between epoxide group from poly(GMA) and N–H bonds in poly(NIPAAm). Strong hydrogen bond can effectively act as a physical cross-linker, thus reducing segment mobility [30]. Both pure constituents, copolymer GN73 and magnetic copolymer GN73, show a single  $T_g$  as shown in Figure 5. It has been shown in the literature [31] that when the polymers are fully miscible, it will exhibit single glass transition temperatures. Furthermore, the thermogram for magnetic copolymer GN73 exhibited slightly higher  $T_g$  (180°C) than copolymer GN73 (172°C) after iron oxide was added to copolymer. As it can be observed, only small amount of magnetite nanoparticles is effective in shifting  $T_g$  to the higher value. Therefore, it can be said that there is an enhancement of glass transition in the magnetic copolymer GN73. This kind of observation was also reported by López et al. for their PVA nanocomposite prepared with Co-Fe<sub>2</sub>O<sub>4</sub> nanoparticles. The proposed explanation is related to the restrictions in segment mobility and to the reduction of diffusivity of attacking agents within the polymer matrix, both due to the polymer-filler interactions [32]. The thermal stability of magnetic copolymer GN73 was improved by the presence of magnetite nanoparticles which act as a heat barrier due to the nanoparticle-polymer interaction. The nanoparticle-polymer interaction could be type of adhesive forces. This kind of interaction has been accepted by several authors to exist between magnetite particles and a polymer [33, 34].

**3.5. SEM Analysis.** Scanning electron microscopy (SEM) is used to elucidate the morphology of the copolymer and the location of pores [35]. Figure 6(a) shows the micrograph of copolymer beads surface without iron oxide nanoparticles, while Figure 6(b) refers to the distribution of beads for

magnetic copolymer GN73. From the figures, it can be found that the surface of a bead copolymer GN73 exhibited a loose shallow porous with average pore diameter between 1.0 and 1.5  $\mu\text{m}$  which is estimated based on the SEM micrograph. However, no porous structure was observed in the magnetic copolymer GN73 as seen in Figure 6(b). This finding was constant with previous report in the literature [13]. In comparison with the copolymer GN73, the magnetic copolymer GN73 surface was smoother than copolymer GN73 without magnetic. This is because the iron oxide (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles are mostly entrapped within the interstitial spaces of a cross-linked water-insoluble polymer during *in situ* polymerization of the monomers forming the copolymer [36]. Polymer surfaces are believed to be nonporous because of their very small specific surface area and pores size after substituting iron oxide nanoparticles [37]. As we can see, the magnetic copolymer GN73 has narrow distribution size of beads in the range of 0.34–0.57  $\mu\text{m}$  and dispersed on the surface of the copolymer. This finding reveals that the iron oxide (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles were found to be inside and of the microspheres particle surface agree with previous report [38].

**3.6. AAS Analysis.** Iron oxide (Fe<sub>3</sub>O<sub>4</sub>) is a biocompatible superparamagnetic material that has low toxicity and strong magnetic properties [20]. The relevant kinetic data has been correlated with one or more of the physiochemical factors that include the ionic activity of H<sup>+</sup>, interaction with OH<sup>-</sup> or SO<sub>3</sub><sup>2-</sup>, electrochemical surface reaction, and changes in surface area [39]. Note that the leaching of iron oxide (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles was measured in three different media including acetic acid solution (50%, v/v, pH 3.0), phosphate buffer solution (pH 7.0), and sodium citrate/NaOH buffer solution (pH 12.0). The highest iron concentration obtained was 2.048 mg/L in 50% acetic acid solution at pH 3.0. It has been reported [37] that the optimum pH for dissolving iron oxide is pH 2.5–3.0. In acidic medium, the degree of freedom for poly(NIPAAm) chains was bigger compared to neutral and alkaline medium [13]. So, more iron oxide is eluted at pH 3.0 compared to other pH. Figure 7 shows that the iron oxide (Fe<sub>3</sub>O<sub>4</sub>) nanoparticle has the lowest solubility in neutral medium (0.028 mg/L), while the concentration of

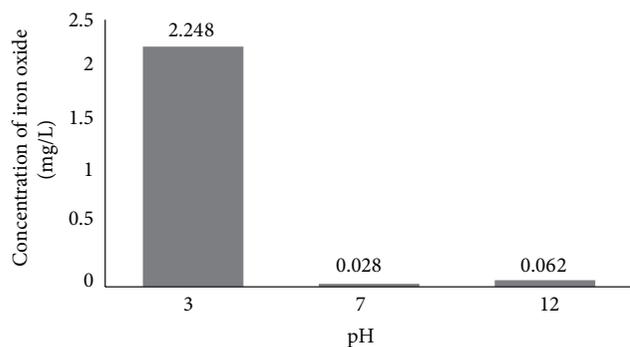


FIGURE 7: Concentration of leached iron oxide ( $\text{Fe}_3\text{O}_4$ ) from magnetic copolymer GN73 in different medium (acetic acid solution (50%, v/v, pH 3.0), phosphate buffer solution (pH 7.0), and sodium citrate/NaOH buffer solution (pH 12.0)) measured by atomic absorption spectrophotometer (AAS).

leached iron oxide ( $\text{Fe}_3\text{O}_4$ ) nanoparticles in alkaline solvent was 0.062 mg/L. It has been previously shown that the iron ions that were entrapped into the polymer matrix can be eluted if there are changes in ionic strength in medium or pH solution [40].

#### 4. Conclusions

In summary, magnetic copolymer GN73 microspheres can be rapidly synthesized by suspension photopolymerization in the presence of iron oxide nanoparticles. The synthesized magnetic copolymer GN73 microspheres exhibited narrow distribution size in the range of 0.34–0.57  $\mu\text{m}$ . The pH value of external buffer solution had influenced the leached iron oxide ( $\text{Fe}_3\text{O}_4$ ) nanoparticles from the copolymer microspheres. The result was confirmed by AAS analysis that revealed that the highest amount of leached iron oxide ( $\text{Fe}_3\text{O}_4$ ) occurred in acidic medium. Besides that GN73 copolymer has good miscibility that was led to increase  $T_{\text{mg}}$  value compared to the homopolymer. The addition of small amount of  $\text{Fe}_3\text{O}_4$  has successfully improved the thermal properties of the polymer. This work has potential in biosensor matrix fabrication because of the presence of epoxy ring that can be easily modified to bind with enzyme. Furthermore, a small size of microspheres promotes higher surface area.

#### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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