INTRODUCTION

Among the family of conjugated polymers, polyaniline (PANI) is one of the most useful since it is air and moisture-stable in both its doped, conducting form, and in its de-doped, insulating form [1–4]. PANI is also unique among conducting polymers due to a very simple acid/base doping/dedoping chemistry. It has a great variety of potential applications including anticorrosion coatings, batteries, sensors, separation membranes, antistatic coatings, electro optics, and light-emitting diodes [5–10]. The commercial application of PANI, like most conductive polymers, is limited due to its insolubility and infusibility. Lack of solubility of PANI may be resulted from the stiffness of its main chain and the existence of a strongly conjugated, n-electron system. Therefore, in order to increase the solubility and induce fusibility of the stiff chain of this polymer, a large number of methods have been studied. Such as polymerizing a derivative of aniline with solubilizing property; substituents used to increase the solubility can range from ring–alkyl [11] or alkoxy [12] and N-alkyl [13, 14] groups to sulphonic acid [15] groups. Also, copolymerization of aniline with N-substituted anilines leads to polymers which have conductivity like PANI and solubility of substituted anilines [16, 17]. Yue and Kohlman have synthesized the sulfonic acid ring-substituted PANI by a reaction of emeraldine base (EM) with fuming sulfonic acid, which is soluble in water only after conversion to the salt form [18, 19]. Another approach towards soluble polyaniline may be an incorporation of flexible polymers into the PANI structure by N-substitution method. Wang et al. [20] synthesized poly(ethylene glycol)-grafted polyaniline with enhanced solubility in common organic solvents and water. Nabid et al [21] reported an enzymatic method for the synthesis of a water soluble conducting poly(o-toluidine) in the presence of sulfonated polystyrene as template. Gheybi et al. reported that the solubility of polystyrene-graft-polyaniline copolymers in common organic solvents such as THF and chloroform is improved by increase the degree of N-grafting [22]. Several functional sulfonic acids have been found to render PANI soluble in organic solvents in its doped form.

Cao et al. reported that the PANI doped with dodecylbenzene sulfonic acid or camphor sulfonic acid could be soluble in various organic solvents such as m-cresol and xylene [23, 24]. Angelpolos et al developed water soluble electrically conducting PANI doped with polyacids such as polystyrene sulfonic acid [25]. Many attempts have been made to produce colloidal PANI by using polymeric surfactants [26, 27]. The incorporation of the side groups into polyaniline has enhanced its solubility and processability and changed its properties [28, 29]. Hosseini reported the grafting of aniline onto functionalized polystyrene [30]. However, the above mentioned procedures differ from the method used in the present research. A. A. Entezami and co-workers [4] have prepared soluble polyaniline by grafting poly(N-isopropyle acrylamide).

The main goal of the present research was to prepare PANI soluble in water and some organic solvents (methanol, DMSO, etc.) by grafting poly(2-hydroxy ethyl metacrylate) using ATRP. Only a few works have been published on ATRP, starting from PANI as a
macroinitiator [22, 31]. Peng synthesized polyaniline grafted poly(methyl methacrylate), which was not soluble in water [31]. We have synthesized the PANI-graft-poly(2-hydroxy ethyl metacrylate) with higher content of grafted to PANI poly(HEMA).

EXPERIMENTAL

Materials

Ammonium persulfate, phenyl hydrazine, triethylamine, sulfuric acid, ammonia, methanol, acetone, chloroacetyl chloride (CAC), and N, N, N, N', N'-pentamethyl diethylene triamine (PMDETA) were obtained from Fluka and were used as received. Aniline purchased from Merck was distilled twice under vacuum prior to polymerization. Copper (I) chloride purchased from Merck was used for stirring in glacial acetic acid, then washing with methanol and finally drying under reduced pressure. 2-hydroxyethyl methacrylate was purchased from Aldrich and distilled under a reduced pressure before use. Dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), toluene, and diethyl ether were obtained from Fluka, and were totally dried and then distilled under reduced pressure.

Methods

The FTIR spectra (Shimadzu FTIR 8600s, Japan) were recorded at room temperature; samples were prepared in KBr pellets. 1H NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer at ambient temperature in DMSO-d6 as solvent and using tetramethylsilane as an internal standard. A differential scanning calorimeter (NETZSCH DSC 200 F3) was used to determine the thermal transition temperatures under nitrogen atmosphere in the range of 30–300°C at a rate of 10 grad/min. Thermal stability of obtained poly(2-hydroxyethyl metacrylate)-graft-PANI was studied by thermal gravimetric analysis using Perkin-Elmer, USA. SEM micrographs of polymer were obtained by Stereoscan 360 Oxford. In order to observe the images clearly, a thin film of gold was sputtered at 10 mA for 20 s on the surface of the probe using a Hummer-600 sputtering system. The morphology of polymers was observed by AFM (AFM C26-DME). Images were gathered at room temperature in air using nano-sensors microfabricated silicon cantilevers. Scan speed was at one line per second and 512 data points per line. Multiple images were collected for the same area with no observable changes in surface morphology for these particular scanning parameters, indicating that little or no damages were done to polymer film surface. Cyclic voltammetry studies were carried out using a glassy carbon (GC) disk electrode with 2 mm diameter as working electrode and Ag/AgCl electrode served as the reference electrode. Cyclic voltammograms (CVs) were recorded by AUTO-LAB model 4.9006 Metrohm, Switzerland and by using a three-electrode cell with a GC (2 mm diameter) with a cast film of copolymer as the working electrode, a Pt wire as a counter electrode and Ag/AgCl electrode as the reference electrode. The cyclic voltammograms were obtained at room temperature in 1 M \( \text{H}_2\text{SO}_4/\text{H}_2\text{O} \), and scanned between –0.2 and 0.8 V at scan rates between 25 and 225 mV/s. The elemental composition of the material was determined by using vario MAX CHN elementary analyzer.

Synthesis of Emeraldine Base Polyaniline

Emeraldine salt polyaniline (PANI-ES) was prepared via a chemical polymerization method. Distilled aniline (0.064 mol) was dissolved in chloroform (200 mL) as an organic solvent. Ammonium persulfate (0.016 mol) was dissolved in 200 mL of 1 M \( \text{H}_2\text{SO}_4 \). The organic phase was transferred to a two-necked flask, equipped with a dropping funnel and argon inlet, and the aqueous phase was added drop wise into the organic solution during 7 h at room temperature (in general, the two solutions are carefully transferred to a beaker, generating an interface between the two layers [31]). The polymerization reaction occurred during 18 h without stirring. The aqueous phase was collected and filtrated. The filtrate was washed with water and methanol followed by washing with acetone. The collected dark green polyaniline salt was then converted into its base form by stirring in ammonia solution 5 wt % for 2 h. This de-doped polyaniline was filtered and washed several times with water. The resulted dark-blue powder was dried under a reduced pressure.

Leucoemeraldine Base Polyaniline

In order to prepare a fully reduced polyaniline, 3.8 mL (0.038 mmol) of phenylhydrazine was added to 0.6 g of the prepared emeraldine base form of polyaniline in a flask equipped with a magnetic stirrer at room temperature. The reaction mixture was stirred for 1 h, and then 300 mL of diethyl ether was added which stirred again for less than 5 min. The resulted gray-white polymer was filtered and dried under vacuum.

Preparation of the Macroinitiator

For preparation of macroinitiator, (0.5 g) of the reduced polyaniline (PANI-LEB) powder was solubilized in 50 mL of NMP at room temperature under argon atmosphere. Then, triethylamine (0.4 mL, 0.0029 mol) and chloroacetyl chloride (0.8 mL, 0.011 mol), were slowly added drop wise to the PANI-LEB solution and then the mixture was left to react at 25°C for 24 h on stirring. The mixture was poured in methanol to precipitate the obtained polymer. The prepared polymer was washed with methanol/water mixture and diethylether to remove the insoluble salts.