Synthesis of Water-Soluble and Conducting Polyaniline by Growing of Poly (*N*-isopropylacrylamide) Brushes via Atom Transfer Radical Polymerization Method

Marjan Ghorbani, Homa Gheybi, Ali Akbar Entezami

Laboratory of Polymer, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

ABSTRACT: Polyaniline-*graft*-Poly(*N*-isopropylacrylamide) copolymers were synthesized by atom-transfer radical polymerization (ATRP) of *N*-isopropylacrylamide using polyaniline macro-initiators. Polyaniline-chloroacetylchloride and polyaniline-chloropropionylchloride macroinitiators were obtained by the reaction of amine nitrogens of polyaniline with chloroacetyl chloride and 2-choloropropionyl choloride, respectively. Both macroinitiators and graft copolymers were characterized by FT-IR and ¹H-NMR spectroscopy. The cyclic voltammetry (CV) and UV-Vis spectroscopy studies showed that these copolymers are electroactive. The solubility test revealed that the polyaniline-*graft*-poly (*N*-isopropylacrylamide) copolymers are water soluble or water/methanol soluble. The Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) images showed the growing of poly (*N*-isopropylacrylamide) chains on polyaniline backbone. Investigation of thermal behavior of graft copolymers by thermal gravimetry analysis (TGA) confirmed the results obtained from AFM and SEM images. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2299–2308, 2012

Key words: conducting polymers; graft copolymers; water soluble polymers; atom transfer radical polymerization (ATRP); polymer synthesis; characterization

INTRODUCTION

Polyaniline (PANI) is a conducting polymer that has received special attention due to its high stability toward air and moisture and unique electrical conductivity properties.[1] This polymer is also important in applications such as rechargeable batteries, electromagnetic shielding materials, sensors, electro optics, and light-emitting diodes.[2] PANI is poor in processability due to its insolubility in common organic solvents.[3,4] Lack of solubility for PANI may be attributed to the stiffness of its main chain because of the existence of a strongly conjugated π electron system.[5] Recently many research efforts have been devoted to enhance the solubility of PANI in common solvents. Flexible groups induce distortions in the polymer chain and the presence of polar groups increase the polarity of the polymer chain which result better solubility.[6] In general, the polymer can become more soluble in solvents such as tetrahydrofuran (THF), with the introduction of alkyl and aryl substituent.[7,8] Ring alkyl,[9] alkoxy,[10–13] and *N*-alkyl-substituted[14] PANI were reported to be soluble in organic solvents. In our previous work, it was reported that the solubility of polystyrene-*graft*-polyaniline (PS-g-PANI) copolymers in common organic solvents such as (THF) and chloroform is improved by increasing the degree of *N*-grafting, and also the samples are partially soluble in xylene.[15] While water-soluble conducting polymers of PANI are synthesized by introducing sulfonic acid groups to the polymer backbone.[16–18] Yue and Epstein[19,20] have synthesized the sulfonic acid ring-substituted PANI (SPAN) by a reaction of emeraldine base (EM) with fuming sulfuric acid, which is soluble in water only after conversion to the salt form (by undoping in basic aqueous solutions). Finally, solubility of conducting polymers has always been a matter of discussion and many reports have been published in the literature discussing of solubility of PANI.[21–23] We have recently reported several methods for synthesis of water-soluble polyaniline. For example, Nabid[24] reported an enzymatic method for the synthesis of a water-soluble conducting poly (*o*-toluidine) (POT) in the presence of sulfonated polystyrene (SPS) as template. The enzyme horseradish peroxidase was used to polymerize *o*-toluidine to form a water-soluble conducting POT/SPS complex, which exhibits moderate electrical conductivity. However these procedures are different from the method has been explained in this article. In the present work, the synthesis and characterization of water-soluble and

Correspondence to: A. A. Entezami (aaentezami@yahoo.com or aentezami@tabrizu.ac.ir).

methanol-soluble polyaniline via atom transfer-radical polymerization of N-isopropylacrylamide as a water-soluble monomer initiated by chloroacetylated and chloropropionated PANI macroinitiators in the homogeneous mild conditions is reported. Functionalized initiators, including a-haloesters and benzyl halides that contain hydroxyl, amino, ester, amide, epoxy, vinyl, allyl and cyclophospazine groups, have been used successfully to initiate ATRP.[25] Over the past decades, many polymerization strategies have been applied in the synthesis of polymer brushes, such as living ring-opening, anionic, cationic and radical polymerization. Among all of the controlled radical polymerization methods, atom transfer radical polymerization (ATRP) is one of the most commonly used ones owing to its specific features such as the use of commercially available and facility synthesize initiators and wide range of accessible monomers, as well as mild reaction conditions.[26] In summary, ATRP is an excellent method for preparation of grafted copolymers with better control over molecular architecture.[27,28]

Poly(N-isopropylacrylamide) is an interesting polymer which is water soluble at room temperature and may therefore be applied in drug delivery systems, biomedical field as a stimulus-sensitive material, cell culture substra, industry, and bioengineering.[29] It should be mentioned that the preparation of water-soluble polyaniline by the use of ATRP technique has not previously been reported in the literatures. Also only a few works have been published on ATRP starting from macroinitiator of PANI.[30] All obtained grafted copolymers were be analyzed by FT-IR, ^{1}H-NMR, UV-Vis spectroscopies, SEM, AFM, cyclic voltammetry (CV), elemental analysis (CHN), and thermal gravimetry analysis (TGA).

EXPERIMENTAL

Materials

Aniline, ammonium peroxodisulfate (APS), and copper (I) chloride were purchased from Merck. Aniline was doubly distilled under vacuum prior to polymerization. Ammonium peroxodisulfate was recrystallized at room temperature from EtOH/water; copper(I) chloride was purified by stirring in glacial acetic acid, then washing with methanol and finally drying under reduced pressure. N-isopropylacrylamide (NIPAAm) (97%) monomer, 2-chloropropionyl chloride (CPC), chloroacetyl chloride(CAC) and N, N, N′, N′, N″-penthamethyldiethylenetriamine (PMDETA) were obtained from ç-Aldrich. N-isopropylacrylamide was recrystallized from hexane. Dimethylsulfoxide and N-methyl-2-pyrrolidone (Fluka) was totally dried and then distilled under reduced pressure.

Characterization

^{1}HNMR spectra were recorded at 25°C on a Bruker 400 MHz NMR spectrometer. The Samples were dissolved in either dimethylsulfoxide-d$_6$ or D$_2$O at room temperature. Fourier transform infrared (FT-IR) spectra were recorded at room temperature using Shimadzu FTIR-8101M. The thermal behavior was studied with thermogravimetric analysis (TGA; Perkin–Elmer). Thermal decomposition was studied under a nitrogen atmosphere at a heating rate of 10°C min^{-1}. The morphology of polymers was observed by a scanning electron microscopy (SEM; LEO 14557p) and atomic force microscopy (AFM; C26-DME). The UV-Vis absorption spectra of dilute polymer solutions were recorded on a Shimadzu UV-1700 spectrometer. Cyclic voltammetry studies were carried out using a glassy carbon disk electrode with 2 mm diameter as working electrode. A platinum wire was employed as counter electrode and Ag/AgCl electrode served as the reference electrode. Voltammograms were obtained with PGSTAT 20 Autolab potentiostat from ECO Chemie (the Netherlands). The elemental composition of the material was determined by using vario-MAX CHN elementar analyzer.

Preparation of the macro-initiators

Aniline was polymerized using $(NH_4)_2S_2O_8$ (1M) in air according to the method described in the literature.[31] Typically, the interfacial reaction was performed in an aqueous/organic biphasic system. Aniline (0.1 mol, 9 mL) was dissolved in 360 mL chloroform as an organic phase. Ammoniumperoxodisulfat (0.025 mol, 5.7 g) was dissolved in 24 mL of 1M H_2SO_4. Then two solutions are carefully transferred to a beaker, generating an interface between two layers. After 24 h, the entire water phase was filled homogeneously with dark-green PANI. The precipitate was subsequently filtered, washed several times with methanol and finally a colorless filtrate was obtained. The undoped PANI was obtained by washing it with 1M NH_3/H_2O. The leucoemeraldine (LM) base was prepared by the reduction of EM with phenylhydrazine in a diethylether suspension at room temperature. For preparation of PANI-CAC macroinitiator, LM powder (0.5 g) was initially solubilized in 50 mL NMP at 25°C under argon atmosphere. Then, triethylamine (0.88 mL, 0.00293 mol), and chloroacetyl chloride (0.88 mL, 0.011mol), were slowly added dropwise to the LM solution and then the mixture was left to react at room temperature for 24 h under stirring. The mixture was poured in methanol to precipitate the polymer. The obtained polymer was washed with water and diethylether to remove the insoluble salts and unreacted chloroacetyl chloride. The polyaniline
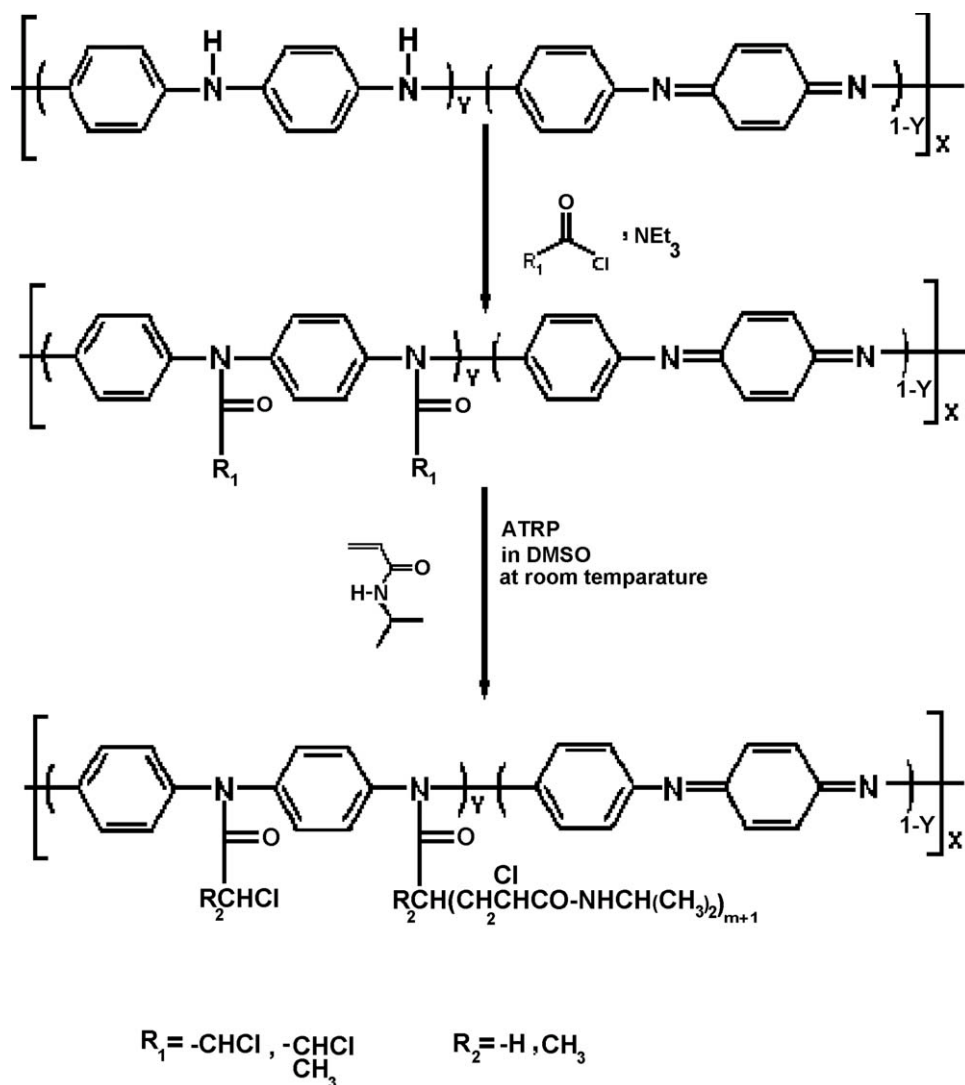
Scheme 1 Synthetic procedure of PANI-g-PNIPAAm copolymers.

macroinitiator was dried in vacuum at 50°C. PANI-CPC macroinitiator was synthesized by this method.

Growing of NIPAAm on the PANI macroinitiators

In a typical polymerization, in order to prepare (PANI-g-PNIPAAM), [NIPAAm]/ [CuCl]/ [PMEDTA] with mole ratio of 50 : 1 : 2 was used. The polymerization of NIPAAm was undertaken in DMSO to allow for solubilization of all components. First, PANI macroinitiator (0.5 g) and NIPAAm (4 g,0.035 mol) were dissolved in DMSO in two flasks separately to prepare initiator and monomer solutions, then the flasks were evacuated and refilled with argon repeatedly three times. The polymerization solution was prepared by adding the solution of NIPAAm monomer and organometallic catalyst to the macroinitiator solution. The organometallic catalyst was formed in an argon atmosphere by adding CuCl (0.07 g, 0.7 mmol)

and PMDETA (300 μL, 1.4 mmol) as ligand to 2 mL of DMSO as solvent. The mixture was then stirred for 5 min to form the CuCl/PMDETA complex. The reaction mixture was allowed to polymerize at 25°C for 72 h under stirring. For isolation and purification of the polymer, the polymerization solution was diluted with water and subjected to dialysis-bag to remove unreacted monomer and catalyst. The polymer was then collected after freeze-drying.

RESULTS AND DISCUSSION

Polyaniline is a conducting polymer that presents good stability and interesting electrochemical and optical properties. Use of polyaniline is still limited because of its poor processability, environmental incompatibility, and poor solubility in common solvents. For practical applications, it is necessary to obtain a polyaniline with improved processability

and high molecular weight. To improve melt and solution processability of polyaniline, the majority of polyaniline modifications have been made by grafting on the backbone of polyaniline. In recent years, methods of living free radical polymerization have been developed to provide a potential for grafting reactions. Apart from the general free-radical mechanism, atom transfer radical polymerization is also an interesting technique to carry out grafting. ATRP requires less stringent reaction conditions as compared to other living polymerization methods. In addition, because of its radical nature, it is a robust technique i.e., it tolerates aqueous conditions, impurities, various functional groups in monomers and can be carried out in bulk or solution.

From the practical point of view, PNIPAAm grafted polyaniline copolymers were prepared through introduction of ATRP initiating groups on the polyaniline and growing N-isopropylacrylamide on the backbone of polyaniline by ATRP method. The synthesis procedures for macroinitiators and PANI-g-PNIPAAm copolymers are presented in Scheme 1. The macroinitiators were synthesized from the reaction of amine nitrogenes of polyaniline with chloroacetyl choloride or 2-chloropropionyl chloride in the presence of triethylamine.

The functionalization was studied by ^{1}HNMR and FT-IR spetroscopies. Figure 1 illustrates the FT-IR spectra for leucoemeraldine base form of PANI (a), PANI-CAC (b), PANI-CPC (c), and PANI-g-PNIPAAm copolymers resulted from PANI-CAC (d), and PANI-CPC (e), respectively. For leucoemeraldine base, the characteristic bands were observed at 1458–1490 cm^{-1} due to benzenoid ring stretching frequency, and a small band at 1576–1586 cm^{-1} attributed to residual quinoid ring stretching mode [Fig. 1(a)]. The FT-IR spectrum of PANI-CAC was characterized by specific carbonyl band at 1680 cm^{-1} [Fig. 1(b)], confirming the immobilization of initiator on the polyaniline. PANI-CAC was prepared by a amid formation reaction between -NH- groups of PANI and CAC. Finally, the addition of N-isopropylacrylamide (NIPAAm) to the solution of N-chloroacetylated polyaniline as ATRP initiator started the ATRP of NIPAAm in the presence of copper chloride/PMDETA as a catalyst system. The formation of the obtained graft copolymer was confirmed by FT-IR and ^{1}HNMR spectroscopies. The reaction between PANI and CAC dissolved in NMP occurred in a homogeneous system which would resulting in a rich amid formation efficiency. Figure 1(d) day shows a typical FT-IR spectrum of PANI-g-PNIPAAm (obtained from PANI-CAC macroinitiator) conjugated with the characteristic bands of the related systems. The absorption peak at 3400 cm^{-1} in Figure 1(d) can be attributed to the stretch of hydrogen bonded N—H group. The anti symmetric
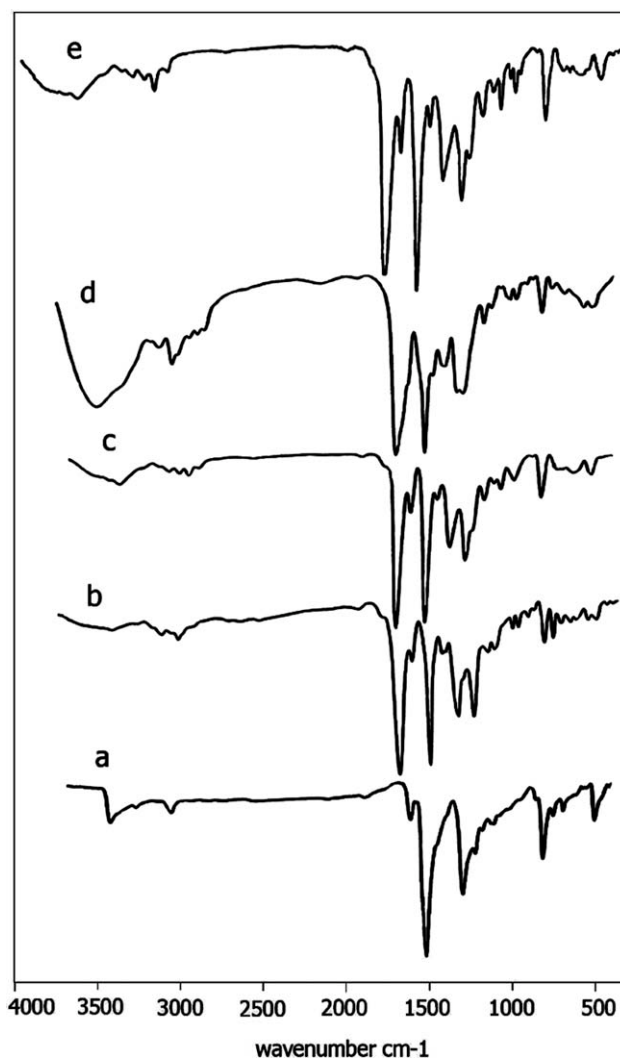

Figure 1 FT-IR spectra of the leucoemeraldine, macroinitiators and graft copolymers (a) leucoemeraldine base, (b) PANI-CAC macroinitiator, (c) PANI-CPC macroinitiator, (d) PANI-g-PNIPAAm copolymer resulted from PANI-CAC macroinitiator, (e) PANI-g-PNIPAAm copolymer resulted from PANI-CPC macroinitiator.

stretching vibration of CH_3 group of N-isopropylacrylamide occurs at 2970 cm^{-1} and the anti symmetric bending deformation of CH_3 occurs at 1460 cm^{-1}. The band at 1395 cm^{-1} may be interpreted considering the methyl groups in the isopropyl functionality.

Supporting evidence for the structural elucidation was revealed by ^{1}HNMR analysis (Fig. 2). The ^{1}HNMR spectra of the PANI-CAC [Fig. 2(a)] and PANI-CPC [Fig. 2(b)] macroinitiators revealed the presence of signals characteristic of PANI at 6.30–7.32 ppm (benzenoid and quinoid protons), 4.3 ppm (CH_2 of CAC), 4.5 ppm (CH of CPC), and 1.7 ppm (CH_3 of CPC). Figure 2(c) shows the ^{1}HNMR spectrum of the PANI-g-PNIPAAm. According to this Figure, the appearance of a strong peak at about 1.0 ppm can be attributed to the methyl protons of isopropyl group related to the PNIPAAm side chains.
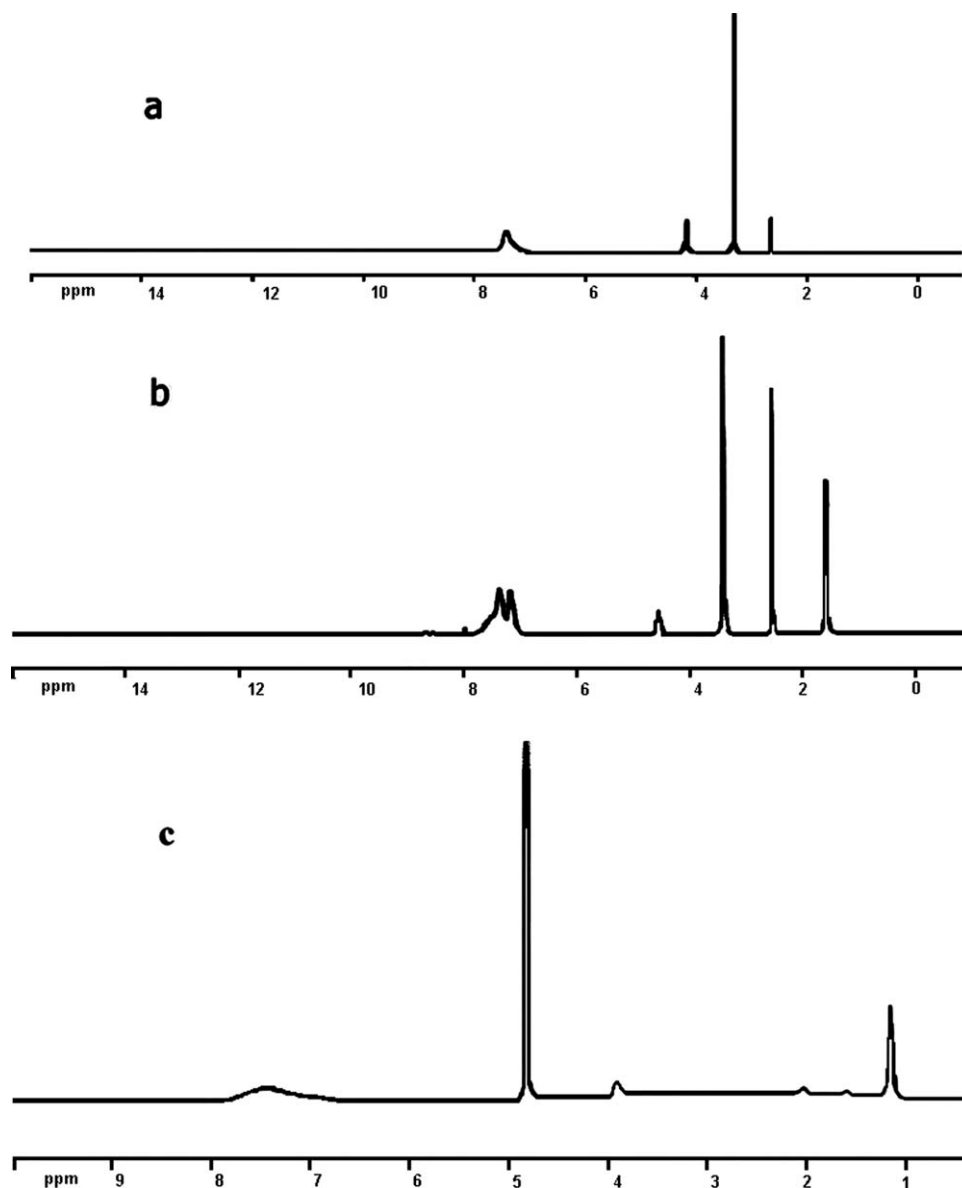
Figure 2 ¹H NMR spectra of macroinitiators in (DMSO-d₆) and ¹H NMR spectrum of PANI-g-PNIPAAm copolymer in D₂O (a) PANI-CAC macroinitiator, (b) PANI-CPC macroinitiator, (c) PANI-g-PNIPAAm copolymer obtained from PANI-CAC macroinitiator.

In addition, the resonances at about 1.5, 2, and 4 ppm are assigned to CH_2, CH and CH—N units in the PNIPAAm chains, respectively. Furthermore, the aromatic and N—H protons are detected at 6.8–7.4 ppm. Overall, the results indicate a successfully formation of PANI-CAC and PANI-CPC macroinitiators and PANI-g-PNIPAAm.

Solubility

Normally, when a pinch of PANI doped with mineral or organic acid is added to highly polar solvents such as dimethyl sulfoxide (DMSO) or N-methyl-2-pyrrolidone (NMP), part of the polymer material is dissolved but a residual is always present in the mixture. In other words, slight solubility is also observed for PANI in NMP and DMSO. In this article when it is quoted "completely soluble," it means that the PANI is dissolved in the solvent without leaving any solid residue. Because of growing of N-isopropylacrylamide as water-soluble monomer to the polyaniline backbone, solubility of PANI-g-PNIPAAm samples are increased in the polar solvents such as water, EtOH, and MeOH. PANI-g-PNIPAAm produced in this way is completely soluble in water, a 1 : 1 mixture of water/EtOH and water/MeOH. The graft copolymer with PANI-CAC macroinitiator can be dissolved 150 g L^{-1} in water or MeOH, and 50 g L^{-1} in EtOH. The other copolymer with PANI-CPC macroinitiator can be dissolved 100

g L^{-1} in EtOH or the mixture of 50% V/V H$_2$O/MeOH and 50 g L^{-1} in MeOH or the mixture of 50% V/V H$_2$O/MeOH.(Table I).

Topography investigation by AFM analysis

The surface topography of graft copolymers was studied by AFM. In this section, the chains of PNIPAAm grafted on the surface probed by AFM are considered. Figure 3 shows the AFM topography images of the PANI-CAC and PANI-CPC macroinitiators [Fig. 3(a,b), respectively], PANI-g-PNIPAAm synthesized by PANI-CAC macroinitiator [Fig. 3(c)], and PANI-g-PNIPAm synthesized by PANI-CPC macroinitiator [Fig. 3(d)]. According to these Figures, the surfaces of macroinitiators are relatively smooth, whereas the surfaces were dramatically changed and the surfaces roughness was increased after grafting reaction. It clearly shows the growth of Poly (N-isopropylacrylamide) (PNIPAAm) side chains on PANI backbone. Comparison of Figure 3(c,d) reveals that the surface roughness has been increased for the graft copolymer synthesized by PANI-CAC macroinitiator. These results have good agreement with solubility tests because PANI-g-PNIPAAm synthesized with PANI-CAC macroinitiator is completely soluble in water, while PANI-g-PNIPAAm synthesized with PANI-CPC macroinitiator (low graft density), is slightly soluble in water and completely soluble in methanol/water solution (50% V/V). In other word, the increasing of graft density improves the solubility of graft copolymer in water.

Morphological analysis

As shown in Figure 4, SEM images reveal some variations in the morphological structure of macroinitiators and PANI-g-PNIPAAm sample. Macroinitiators exhibit a spong-like structure with small paticle size [Fig. 4(a)(PANI-CAC) and 4(b)(PANI-CPC)], whereas in grafted sample, prepared by PANI-CPC macroinitiator, we can see the globular structure on the polyaniline backbone by the growing of PNIPAAm chains [Fig. 4(c)]. As shown in Figure 4(d), the surface morphology of PANI-g-PNIPAAm prepared by PANI-CAC macroinitiator is smoother, illustrating larger segments and more compressed structure for growing chains of PNIPAAm.

UV-Vis analysis

Counducting PANI shows three absorbance bands in its UV-Vis spectrum with maxima located at 350, 420, and 800–880 nm and they are related to $\pi \rightarrow \pi^*$, polaron π^*, and π-polaron electronic transitions, respectively. On the other hand, the UV-Vis spectrum of undoped emeraldine-base PANI shows two

TABLE I
Solubilities of the Macroinitiators and PANI-g-PNIPAAm Samples in Water, Methanol, Ethanol, and Polar Organic Solvents

	NMP	DMSO	DMF	THF	MeOH	H2O	CHCl3	EtOH	25/75 H2O/MeOH	50/50 H2O/MeOH	50/50 H20/EtOH	25/75 H20/EtOH
PANI	+	+	+	+	−	−	+	−	−	−	−	−
PANI-CAC	++	++	++	+	−	−	+	−	−	−	−	−
PANI-CPC	++	++	++	+	−	−	+	−	−	−	−	−
PANI-CAC-g-PNIPAAM	++	++	++	−	++	++	−	++	++	++	++	++
PANI-CPC-g-PNIPAAM	++	++	++	−	++	+	−	++	++	++	++	++

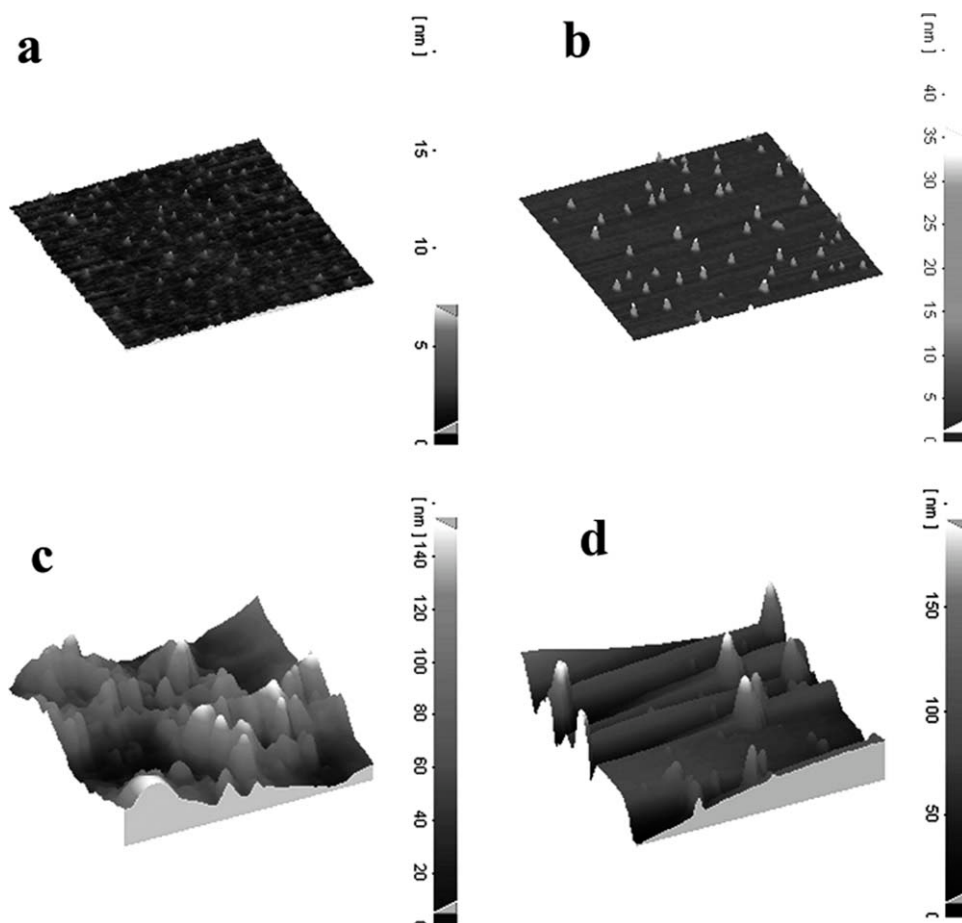++, Soluble; +, partially soluble; −, insoluble.

Figure 3 AFM topography images of macroinitiators and PANI-g-PNIPAAm copolymers (a) PANI-CAC macroinitiator, (b) PANI-CPC macroinitiator, (c) PANI-g-PNIPAAm synthesized with PANI-CAC macroinitiator, (d) PANI-g-PNIPAAm synthesized with PANI-CPC macroinitiator.

bands: one with a maximum at 320–330 nm and second band with a maximum at 600–650nm. Ito et al. have prepared polyaniline that can be dissolved up to 88 g L^{-1} in water.[32] They adapted a difficult procedure to sulfonate the emeraldine base by which the solubility of the resulting material depends on the S/N ratio. However, the conductivity of the PANI is low in the range of 0.02 to 1×10^{-5} S cm^{-1}. According to the literature, increasing solubility of polyanilie in water, leads to a decrease in its conductivity. Figure 5(a) shows the absorption spectrum of PANI-g-PNIPAAm copolymer after dissolving the polymer in aqueouse solution by dodecylbenzen solfunicacid. The acidity of solution was regulated in pH = 1 by addition of DBSA. The bands at 1020 nm are related to polaron transition (bezenoid form) and the band at about 620 is related to bipolaron transition(quinoid form). The UV-Vis spectrum of methanol-solube copolymer is the same as water-soluble copolymer [Fig. 5(b)]. These results show that PANI-g-PNIPAAm samples are electroactive copolymers. As it can be seen, the position of polaron band at 1000–1100 appears at lower energy

for PANI-g-PNIPAAm in comparison with unsubstitution PANI. Thus, the reduction of the extent of conjugation with N-grafting on the polyaniline may be a reason for decreasing the conductivity of the copolymer decreases through N-grafting reaction on the backbone of polyaniline. The steric effect of PNIPAAm chains substituent might be increased due to the torsional angle between adjacent phenyl rings thus disturbing the overlapping of orbitals between the phenyl π-electrons and the nitrogen lone pairs, and resulting in lowering the degree of conjugation. The red shift can be expected to decrease with increasing the degree of N-grafting in polymer backbone.

Cyclic voltammetry analysis

Cyclic voltammetry was employed to study the electrochemical behavior of polymers. Cyclic voltammetry curves of PNIPAAm-substituted PANI samples recorded at different scan rates between -0.5 and 1 v for PANI-g-PNIPAAm resulted from PANI-CPC and -0.2 to 1 v for PANI-g-PNIPAAm resulted from
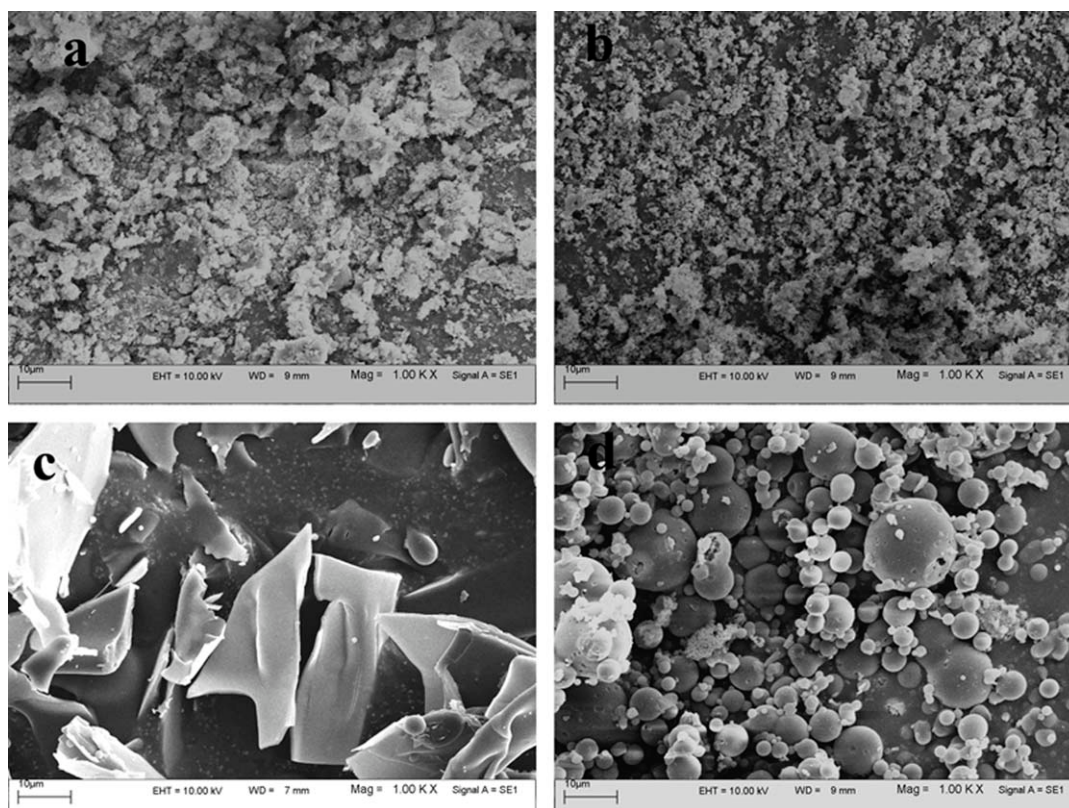
Figure 4 SEM of macroinitiators and PANI-g-PNIPAAm samples (a) PANI-CAC macroinitiator, (b) PANI-CPC macroinitiator, (c) PANI-g-PNIPAAm copolymer obtained from PANI-CAC macroinitiator, (d) PANI-g-PNIPAAm copolymer obtained from PANI-CPC macroinitiator.

PANI-CAC versus SCE in dodecylbenzen sulfonic acid show they are conducting polymers. As shown in Figure 6(a,b), cyclic voltammograms of PANI-g-PNIPAAm copolymers exhibit that only one set of

Figure 5 Absorption spectra of PANI-g-PNIPAAm copolymers (a) PANI-g-PNIPAAm synthesized with PANI-CAC macroinitiator, (b) PANI-g-PNIPAAm synthesized with PANI-CPC macroinitiator.

redox peaks is observed at $E_{1/2} = -0.1$V and $E_{1/2} = -0.25$V for water soluble polyaniline [Fig. 6(a)] and methanol soluble polyaniline [Fig. 6(b)], respectively. The absence of two anodic peaks probably is due to the resistance of the PANI-g-PNIPAAm copolymers to oxidation to the other state.
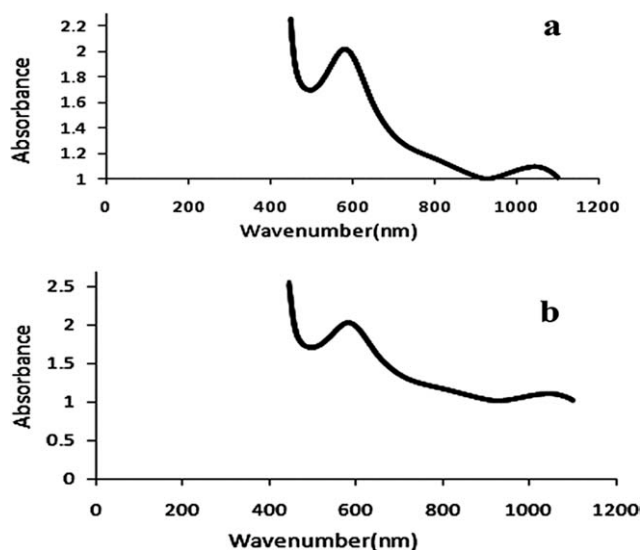
Thermogravimetric analysis

Another interesting behavior of the copolymers became apparent in the thermal degradation experiments. Thermograms of PANI-g-PNIPAAm copolymers are shown in Figure 7(a) obtained from (PANI-CAC) and 7(b) from (PANI-CPC). The weight loss observed below 100°C for the samples corresponds to the loss of water molecules/moisture, which is due to the hydrophilic nature of the copolymers. As seen from the TGA curves, the rate of weight loss of PANI-g-PNIPAAm copolymer resulted from PANI-CPC is much fast, while the rate of weight loss of PANI-g-PNIPAAm copolymer resulted from PANI-CAC is slower. A weight loss of $\sim 17\%$ in the temperature range between 200 and 350°C was observed for the PANI-g-PNIPAAm copolymer resulted from PANI-CPC macroinitiator, whereas for PANI-g-PNIPAAm copolymer obtained from PANI-CAC, a loss of $\sim 40\%$ mass was observed at the 170–400°C. This
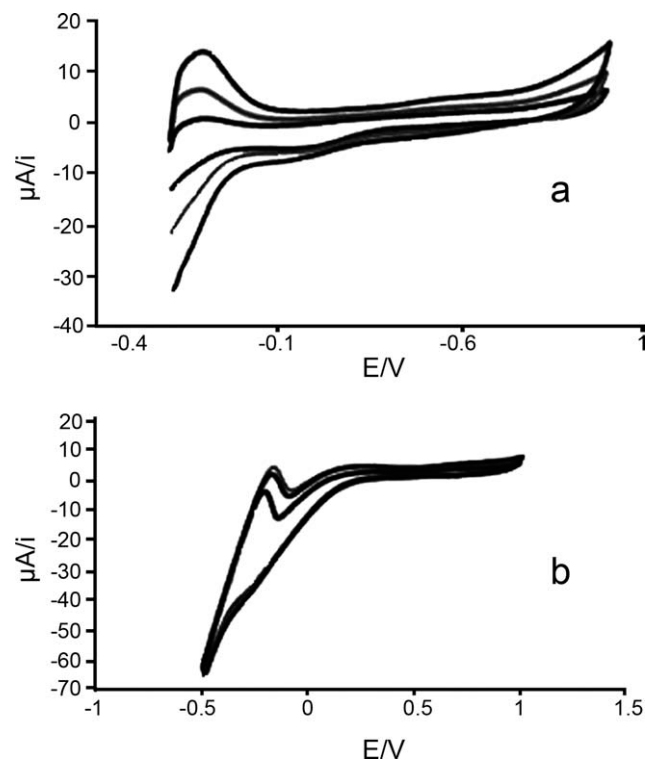
Figure 6 Cyclic voltammograms of PANI-g-PNIPAAm samples (a) water-soluble polyaniline synthesized with PANI-CAC macroinitiator, (b) Methanol-soluble polyaniline synthesized with PANI-CPC macroinitiator.

Figure 7 Thermograms of PANI-g-PNIPAAm copolymers (a) PANI-g-PNIPAAm obtained from(PANI-CAC), (b) PANI-g-PNIPAAm obtained from(PANI-CPC).

phenomena indicates that the high graft density in the PANI-g-PNIPAAm copolymer synthesized via PANI-CAC retard the thermal decomposition of this copolymer more than that of the copolymer prepared from PANI-CPC macroinitiator. The weight loss was recorded for the polymer chain of PANI up to 400°C. The obtained result of thermal gravimetry confirmed AFM and solubility tests.

Elemental analysis

The elemental analysis was carried out to obtain the chemical composition of the macroinitiators with various elements such as C, H, and N in the polymer matrix. The experimental and calculated compositions obtained from elemental analysis of the PANI
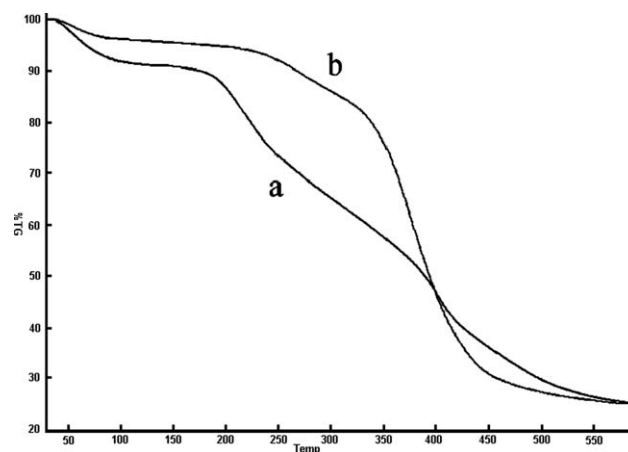
and macroinitiators are given in Table II. The measured compositions agree very well with the calculated values. These results also support that macroinitiators are successfully synthesized. As shown in Table II, because of increasing the incorporation of chloroacetyl chloride to the polyaniline backbone, the grafting percentage of PNIPAAm is higher for PANI-CAC macroinitiator in comparison with PANI-CPC macroinitiator confirming results obtained from AFM and solubility test.

CONCLUSIONS

Polyaniline was polymerized according to the interfacial method. Then the leucoemeraldine (LM) base was prepared by the reduction of emeraldine state. The reaction of polyaniline in the leucoemeraldine state with Chloroacetyl chloride and 2-chloropropionyl chloride was investigated for the synthesis of macroinitiators. The ^{1}H NMR and FT-IR spectroscopies results indicated that the macroinitiators could be successively prepared. Water-soluble copolymers with intermediate conductivity were synthesized from polyaniline macroinitiators and growing NIPAAm by ATRP method. Investigation of AFM and SEM images showed the growing of

TABLE II
Composition of the Macroinitiators and PANI-g-PNIPAAm

Sample	Experimental (%)			Calculated (%)			Percentage of graft
	H	N	C	H	N	C	
PANI	5	15.4	79	4.9	79.5	15.4	–
PANI-CAC	4.5	9	58.6	3.72	8.88	58.9	87%
PANI-CAC-g-NIPAAm	6.5	12.3	59.8	–	–	–	–
PANI-CPC	5.3	10	61.3	4.9	8.57	61.5	49%
PANI-CPC-g-NIPAAm	8.2	11.7	63.2	–	–	–	–

PNIPAAm chains on the backbone of polyaniline. The PANI-g-PNIPAAm copolymers exhibited solubility in water, water/methanol, and enhanced solubility in highly polar solvents such as NMP and DMSO. The properties of resulted copolymers are attributed to the degree of *N*-grafting. Therefore, by using the NIPAAm as a water-soluble monomer the problem of solubility of PANI can be solved and a conducting form of polymer is obtained. The conductivity and electroactivity of the obtained copolymers were studied by cyclic voltammetry and UV-Vis spectroscopy, respectively. All results obtained from the percentage of growing NIPAAm confirmed AFM, TGA and elemental analysis results.

References

1. Gustafsson, G.; Cao, Y.; Trace, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. Nature 1992, 357, 477.
2. Jiaxing, H. Pure Appl Chem 2006, 78, 15.
3. Morrin, A.; Wilbeer, F.; Ngamna, O.; Moulton, S. E.; Killard, A. J.; Wallace, G. G.; Smyth, M. R. Electro Chem Commun 2005, 7, 317.
4. Srinivasan, P.; Amalraj, J. Prog Polym Sci 2008, 33, 732.
5. Nabid, M. R.; Sadeghi, R.; Entezami, A. A. J Appl Polym Sci 2007, 103, 3724.
6. Tiwari, A.; Singh, V. Express Polym Lett 2007, 1, 308.
7. John, A.; Palaniappan, S.; Djurado, D.; Pron, A. J Polym Sci Part: A Polym Chem 2008, 46, 1051.
8. Mikhael, G. M.; Padias, A. B.; Hall, H. K. J. R. J Polym Sci Part: A Polym Chem 1996, 35, 1673.
9. Arsalani, N.; Khavei, M.; Entezami, A. A. Iranian Polym J 2003, 12, 237.
10. Feng, W.; Fujii, A.; Lee, S.; Wu, H. C.; Yoshino, K. Synth Met 2001, 121, 1595.
11. Macinnes, J. D.; Funt, B. L. Synth Met 1998, 25, 235.
12. Dhawan, S. K.; Trivedi, D. C. Synth Met 1993, 60, 67.
13. Storrier, G. D.; Colbran, S. B.; Hibbert, D. B. Synth Met 1994, 62, 179.
14. Nabid, M. R.; Entezami, A. A. Polym Adv Technol 2005, 16, 305.
15. Gheybi, H.; Abbasian, M.; Moghaddam, P. N.; Entezami, A. A. J Appl Polym Sci 2007, 106, 3495.
16. Thiyagarajan, S. M.; Kumer, L. A.; Cholli, J. J. Am Chem Soc 2003, 125, 11502.
17. Kulkarni, V. M.; Viswanath, K. A. Eur Polym Mater 2004, 40, 379.
18. Lin, H. K.; Chen, S. A. Maromolecules 2000, 33, 8117.
19. Yue, J.; Wang, Z. H.; Cromack, R. K.; Epstein, A. J.; MacDiarmid, A. G. J Am Chem Soc 1991, 113, 2665.
20. Kohlman, R. S.; Zibold, A.; Tanner, D. B.; Ihas, G. G.; Inshigur, T.; Min, Y. G.; MacDiarmid, A. G.; Epstein, A. J Phys Rev Lett 1997, 78, 3915.
21. Laska, J.; Widlarz, J. Synth Met 2003, 135, 261.
22. Athawale, A. A.; Kulkarni, M. V.; Chabukswar, V. Mater Chem Phys 2002, 73, 106.
23. Yin, W.; Ruckenstein, E. Synth Met 2000, 108, 39.
24. Nabid, M. R.; Entezami, A. A. Eur Polym Mater 2003, 39, 1169.
25. Alli, A.; Hazer, B. H. J Biol Chem 2009, 37, 23.
26. Natanya, M. L.; Katja, J.; Soren, H. Eur Polym Mater 2007, 43, 255.
27. Matyjaszewski, K.; Gaynor, G.; Kulfan, A.; Podwika, M. Macromolecules 1997, 30, 5192.
28. Matyjaszewski, K.; Gaynor, G. Macromolecules 1997, 30, 7034.
29. Alli, A.; Hazer, B. Eur Polym Mater 2008, 44, 1701.
30. Peng, L.; Zhixing, S. U. Polym Bull 2005, 55, 411.
31. Jiaxing, H.; Richard, B. K. J Am Chem Soc 2004, 126, 851.
32. Ito, S.; Murata, K.; Teshima, S.; Aizawa, R.; Asako, Y.; Takahashi, K.; Hoffman, B. M. Synth Met 1998, 96, 161.