

# Improvement of Polyaniline Processability by Graft Reaction of Polyaniline on Poly(glycidyl methacrylate-*alt*-maleic anhydride) Copolymer: Synthesis and Characterization

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**Abstract**—The present research describes a method of the synthesis of polyaniline grafted on poly(glycidyl methacrylate-*alt*-maleic anhydride) copolymer in order to improve the polyaniline processability. Polyaniline was prepared by a chemical synthesis under ultrasonic treatment. Then it was chemically grafted onto poly(glycidyl methacrylate-*alt*-maleic anhydride) copolymer to prepare a conductive comb copolymer. The grafted copolymer was identified by the FTIR and UV-visible spectroscopy. The analysis of the solubility and electrochemical properties showed an improved performance of grafted copolymer in comparison with pure polyaniline.

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## INTRODUCTION

Polyaniline (PANI) was first known in 1835 as ‘aniline black’, and it is a black powdery polymeric substance that is obtained from the anodic oxidation of aniline and accompanied a color change upon switching potential, which it latterly was called as an electrochromism [1]. It can be chemically oxidized by ammonium peroxydisulfate (APS) to obtain green powder of the polyaniline with a conductivity of as high as 3 S/cm [2–6]. PANI can exist in a base form and in various protonated H<sup>+</sup> salt forms. Only the protonated salt form of emeraldine is conductive. Polyaniline is one of the typical conducting polymers. It attracts a great attention due to its low cost, environmental stability, easy synthesis, electroactivity, and physical properties, which are controlled by both oxidation and protonation state [7–11]. PANI can be reversibly transformed from conduction to insulation by using acid-base reactions [12–17]. PANI generally has a highly developed p-conjugated system between the quinoid imine and the benzenoid amine structures. This results in such drawbacks as insolubility of PANI in almost all organic solvents and inability to melt; so it has a poor processability. Considerable progress has been achieved in the last few years in the processability of conducting polymers. More recently, conducting forms of polyaniline can be processed by using the acidic dopant such as dodecylbenzene sulfonic acid or camphorsulfonic

acid in a polar or non-polar solvent [18] or by doping polyaniline emeraldine base with extended organic alkyls of sulphonic acids [19–24]. Numerous attempts have been also undertaken to prepare polyaniline by using colloidal polymer surfactants to provide its processability [25–27].

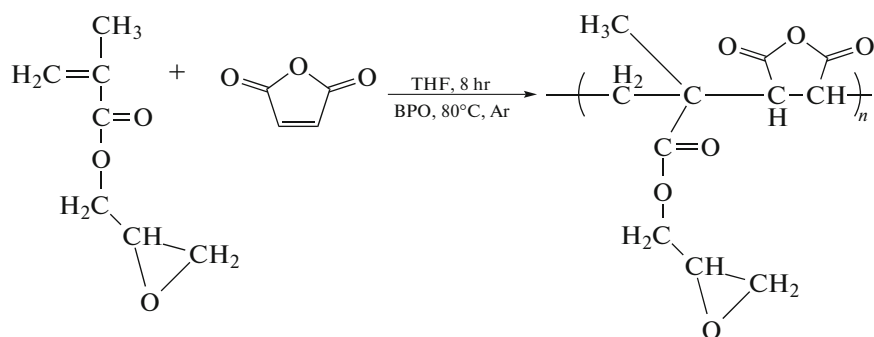
Comb-like polymers are a type of grafted polymers, in which the grafting degree, the length of side groups, and the rigid state of polymer main chains facilitates the preparation of multifunctional and structuralized comb-like polymers [28–30]. Various approaches that have been reported include grafting of polymers to a non-conducting polymer, direct polymerization of intractable polymers into the final desired shape, making a composite of blend of conducting polymers and copolymerization and so on.

The aim of our work is the synthesis of PANI-g-poly(glycidyl methacrylate-*alt*-maleic anhydride) by a grafting reaction of polyaniline onto poly(glycidyl methacrylate-*alt*-maleic anhydride).

## EXPERIMENTAL

### Materials and Chemicals

All chemicals were used as received without further purification except the aniline. Aniline was purified by distillation under reduced pressure to remove impurities prior to use. Glycidyl methacrylate (GMA),



Scheme 1.

maleic anhydride (MAN) (>99%), ammonium peroxydisulfate, benzoyl peroxide (BPO) (>75%), and tetrahydrofuran (THF) (>99%) were supplied by Merck (Germany).

#### *PANI Synthesis by the Ultrasonic Method*

The aniline chemical oxidative polymerization is an effective approach to produce polyaniline [30]. Polyaniline in the emeraldine salt was synthesized via chemical oxidative polymerization in the presence of ammonium peroxydisulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) and dilute hydrogen chloride under ultrasonic treatment. A quantity of aqueous solution of hydrochloric acid 1 M (40 mL) was poured into the three-necked round-bottom flask equipped with ultrasonic probe, then 1 mL (0.011 mol) of the aniline was added to the solution and dispersed by an ultrasonic disperser. The solution was kept at 0–4°C under argon atmosphere. Then 3.12 g of ammonium peroxydisulfate was dissolved in 20 mL of water and slowly dropped into the aniline salt solution under ultrasonic treatment using a power of 100 W operating at 40 kHz for 1 h. The reaction continued in the ultrasonic disperser at 0–4°C for 4 h. The dark green polyaniline dense precipitate was subsequently collected by gravity filtration and washed with water and methanol for several times to remove the excess of reducing agent. The washed product was immersed in ammonia solution (5 wt %) and stirred for about 3 h to dedopping of the product. The residue was collected by filtration, followed by final washing with excess distilled water, and dried at 40°C in a vacuum dryer.

#### *Preparation of Poly(glycidyl methacrylate-*alt*-maleic anhydride)*

A round-bottom flask equipped with a stirrer and reflux condenser was charged with appropriate quantities of GMA, MAN, THF, and BPO (0.1 mol % based on total monomer). Agitation of the mixture was begun and the system was purged by bubbling argon for 20 min. The reaction mixture was then heated to 80°C for 8 h with stirring. The slurry was cooled down

to room temperature and the reaction mixture was poured into an excess of *n*-hexane to precipitate the copolymer. The copolymer was purified by washing with *n*-hexane several times and filtration. Then, the obtained white-cream powder was dried in a vacuum oven at a temperature of approx. 40°C [31]. The process which led to the poly(glycidyl methacrylate-*alt*-maleic anhydride) PGMA-MAN copolymer is summarized in Scheme 1.

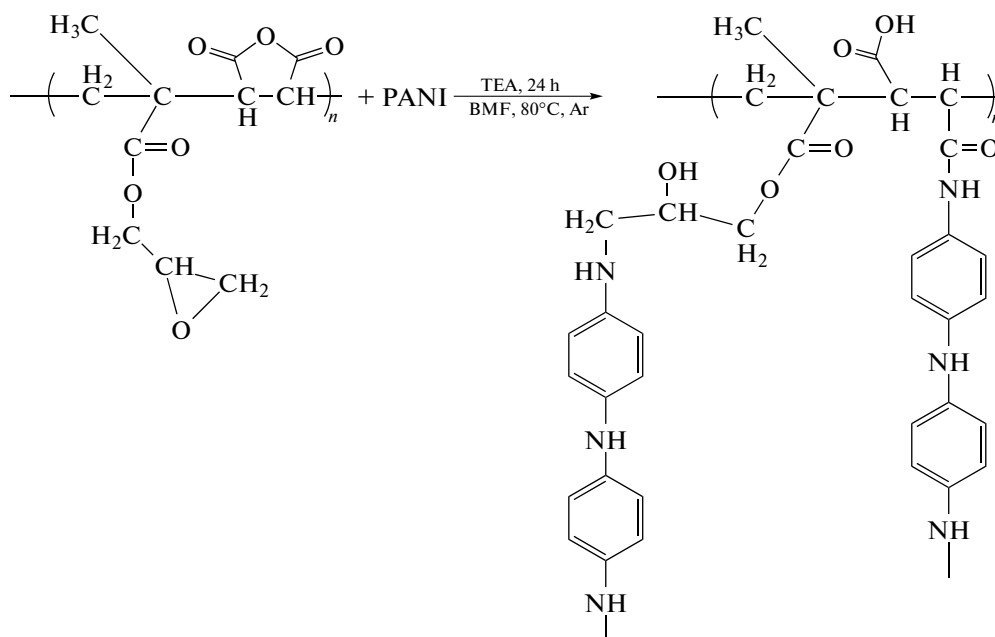
#### *Preparation of Grafted Polyaniline PANI-g-PGMA-MAN*

A 100 mL round bottom flask containing 40 mL of DMF and 1.00 g (4.42 mmol) of the PGMA-MAN was equipped with a mechanical stirrer under argon atmosphere. Then, 0.44 g triethylamine (4.42 mmol) was added and stirred at room temperature until complete dissolution followed by the addition of 2 g of undoped PANI in emeraldine base. The reaction mixture was continuously agitated for 24 h at 80°C under inert atmosphere. The product was cooled down to room temperature and precipitated into excess diethylether. The precipitate was collected by filtration and thoroughly washed with distilled water and methanol. The obtained PANI-g-PGMA-MAN was dried at 40°C for 24 h.

For preparation of PANI-g-PGMA-MAN with different wt/wt ratio of the PANI to the PGMA-MAN, similar procedure was used except ratio of the materials in feed of graft reaction (PANI : PGMA-MAN = 0.5 : 1 and 1 : 1 wt/wt).

#### *Characterization*

Scanning electron microscope a Netherlands XL30 Philips SEM was employed to study the type of surface morphology of the polymer.  $^1\text{H}$  NMR spectrum was measured on a Bruker 400 MHz NMR spectrometer using deuterated DMSO- $d_6$  as solvent. A Fourier transform infrared spectrometer (FT-IR), Nexus-670, Thermo Nicolet (USA) was used in spectral measurements of the polymer and graft copolymer. The



Scheme 2.

UV–Vis spectra were recorded with Agilent 8453 spectrometer. Electrochemical polymerization was conducted using digital potentiostat (Shanghai Chenhua, Shanghai). Cyclic voltammetry was performed using a conventional three electrode system in 0.1 M phosphate buffer solution (PBS) where a platinum wire was used as the auxiliary electrode and saturated calomel (SCE) as the reference electrode. The working electrode was prepared by solution casting of 50 mL of nanomaterial/DMF dispersion (1 mg/mL) on graft plates and dried.

## RESULTS AND DISCUSSION

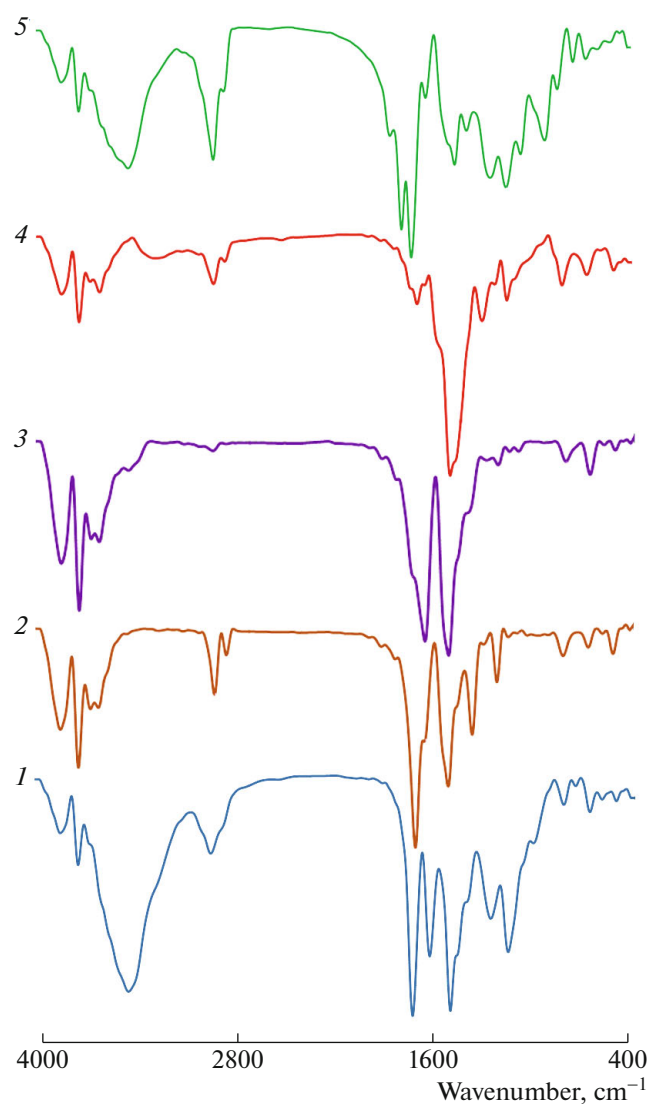
One of the most widely used methods to overcome the poor processability of PANI is its chemical modification. In this work this idea was developed by post modification of PANI via grafting the dedoped PANI on poly(glycidyl methacrylate-*alt*-maleic anhydride) with a good processability nature. The FTIR spectra and solubility testes show that the method runs successfully however, the presence of unreacted PANI in final product is possible. We have separated insoluble part of the final product using DMSO, which can dissolve the main grafted product. The yield of the soluble fraction was 67.64%. The grafting reaction is shown in Scheme 2.

Figure 1 shows the FTIR spectra of the pure PANI, PGMA-MAN, and PANI-*g*-PGMA-MAN with various weight ratios of PANI to PGA-MAN. The FTIR spectrum of PANI-*g*-PGMA-MAN (0.5 : 1 wt/wt) (Fig. 1, curve 1) shows a wide absorption band of the N–H appearing at 3395  $\text{cm}^{-1}$ . A sharp peak at the

3027  $\text{cm}^{-1}$  with a shoulder at 2943  $\text{cm}^{-1}$  can be assigned to the stretching vibration of the aliphatic and the aromatic C–H. Two absorption bands at 1732 and 1633  $\text{cm}^{-1}$  correspond to the ester or acidic and amidic carbonyl groups. The appearance of the latter band indicates that polyaniline was chemically grafted onto PGMA-MAN. Moreover, the bands at 1504 and 1462  $\text{cm}^{-1}$  correspond to the stretching vibration of the quinoid and benzenoid rings.

FTIR spectra of PANI-*g*-PGMA-MAN with a weight ratio of the PANI to PGMA-MAN with 1 : 1 and 2 : 1 are shown on Fig. 1 (curves 2 and 3). As is seen, increasing of PANI in the feed leads to an increase in the intensity of the amidic carbonyl groups. As a result, the carbonyl of amid shifts toward a lower wavenumber (1658  $\text{cm}^{-1}$ ) and ester and acidic carbonyl groups shift to a higher wavenumber (1714  $\text{cm}^{-1}$ ), so they are nearly overlapped with each other. For a better comparison, the FTIR spectra of the PANI (Fig. 1, curve 4) and the PGMA-MAN (Fig. 1, curve 5) are depicted. The most important bands of PANI are observed at 1502 and 1463  $\text{cm}^{-1}$  corresponding to the stretching vibration of the quinoid and benzenoid rings, while the bands at 1149 and 1315  $\text{cm}^{-1}$  are due to the C–N and C=N stretching modes. The bands at 1730, 1786, and 1863  $\text{cm}^{-1}$  are characteristic for maleic anhydride carbonyl groups and ester carbonyl groups of PGMA-MAN.

Figure 2 shows the  $^1\text{H}$  NMR spectrum of the PANI-*g*-PGMA-MAN with 1 : 1 wt/wt ratio of PANI to PGA-MAN in DMSO- $d_6$ . Due to the various repeating groups in the final grafted copolymer, the variety of protons in spectra is high. So, we referred to



**Fig. 1.** (Color online) The FTIR spectra of the PANI-g-PGMA-MAN with weight ratio (1) 0.5 : 1, (2) 1 : 1, (3) 2 : 1, (4) the pure PANI, and (5) the PGMA-MAN.

only pick area in the spectrum. Polyaniline aromatic protons appear from 7.01 to 7.72 ppm, the N–H protons of the polyaniline repeated groups appear at

7.94 ppm. Also the protons of the PGMA-MAN appear in the aliphatic area at about 0.841–4.01 ppm.

A granular morphology of the graft copolymer by SEM (Fig. 3) was observed for samples prepared by grafting the PANI onto the PGMA-MAN with 1 : 1 and 2 : 1 wt/wt in feed of graft reaction. This morphology confirms a uniform compact globular structure. Also by increasing the PANI ratio in graft copolymer, the size of granules becomes smaller and the surface of copolymer becomes smoother.

Figure 4 shows the cyclic voltammetry (CV) of PANI-g-PGMA-MAN with different ratios of the PANI to the PGMA-MAN in feed of graft copolymerization. The study of the CV shows that by increasing the PANI content, the current flow increases and also the peak tightens. It seems that the appearance of the peaks can be correlated to an increase in the conductivity by increasing of the PANI, and an increase in the number of residual spins in the polymer upon potential cycling.

The UV-vis absorption spectra of the PANI-g-PGMA-MAN are presented in Fig. 5. The samples were examined immediately after preparation with specified concentration of the *N,N*-dimethylacetamide. The UV-Vis spectrum shows two characteristic absorption peaks assigning to the  $\pi$ – $\pi^*$  electron transition within the benzenoid segments at 280 nm. Moreover, the absorption peak at around 360 nm is attributed to the polaron formation and polaron to  $\pi^*$  transition. After protonation, a red shift of the absorption peak at 650 nm corresponding to nonconducting PANI to 800 nm is observed, and it is attributed to  $n$ – $\pi^*$  transition of quinoid moieties to benzenoid species. The spectra reveal the same ultraviolet absorption which is observed in the mentioned areas for other ratios. By decreasing the PGMA-MAN content, the induced bands remain the same. Furthermore, the color conversion of the solution in the acidic and basic media confirms the grafting reaction.

One of the criterions for showing the improvement in processability is the solubility test. For this purpose, the synthesized grafted copolymers were tested for their solubility in different common solvents. Table 1 shows the results of the solubility test of the grafted

**Table 1.** Solubility of grafted copolymers in various solvents

PGMA-MAN : PANI	NMP	DMSO	THF	DMF	DMA	Xylene	Chloroform	Water
0 : 1	+	–	–	–	–	+	+	–
1 : 0.5	++	+++	–	++	+++	–	+	–
1 : 1	+++	+++	+	+++	+++	–	+	–
1 : 2	+++	+++	+	+++	+++	+	+	–

The solubility was determined using 0.5 g of sample in 100 mL of the solvent. Soluble at room temperature (+++), soluble on heating at 60°C, partly soluble on heating at 60°C, insoluble on heating at 60°C (–).

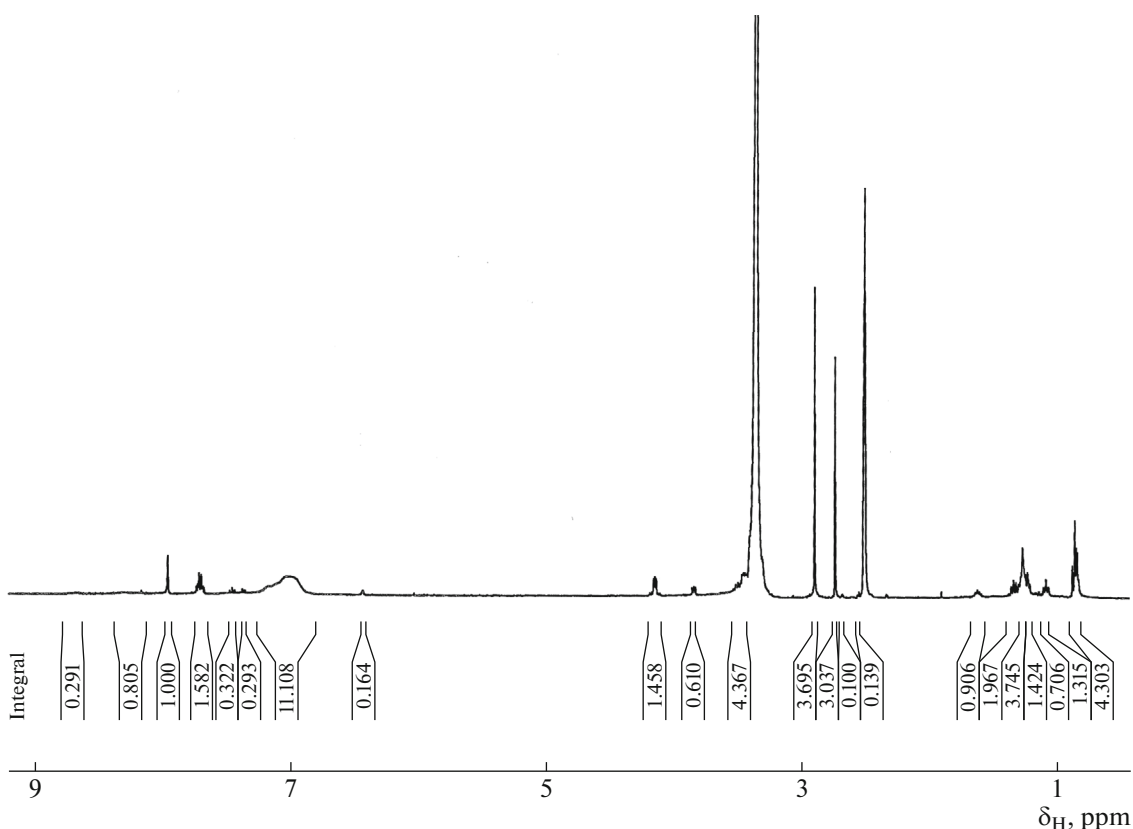


Fig. 2. The  $^1\text{H}$  NMR spectrum of the PANI-g-PGMA-MAN with weight ratio 1 : 1.

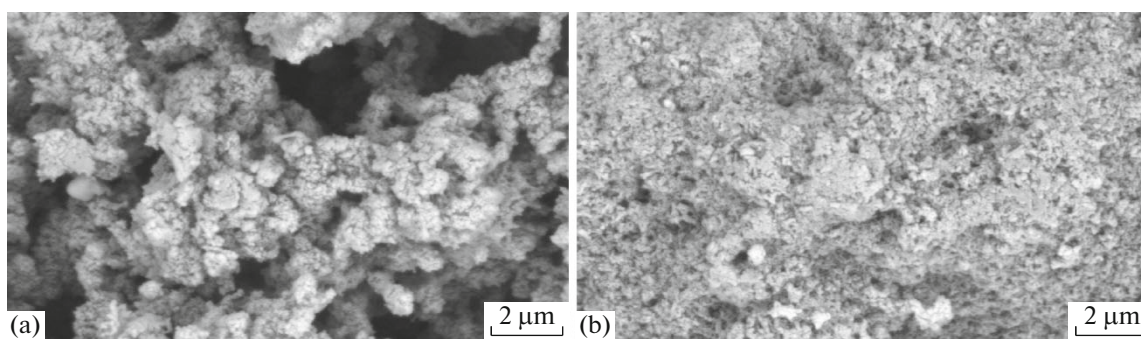
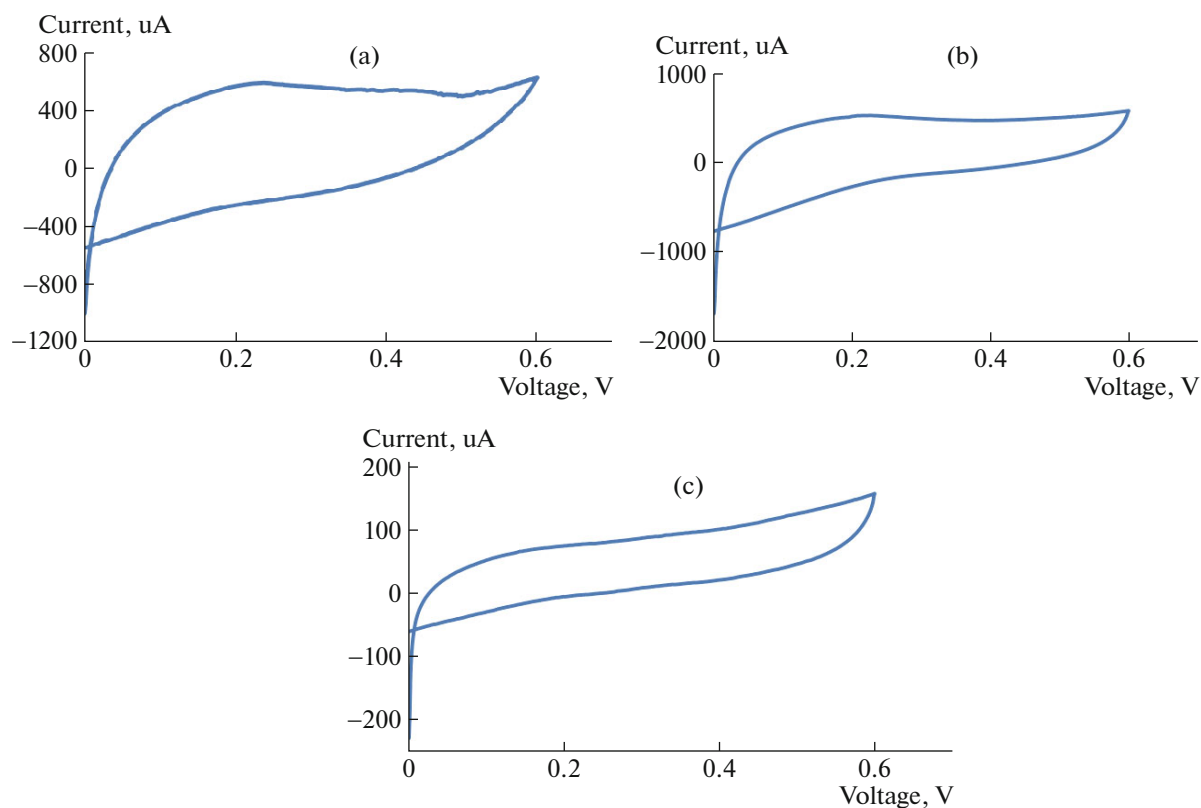


Fig. 3. The SEM images of the PANI-g-PGMA-MAN with weight ratio (a) 1 : 1 and (b) 2 : 1.

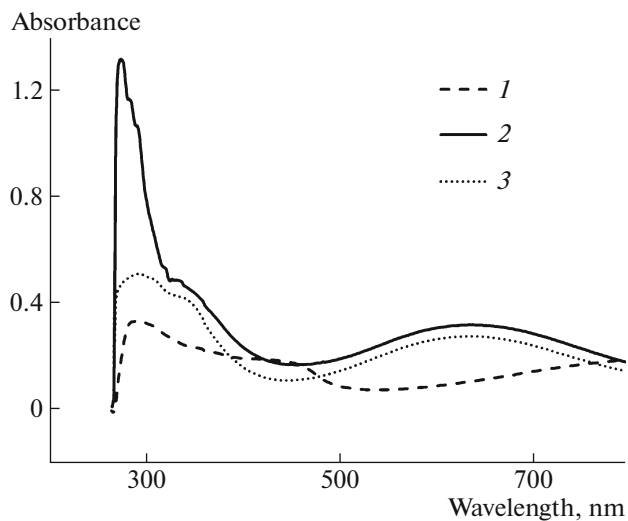
copolymers in different solvents. The comparison of the results shows that the grafting of the PANI on the selected copolymer backbone improves the solubility of PANI to a large extent. Generally, the grafted copolymers show good solubility in polar solvents such as *N*-methyl-2-pyrrolidone, DMF, DMA, and DMSO. In fact, it can be said that grafting reaction of PANI on PGMA-MAN copolymer backbone increases the processability of PANI and so enhances its solubility.

The TGA was used to evaluate the thermal stability of the synthesized graft copolymer. Figure 6 demon-

strates the TGA thermograms of the PANI-g-PGMA-MAN with 0.5 : 1 (Fig. 6a) and 1 : 1 wt/wt ratios of the PANI to the PGMA-MAN (Fig. 6b). PANI-g-PGMA-MAN with weight ratio 0.5 : 1 shows a weight loss of about 2.3% up to 100°C which can be attributed to the loss of physically adsorbed water. The latter weight loss about 11% up to 260°C is attributed to decarboxylation and splitting off  $\text{CO}_2$ . Two consecutive and continuous weight losses from 300 to 500°C can be attributed to the separation of the PANI grafted moieties from the copolymer backbone which is fol-



**Fig. 4.** The cyclic voltammetry of PANI-g-PGMA-MAN with weight ratio (a) 0.5 : 1, (b) 1 : 1, and (c) 2 : 1.



**Fig. 5.** The UV-Vis spectra of PANI-g-PGMA-MAN with weight ratio 2 : 1 in various media: (1) acid, (2) base, (3) neutral.

lowed by decomposition of the main copolymer backbone. Final weight loss is related to decomposition of the separated moieties specially PANI. With increase of the content of grafted PANI the thermal stability of the grafted copolymer increases.

## CONCLUSIONS

PANI was synthesized and grafted to the PGMA-MAN to prepare PANI copolymers with improved processability. The prepared grafted copolymer was confirmed by the FTIR and UV-Vis spectroscopy.

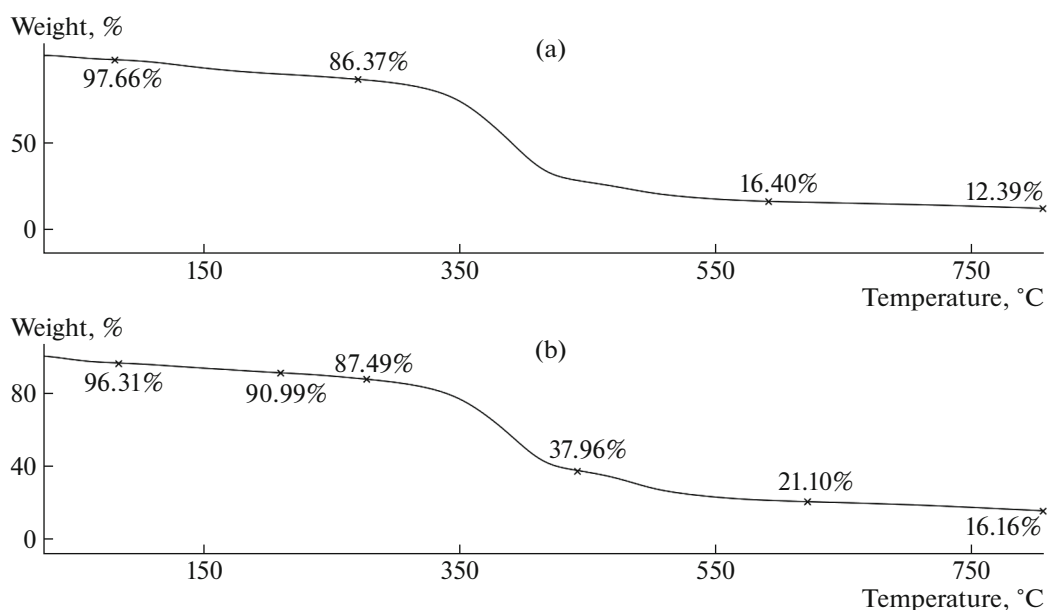


Fig. 6. TGA thermograms of PANI-g-PGMA-MAN with weight ratio (a) 0.5 : 1 and (b) 1 : 1.

The TGA was used to evaluate the thermal stability of the synthesized graft copolymer and the difference of two thermograms after and before grafting reactions could be a good evidence for grafting reaction. The results of the solubility test showed an improved performance of the grafted conductive copolymer in comparison to the pure PANI. The study of the CV showed that by increasing the PANI content, the current flow increases.

#### ACKNOWLEDGMENTS

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