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Chemical and Electrochemical Synthesis of Polyvinyl Propionate Graft Polyaniline

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ABSTRACT

In this work, we have synthesized poly vinyl(alcohol-*co*-3-chloropropionate), (PVA-*co*-PV3CPr) by reaction between 3-chloropropionic acid and polyvinyl alcohol (PVA) in presence dicyclohexyl carbodiimide (DCCI) and (dimethylamino)pyridine (DMAP). Then 1,4-phenylene diamine was added and poly[vinylpropionate-*co*-3-(*N*-p-aminoaniline)propionate], (PVPr-*co*-P3NPAAPr) was prepared. This polymer dissolved in solution of chloroform/toluene containing polyvinylpyrolidone. Then sufficient fresh aniline was added to the solution and stirred at temperature 0-5^{o}C. To continue, we added solution of ammonium persulphate, *p*-toluenesuphonic acid in water drop by drop by a dropping funnel. The solution was diluted with warm DMF and filtered under vacuum and then precipitated to ice methanol and produced polyvinylpropionate-*graft*-polyaniline, (PVPr-*g*-PANi). This polymer was doped in NMP or warm DMF solution with camphorsulphonic acid (CSA), *p*-toluenesulphonic acid (PTSA), dodecylbenzene sulphonic acid (DBSA) or methansulphonic acid (MSA) and then produced their films by casting method. The electrical conducting charges versus dopants concentration, doping time and doping temperature were determined. Electropolymerization carried out by coating (PVPr-*co*-P3NPAAPr) on surface GC disk electrode, then grew graft copolymer (PVPr-*g*-PANi) in presence of fresh aniline and acidic solution. Electrical conductivity of copolymer have been studied by a four-probe method and conductivity of 4.6 × 10^{-2} S/cm was achieved.

Key Words:
chemical and electrochemical synthesis;
graft copolymer;
polyaniline;
polyvinylpropionate.

INTRODUCTION

Conducting polymers have attracted considerable attention because of their electrical and optical properties and many potential applications such as energy storage [1], electromagnetic interference shielding [2], mechanical [3,4], acoustic [5], radiation [6] and sensor [7-9]. So far, however, only a few technical applications for this class of compounds have been realized, since organic conductive materials are, in general, very difficult to be processed. One of the interesting subjects in conducting

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polymers is the connection of these polymers with base polymers in different properties and creating new properties. These polymers can be connected as block or graft and cause changes in their solubility. The most common approach for this involves electrochemical polymerization of pyrrole on an electrode which is already coated with an insulating polymers [10]. The basic aim is to obtain homogeneous composites with good mechanical properties, at least to a certain extent. In these studies low percolation thresholds were achieved with the help of hydrogen bonding between host matrix and polypyrrole (PPy) [11]. Graft polymers were also obtained via the chemical polymerization method [12]. The graft polymer films showed different behaviours in differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and FTIR (ATR), as compared with the mechanical mixture of the two polymers. Insolubility of the insulating polymer in a suitable solvent suggested that the composite may be a graft rather than a mixture of two polymers.

Vatansever and Toppare [13] have reported about conducting polymer composites from polythiophene. Balci and coworkers [14] have experienced the same result with composites of PPy and poly(vinyl chloride-vinyl acetate), and have reported that graft copolymers of PPy and poly(methyl methacrylate) derivative [15] from a good solution with a favourable degree of conductivity. These graft copolymers have been connected to each other by an ethylene intermediate and they have good physical properties as well as conductivity.

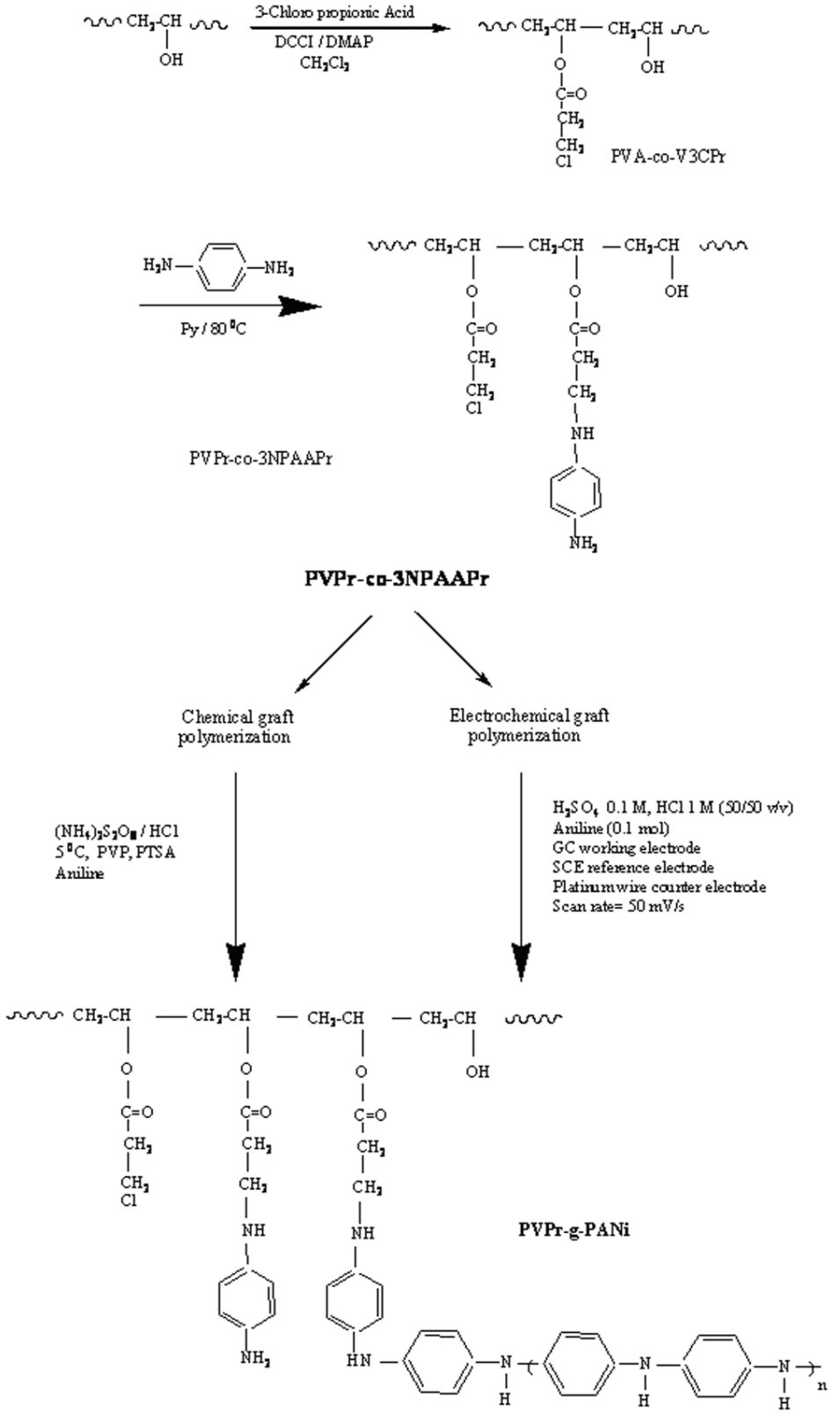
Copolymers in general exhibit physical and mechanical properties far different from those of blends of the same individual homopolymers. For example the butadiene-styrene copolymer in a 3:1 ratio (synthetic rubber) has desirable properties which cannot be achieved with either of the homopolymers or any of their blends. The properties of copolymers can also be modified by varying either the ratios of the various constituents or the manner by which they are chemically attached. A large variety of copolymers should thus be obtainable by varying the nature, number and ratios of the polymers copolymerized with PPy. Polyaniline (PANi) is an important conducting polymer because of its good environmental stability [16]. In addition to the oxidation doping as for the other conducting polymers, PANi can also be doped through protonation by exposure to an appropriate protonic acid without changing the number of π-electrons in the polymer, making its properties unique [17]. We have reported blends and graft copolymers of polyvinyl acetate and polypyrrole [18,19] without increasing the conductivity. In this research, we have replaced PPy by PANi in order to increase solubility and conductivity (Scheme I).

EXPERIMENTAL

Instrumentals and Materials

The electrical conductivity of polymer was measured at room temperature by a four-probe technique (ASTM Standards, F 43-93). Elemental analysis was determined with Perkin-Elmer 2400 CHN. A Fourier-transform infrared spectrometer (8101 M-Shimadzu) was used in spectral measurements of the film. Cyclic voltammetry and electrochemical polymerization was carried out using digital potentiostat DP8 (homemade). Proton and carbon nuclear magnetic resonance (FT-H^1, ^{13}C NMR) spectra were recorded at 250 MHz on a Bruker WP 200 SY spectrometer. NMR Data are reported in the following order: chemical shift (ppm), spin multiplicity (s=singlet, d=doublet, t= triplet, q=quartet, m=multiplet), and integration. Visible spectra were obtained by Perkin Elmer Lambda 15 spectrophotometer. Molecular weights were measured at 30°C with a gel permeation chromatography (GPC) (Waters Associates, model 150-C). Three styragel packed columns with different pore sizes (10^4-10^6-Å) were used. The mobile phase was tetrahydrofuran (THF) with flow rate of 1.5 mL/min. The solution concentration was 0.2 wt%. Calibration of the instrument was performed with nine standard samples of monodisperse polystyrene having molecular weights between 3.0×10^3 and 1.4×10^6. The thermal properties of polymer was studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) of PL Thermal Science. Scanning electron microscopy (SEM) was employed to study the type of surface morphology of polymer. A Cambridge S-360 SEM was used for this purpose.

Aniline (Merck) was dried with NaOH, fractionally distillated under reduced pressure from sodium or CaH_2. Polyvinylalcohol (Merck, 72000 molecular weight) was used as matrix polymer. Acetonitrile



Scheme I

(Merck) was dried on silica gel, distillated on P_2O_5 in the presence of nitrogen gas. 1,4-Phenylenediamine (Aldrich) purified by recrystallization in benzene. All the other materials and gases used in this work were purchased from Merck Chemicals and purified, or were prepared by literature methods.

Preparation of Poly(vinylalcohol-co-3-chloropropionate), PVA-co-PV3CPr

A 250-mL three-necked flask was equipped with a mechanical stirrer, condenser and a dropping funnel. A solution of 11 g (0.25 mol) of poly(vinyl alcohol) in 75 mL of dichloroethane was placed in the flask and 20 mL saturated solution of *p*-toluenesulphonic acid (PTSA) in dichloroethane was added in the dropping funnel. Then, 32.56 g (0.3 mol) 3-chloropropionic acid in 75 mL of dichloroethane was placed inside flask and produced suspension solution by refluxing for 5 min. Then PTSA solution was added till the appearance of clear solution. Stirring was continued by refluxing at room temperature for 3 and 10 h, respectively. The product was precipitated in ice ethanol and filtered, then washing produced solids with acetone and ethanol and dried above vacuum. (yield = 87%)

UV-Visible in THF: λ_{max}; 302 nm (3.9 intensity), 309 nm (3.8 intensity), 359 nm (2.4 intensity), 496 nm (1.39 intensity)

FTIR; 3516(m), 2961(sh), 1757(s), 1418(m), 1317(m), 1194(m), 1148(s), 953(m), 785(m), 708(m), 577(sh) cm^{-1}

FT-^{1}H NMR ($CDCl_3$); 4.4(t, sharp, 2H), 4.1 (s, sharp, 1H), 3.2(s,weak,0.6H), 2.8(t, sharp, 2H), 1.7 (s, broad, 2H) ppm

Preparation of poly[(vinyl-3-chloropropionate)-*co*-3-(N-p-aminoaniline)propionate], poly(V3CPr-*co*-3NPAAPr)

A 0.5 g poly(vinylchloropropionate) was dissolved in 10 mL DMF, then 1.62 g (0.0149 mol) was added in 4 mL pyridine continue stirring at refluxed for 2 h, then stirred at room temperature for 3 h. Finally, it was precipitated in iced methanol and filtered, then washing produced solids with ice methanol and dried above vacuum.

UV-Visible in THF: λ_{max}; 235 nm (2.9 intensity), 288 (1.8 intensity), 310 nm (2.5 intensity), 365 nm (1.9 intensity), 505 nm (0.7 intensity).

FTIR; 3360-3600 (w), 3009 (sh), 2970 (sh), 1760 (s), 1540 (sh), 1450 (s), 1420 (s), 1370 (m), 1330 (m), 1201 (m), 1160 (m), 1111 (s), 960 (m), 860 (m), 780 (m), 710 (m), 680 (sh).

FT-^{1}H NMR ($CDCl_3$); 7.1(d, 2H), 6.7(d, 2H), 4.2(t, sharp, 2H), 3.9(s, sharp, 1H), 3.1(s, weak, 0.7H), 2.6(t, sharp, 2H), 1.8(s, broad, 2H)

^{13}C NMR ($CDCl_3$) 23.1, 25.6, 33.2, 47.3 48.2, 122, 134, 155 ppm.

Chemical Preparation of Polyvinylpropionate-*g*-polyaniline, (PVPr-*g*-PANi)

A 0.5 g poly(V3CPr-*co*-3NPAAPr) is completely dissolved in 20 mL of DMSO. One g aniline and 0.5 g p-toluensulphonic acid are added to the above solution. The mixture was vigorously stirred and temperature reduced to 5°C. In a separate container 2 g (0.0088 mmol) $(NH_4)_2S_2O_8$ (ammonium peroxydisulphate) was dissolved in 10 mL tosic acid solution. The oxidant solution was slowly added at a rate of approximately 5 mL/ min to the mixture.

After the mixture was allowed to stir for 10 min, a solution containing 1 g sodium sulphite in water/ DMSO was added to the mixture. The mixture was stirred for about 2 h and polymer solution was filtered using G2 sintered glass filter, then precipitated into ice methanol. The product was washed successively by distilled water and methanol and dried at 60°C for 24 h.

UV-Visible in DMSO: λ_{max}; 240 nm (3.4 intensity), 290 nm (2.2 intensity), 315 nm (1.8 intensity), 370 nm (1.5 intensity), 680 nm (0.7 intensity).

FTIR; 3300-3600 (w), 3010 (sh), 2990 (sh), 1710 (s), 1550 (w), 1530 (sh), 1460 (s), 1425 (s), 1372 (m), 1340 (m), 1210 (m), 1165 (m), 1110 (s), 955 (m), 880 (m), 780 (m), 715 (m), 650 (m), 685 (sh) cm^{-1}.

FT-^{1}H NMR (d_6-DMSO); δ 6.45-7.61(b and m, 12H), 4.4(t, sharp, 2H), 3.7(s, sharp, 1H), 3.3 (s, weak, 0.6 H), 2.9 (t, sharp, 2H), 1.8 (s, broad, 2H) ppm.

^{13}C-NMR (d_6-DMSO); δ 24.5, 25.38, 25.52, 33.40, 47.57, 48.30, 110, 125, 130, 134, 140, 145, 160 ppm.

Electrochemical Preparation of Polyvinylpropionate-*g*-polyaniline, (PVPr-*g*-PANi)

Electrochemical synthesis of (PVPr-*g*-PANi) was carried out using a conventional three-electrode system with a SCE reference, platinum wire counter electrode and GC disk working electrode. The solution for elec-

trochemical graft copolymerization was HCl 1 M and H_2SO_4 0.1 M (50/50 v/v) solution.

Electrochemical Preparation of PVPr-*g*-PANi films

Electrochemical synthesis of PVPr-*g*-PANi was carried out using a conventional a three-electrode system with a SCE reference, platinum wire counter electrode and GC disk working electrode. The solution for electrochemical graft copolymerization was HCl 1 M and H_2SO_4 0.1 M (50/50 v/v) solution. Firstly a suitable amount PV3CPr-*co*-3NPAAPr) on the GC disk electrode was coated by using casting method and then various amount of anilines were added. Polymer was grown on GC disk electrode under scan potential in the range of -450 to 1700 mV and scan rate 50 mV/s. The cyclic voltammetry curve for PVPr-*g*-PANi under potential in the range of -150 to 900 mV by scan rate 50 mV/s was obtained. The thickness of the film was ca. 35 μm as determined by scanning electron microscopy in 1/1 weight ratio PV3CPr-*co*-3NPAAPr / aniline.

RESULTS AND DISCUSSION

Study of UV-visible Spectroscopy

Conductive polymers have a conjugate system of double bonds in a backbone polymer. These polymers have some of conventional transfers of UV region, such as $n\rightarrow\pi^*$, $\pi\rightarrow\pi^*$, etc. The $\pi\rightarrow\pi^*$ transfers of conjugated double bonds related to the close visible regions, associated to polaron and bipolaron statues as well as solution conductive polymers.

Figure 1 shows UV-visible spectral data for PVPr-*g*-PANi with different PANi/PVPr ratios presented as well as their doping states in *m*-cresol solvent. The

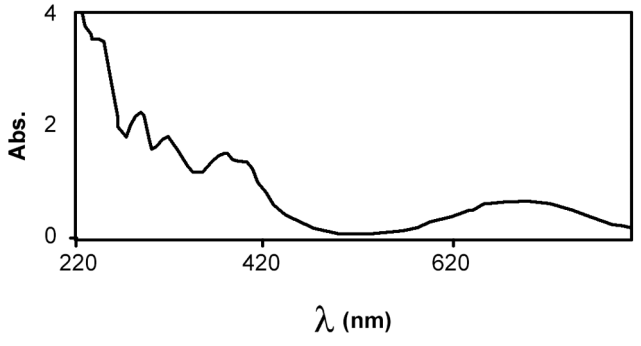


Figure 1. UV-Visible spectroscopy of PVPr-*g*-PANi in *m*-cresol solvent.

above-mentioned polymer (with aniline pattern) should have two peaks in 240 nm with 3.4 intensity and 290 nm with 2.2 intensity. The first transfer could be for the $n\rightarrow\pi^*$ transfer and the second one could be for $\pi\rightarrow\pi^*$ of benzoic system. As we know, by an increase in the length of chain and subsequently increase in conjugated double bonds, a decrease in energy difference $\pi\rightarrow\pi^*$ occurs that causes an increase in the wavelength. UV-Visible spectral data show that spectrum of 290 nm region is for the second peak of aniline groups and the $\pi\rightarrow\pi^*$ is a conjugate couple system for the benzoic states in 350-400 nm regions. Obviously, after doping these polymers, a wide peak in 500-800 nm is for the transfer of $\pi\rightarrow\pi^*$ quinon of aniline groups (for the polaron and bipolaron transfers). Obviously, if the peaks of 350-400 nm and particularly 550-600 nm increase, we will have more conductivity which could be due to the couple length of the dual grafts in the system length. As it is shown in UV-visible data, by an increase in the percentage in polymer structures, the absorption related to the conductivity increases and the conductivity increases accordingly. Obviously, more than 60 % increase in PANi will lead to a decrease in solubility. According to the results of elemental analysis, 10 to 60 % aniline are grafted.

Study of Infrared (IR) Spectroscopy

The IR spectrum has given good information on polymer and can confirm different methods of synthesis as well. The FTIR data for PVPr-*g*-PANi show sharp peak of 650 cm^{-1} for the C-Cl stretching vibration and 1100 cm^{-1} for the C-O stretching vibration, 1710 cm^{-1} for C=O stretching vibration, 2990 cm^{-1} for C-H aliphatic stretching and 3300-3600 cm^{-1} is for the O-H stretching vibration resulted from polyvinyl alcohol. By calculating the amount of chloride in J_{ob} and UV methods, around more of 86% then hydroxyl groups changed into 3-chloropropionate groups by 3-chloropropionic acid. The FTIR data for (PVPr-co- P3NPAAPr) which is used as an intermediate for preparing related graft polymer show sharp peaks in 3440 and 3010 cm^{-1} stretching vibration for N-H and C-H (aromatic) stretching vibration, as well. The other stretch vibrations related to the polymer base, poly(vinylalcohol-*co*-vinylchloropropionate, are developed in agreement with what mentioned before. FTIR of PVPr-*g*-PANi shows the desirable growth of polymer on poly(vinylchloropropionate) base.

Study of NMR Spectroscopy

The FT-^{1}H NMR, PVPr-*g*-PANi shows the spectrum in 1-1.8 ppm region for different protons of CH_2 in chain length is also in lateral chains and different variations of these protons did not cause the appearance of not-reacted and reacted states of these groups either. The spectrum in 2.9 ppm is for methyl groups and multiple spectrum is 3.3 ppm seems to be related to the C-H protons linked to oxygen which are deshield up to this region. The wide spectrum observed in 3.7 ppm is also the specific peak of hydroxyl group along the chain. The existing spectrum in 6.5 ppm is for C-H of PANi quinoide system and spectrum in 7.0-7.5 ppm region is for the aromatic region and benzoic PANi protons. The FT-^{13}C- NMR data of PVPr-*g*-PANi compounds in which, the peaks below 34 ppm is for different types of aliphatic carbons that could be related to the -CH_2- carbons on chain and the -CH_2- carbons are related to the lateral branches. The variation in the carbons of this region does not react solely to CH_2Cl carbons and are nitrogen-linked carbons. The peak in 48.30 ppm region is for the carbon linked to the hydroxyl and oxygen group. The peaks of 110 to 145 ppm are also for the ring carbons in aromatic and quinoide states. The peak related to 160 ppm is also for carbon carbonyl ester.

Results of Elemental Analysis

The elemental analysis is used to determine the percentage of polymers that participate in the resulted compound. Determining polymer percentage in graft copolymer is important in the manner that we may study the electronic conductivity conditions in the graft copolymer properties both in quantity and quality terms. By changing factors such as varying oxidant concentrations, change in solvent, change in monomer concentration and change in the polymer base, in the synthesized polymer, we try to reach desirable conditions to use in sensor applications.

For this purpose, we carried out elemental analysis studies on the films in terms of electric conductivity, stability and mechanical properties. Since the prepared copolymer is on aniline basis and the ground polymer lacks nitrogen; we can obtain the aniline percentage by following up the %N in the elemental analysis. For preparing PVPr-*g*-PANi in each test, we chose specific weight of polymer to have a suitable condition. To determine the weight percent of PANi in the mentioned copolymer the following procedure is taken. The weight percent of nitrogen theory in each monomer (aniline) unit is obtained first.

Table 1. The different percentages of PANi/polymer in 5 samples obtained from elemental analysis.

Sample	Aniline (g)	%N Found	%PANi in PVPr-*g*-PANi
1	0.3	5.17	76.5
2	0.6	9.09	133.8
3	1	16.19	238.2
4	1.5	23.09	339.7
5	2	30.19	444.1

$$\text{Theoretical mass of } \%N_2 \text{ in polymer} = \frac{\text{Molecular mass of } \%N_2}{\text{Mass unit of monomer 3-(}N\text{-}p\text{-aminoaniline) propionate}} \times 100$$

$$\text{Theoretical mass of } \%N_2 \text{ in (PV3CPr-}co\text{-P3NPAAPr)} = \frac{14}{206} \times 100 = 6.80$$

$$\text{Percentage of aniline in copolymer (PV3CPr-}co\text{-3NPAAPr)} = \frac{\text{N (\%) Found}}{\text{Theoretical mass of } N_2 \text{ in polymer}} \times 100$$

$$\text{Aniline (\%)} = \frac{11.5}{6.80} \times 100 = 169$$

$$\frac{169}{2} = 84$$

This means that 84% of the 3-chloropropionated were phenyl-diaminated. Therefore, by having %N, we will be able to calculate the percent of existing PANi in the copolymer. Table 1 shows different percentages of PANi/polymer in five samples obtained from elemental analysis. For calculation of percentages of PANi on graft copolymer, we performed measurement according to the following equations for 5 samples obtained from elemental analysis listed in Table 1.

$$\text{Percentage of PANi in PVPr-g-PANi (\%PANi)} = \frac{\text{N (\%) Found}}{\text{Theoretical mass of nitrogen polymer}} \times 100$$

Which means that aniline would growth on (PV3CPr- -P3NPAAPr) as well.

Therefore, by having N%, we will be able to calculate the percent of existing PANi in the copolymer.

Results of Gel Permeation Chromatography (GPC)

The GPC of PVPr-*g*-PANi was analyzed using poly-

Table 2. The molecular weight distribution averages for the PVPr-*g*-PANi from GPC.

Sample molecular weights	Aniline (g) PVPr-*g*-PANi
Number average	71756
Weight	209611
Z average	466799
Z+1 average	760902
Polydispersity	2.9
Molecular weight	154405

styrene standard. The GPC curves obtained, show a unimodal distribution. The molecular weight distribution averages for the polymer is presented in Table 2. As shown in Table 2, high molecular weight of the polymer shows the growth of PANi on PVPr-*g*-PANi.

Study of Electrical Conductivity and Physical Properties of PVPr-*g*-PANi with Variation PANi%

As noted before, the physical properties of copolymers is a combination of the properties of polymers participating in the copolymer structure and its properties fit with the percentage of each participating element. The electrical properties of this copolymer are not excluded form this principal. So, PVPr-*g*-PANi with different percentages of PANi were prepared, each with their particular physical and electric properties. Obviously, as the PANi ratio in the copolymer increases, in addition to the conductivity, its hardness and thermal resistance increase as well, while their flexibility and smooth film remain almost the same.

This copolymer is doped for 24 h in presence of 1.5 M HCl and its conductivity is improved few times. Table 3 shows the effects of different PANi proportions in the graft copolymer in the conductivity and physical properties of PVPr-*g*-PANi before and after doping with 1.5 M HCl.

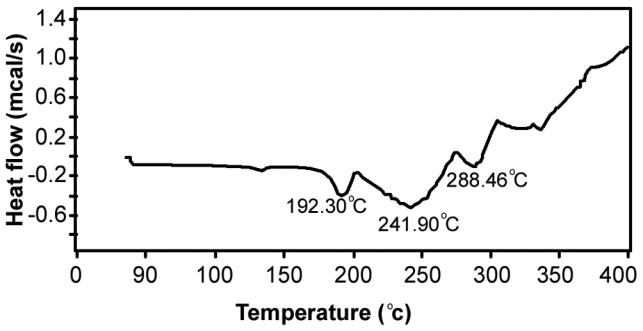


Figure 2. TGA Thermogram of PVPr-*g*-PANi.

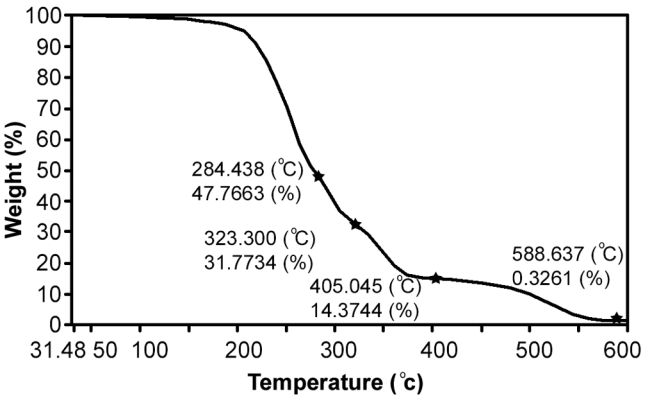


Figure 3. SEM Micrographs of PVPr-*g*-PANi; (a) surface image (b) cross-section image.

Study of Differential Scanning Calorimetry and Thermal Gravimetry Analysis

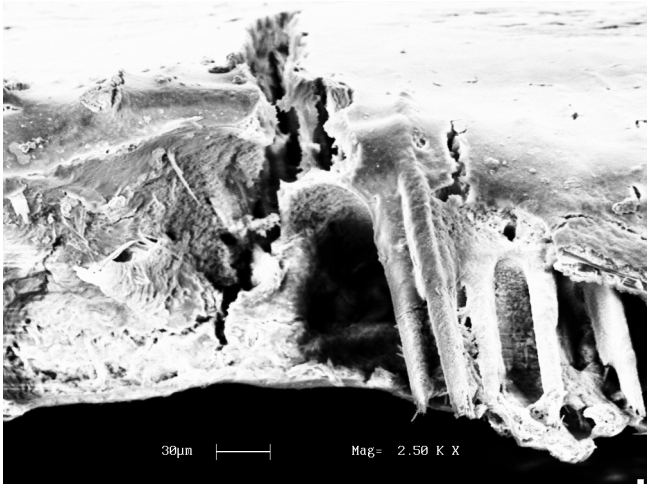
Figures 2 and 3 show DSC and TGA of PVPr-*g*-PANi. The DSC measurement shows the w/g thermal flow in different temperatures. The DSC curve shows that PVPr-*g*-PANi has higher thermal resistance than PVA

Table 3. The effect of change in the %PANi on electrical conductivity and physical properties of PVPra-*g*-PANi.

Sample	Conductivity (before doping)	Conductivity (after doping)[b]	Physical properties
1	8.1×10^{-5}	2.4×10^{-4}	Smooth, flexible, strong
2	4.1×10^{-4}	1.2×10^{-3}	Smooth, flexible, strong
3	9.3×10^{-4}	2.3×10^{-3}	Smooth, flexible, strong
4	2.3×10^{-3}	6.4×10^{-3}	Smooth, flexible, most strong
5	2.1×10^{-2}	8.5×10^{-3}	Smooth, flexible, most strong

(a): Synthetic polymer; (b): Doping carried out by 1.5 M HCl solution after 24 h.

(a)



(b)

Figure 4. SEM Micrographs PVPr-*g*-PANi; (a) surface image and (b) cross-section image.

and PVPr. This curve has a softening temperature at 130ºC and destruction initiation in less than 200ºC and in both polymer PVA and PVPr polymers there is less resistance.

In these curves, the endothermic peaks appear in 180-200ºC (192.3ºC), 220-250ºC (241.9ºC) and (275-300ºC) (288.5ºC) and only one weak exothermic peak is seen in the 300-320ºC region.

As it is shown in PVPr-*g*-PANi thermogram, this polymer at 30ºC started to soften and up to 200ºC it approximately losses 1.5% of its weight which is due to humidity and existing solvent in polymer chains, and at about 400ºC it approximately degraded. PVPr-*g*-PANi is stable below 190ºC and over 200ºC polymer starts its complete distraction and continue at 400ºC. The methods of interpreting TGA results are numerous and also lack standardization. Some of these note the temperature of 5-10% loss, or by inflection temperature of a downward slope, or by the first detectable break in the curve. The STA of PVPr-*g*-PANi for about 10% grafted PANi illustrated that initial decomposition temperature (IDT), polymer decomposition temperature (PDT) and the maximum polymer decomposition temperature (PDTmax) are 200ºC, 284.44ºC and 405.04ºC, respectively. The residual weights (c) of the polymers were reported at 588.64ºC to be 0.3261%. These polymers were stable in normal atmosphere up to presented temperatures.

The results of TGA, DSC and CHN (elemental analysis) for samples with changes to the proportion of PANi in copolymer show that by an increase in the amount of PANi in copolymer, thermal resistance, hardness and ability of film formation increases accordingly. Table 4 shows the changes of thermal resistance to an increase in the proportion of PANi in copolymer.

A comparison between the changes in thermal resistance of PVPr-*g*-PANi and its blends show that PVPr and PANi blends have higher thermal resistance then copolymer. So much that a blend of 30/70 from

Table 4. Changes in thermal resistance of PVPr-*g*-PANi in different of PANi percentages.

Sample	%PANi in PVPr-*g*-PANi	IDT (ºC)[a]	PDT (ºC)[b]	PDT (ºC)max[c]	η_c (%)
1	76.5	188	230	370	4.323
2	133.8	200	240	375	5.326
3	238.2	219	249	380	7.212
4	339.7	225	258	381	10.223
5	444.1	230	270	385	12.0156

(a) Initial decomposition temperature; (b) Polymer decomposition temperature, and (c) Maximum polymer decomposition temperature.

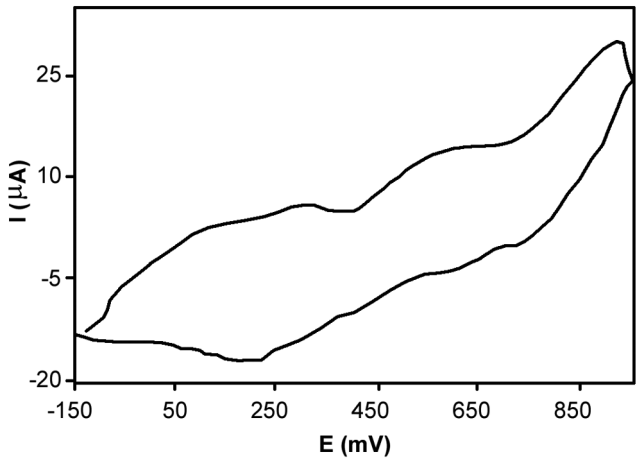


Figure 5. Cyclic voltammogram of PVPr-*g*-PANi, in HCl 1 M and H_2SO_4, 0.1 M (50/50 v/v), GC disk electrode vs. SCE, scan rate=50 mV/s.

PANi/PVPr with PVPr-*g*-PANi, grafted with 40-50 % PANi seems more resistant between 100-150ºC. The reason could be attributed to the freer and longer PANi chains in blends than the graft copolymers; for in the copolymers the chains could be shorter and distributed in the polymer chains solutions of polyvinyl propionate; where, this may cause a decrease in conductivity, thermal resistance and other physical properties in the copolymer.

Studying the Scanning Electronic Microscopy

The investigation results of SEM pictures are among the best methods for morphological study of polymers. Although the surface has some limitations, in SEM, by preparing a tridimensional picture with high depth one may provide suitable information for the topology of surface with approximately 100 Å resolution power. The ordinary application of SEM includes studying scattered pigments in painting colours, peal off or fracture in coats, the phasic borders limit in unmixed solutions, the structure of sponge polymers and disability in surface adhesion. SEM is particularly valuable in assessing how polymer surgical equipment reacts their host environment. Figure 4a,b shows SEM of PVPr-*g*-PANi. As it is shown in pictures, PANi is in form of needle-shape and homogeneous particles. Homogeneity and being single phase of films are the implication of successful graft copolymer. The cross cut of this film shows the homogeneity and preparation of graft copolymer in a good way, as well. The development of PANi chains is sufficient on the base polymer. Figure 4b is the cross-cut of this film which shows the homogeneity and preparation of graft copolymer in a good way. The development of PANi chains is sufficient on the base polymer.

Study of Cyclic Voltammetry

The copolymer prepared in this research work underwent voltammeter study due to its electroactivity. Figure 5 shows the cyclic voltammogram of PVPr-*g*-PANi. As it is shown in the voltammogram, this polymer has a good reversibility and while showing good potential in electron transfer. It also shows good stability on the electrode level. This polymer shows behaviour similar to the pure PANi behaviour and has two oxidation and reduction peaks. Here, by initiation of development from negative potentials (-150 mV) first, the leucoemeraldine is converted into emeraldine in form of oxidation doping in peak and in continuation of the fall in peak, emeraldine is oxidized to pernigraniline and then, in the emeraldine is reduced to of leucoemeraldine. In both reduction system, during transferring electron from polymer chain, to neutralize the load, the anions in the electrolyte Cl^- exits to the polymer structure or leaves it. Two redox systems are in fact two processes of oxidation doping.

CONCLUSION

PVA and PVPr are soluble, flexible film and disperse able as well. So, they can be used in different applications such as dye and adhesive industries. On the other hand, PANi conducting polymer have fibre and film ability formation. So combination of these polymers produces formation a new compound with new properties. PVPr-*g*-PANi is soluble, flexible polymer with good film, fibre, disperse and conductivity ability as a backbone polymer.

This graft copolymer can be used for conducting dye, sensors, antiradar and corrosion protection. Cyclic voltammetry and spectroscopy data confirm the formation of electro and chemical polymerization, respectively. STA and SEM of (PVA-*co*-PVPr-*g*-PANi) shows increased thermal stability and successful copolymerization, respectively.

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