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ORIGINAL ARTICLE

Optimization of amine-terminated polyacrylonitrile synthesis and characterization

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Abstract Amine-terminated PANs were prepared in two steps. The first step includes free radical polymerization of acrylonitrile (AN) using initiator pair of ammonium persulfate and sodium thiosulfate as redox system. In the second step, the amino groups were introduced through the reaction of polyacrylonitrile with excess of different diamines (10-fold) including ethylenediamine (EDA), hexamethylenediamine (HMDA) and octamethylenediamine (OMDA), to yield PAN–EDA, PAN–HMDA and PAN–OMDA, respectively. Optimization of the amine-terminated PANs synthesis was carried out at different temperatures (30–90 °C) and different time intervals (4–24 h). In addition, the introduction of the amino group was followed by the piperidine test and recording of the FT-IR spectra. All polymers were characterized by, ^{1}H NMR spectra, thermogravimetric analysis (TGA), and FT-IR spectra.

1. Introduction

Chemical reactions of polymers have received much attention in which several fundamentally functionalized polymers were prepared by the reaction of linear or crosslinked polymers and by the introduction of reactive polymer chains (Horie et al., 2003). Considerable interest has been focused on functional polymers and on their diverse applications in many fields such as biomedical applications including drug delivery and antimicrobial polymers. Functional polymers have potential advantages over small analogue molecules. Their usefulness is related to both the functional groups and to their polymeric nature whose characteristic properties depend on the extraordinarily large size of the molecules (Kenawy et al., 1998; Akelah and Moet, 1990).

Polyacrylonitrile (PAN) is an important polymer which has many desirable properties like solvent resistance, abrasion resistance, thermal and mechanical stability, high tensile strength and posseses good insect resistance (Jain et al., 2009). Polyacrylonitrile finds many applications in the areas of composites, protective clothing, nanosensors, gas separation technology and in biochemical product purification and for

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biomedical applications (Jain et al., 2009). Active nitrile groups present in polyacrylonitrile allow for the introduction of new functional groups by special reactions. Among the reactions of the nitrile group modification are the hydrolysis and reduction to produce carboxyl and amine functionalities, respectively (Kiani et al., 2011). In recent years, there has been much interest in synthetic polymeric fibers suitable for medical applications. Anirudhan and Ramachandran (2008), Kiani et al. (2011) have reported different methods of modifications of polyacrylonitrile fibers to obtain cathionite, anionite, and ampholyte. Some authors carried out surface modifications of polyacrylonitrile with sodium hydroxide to obtain a significant number of carboxylic groups (Kiani et al., 2011; Bilba et al., 2006) and others have applied modification with hydroxylamine to form hydroxy-functionalized resins (Anirudhan and Ramachandran, 2008; Kiani and Arsalani, 2006; Arsalani and Hosseinzadeh, 2004; Arsalani et al., 2009). Amine functionality on the surface of polyacrylonitrile fibers was introduced by reduction with lithium aluminum hydride (Jain et al., 2009). Recently, aminated polyacrylonitrile fibers have been used for the removal of metal ions such as chromium, copper, and lead, but with low metal sorption capacity (Arsalani et al., 2009; Deng and Bai, 2004; Deng et al., 2003; Bagheri et al., 2010). Also, Lin et al. synthesized polyacrylonitrile fiber-supported palladium catalyst which was used in Heck reactions (Arsalani et al., 2009; Lin et al., 2003).

The objective of the present study was to prepare amine-terminated polymers as functional polymers for use in biomedical applications. The synthesis of amine-terminated polyacrylonitrile was carried out by the reaction of polyacrylonitrile with different types of diamines at different time intervals and different temperatures to reach the optimum conditions.

2. Experimental

2.1. Materials

Acrylonitrile (AN) was purchased from Loba Chemie, Spain. Ethylenediamine (EDA), hexamethylenediamine (HMDA) and octamethylenediamine (OMDA) were purchased from across. Bromophenol blue (BPB) was purchased from PROLABO. Piperidine was purchased from BDH Chemicals Ltd Poole England. All solvents were used as received without further purification.

2.2. Characterization techniques

^{1}H NMR spectra were recorded on a JEOL JNM-PM X90 Si-NMR spectroscopy instrument. Thermal properties were examined by using thermogravimetric analysis (TGA) which was carried on TA-Q500 System of TA; samples of 5–10 mg were heated in the temperature range of 30–800 °C at a scanning rate of 10 °C min^{-1} under nitrogen atmosphere. Fourier-transformer infrared (FT-IR) Spectra were recorded using TENSOR 27, Bruker. UV Spectra was recorded using Perkin–Elmer Lambda 35 UV–vis spectrophotometer.

2.3. Polymer synthesis

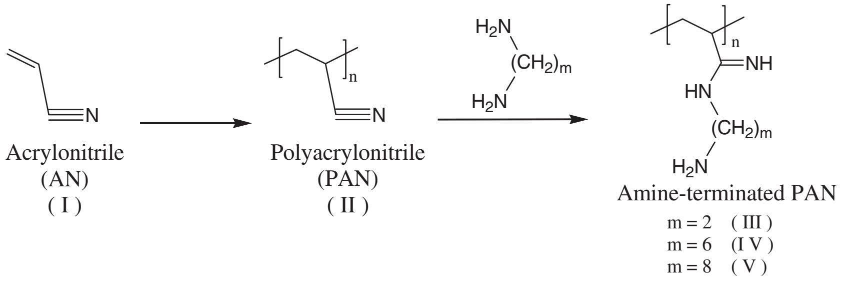
Polyacrylonitrile PAN (II) was prepared by precipitation polymerization using a redox initiation system in aqueous solution according the procedure by Braun et al. (2005). The procedure can be summarized as following; In a 250 mL round-bottomed flask, acrylonitrile (AN) (I) (15 mL, 230.3 mmol) was mixed with distilled water (175 mL) at room temperature with stirring under nitrogen atmosphere. Then, sodium disulfite solution (5%, 0.5 mL, 0.13 mmol) and ferrous sulfate solution (2.5 mL, 9.10 mmol), were added followed by potassium proxodisulfate solution (5%, 2.5 mL, 0.46 mmol). The turbidity was noted after 5 min and stirring was continuing for more than 20 min. The precipitated polymer (II) was filtered and was washed with distilled water (300 mL) and finally with methanol (100 mL). The product PAN (II) was dried in a vacuum oven at 50 °C overnight to yield 8.3 g (55% yields). The ^{1}H NMR spectrum (400 MHz, DMSO-d_6, ppm, Si(CH$_3$)$_4$) of PAN (II) showed peaks at: δ 2.03 ppm (singlet, g, –C$\underline{H}_2$–CH–), δ 2.13 ppm (triplet, –CH$_2$–C$\underline{H}$–).

2.4. Synthesis of amine-terminated polyacrylonitrile PANs (III–V)

2.4.1. General procedure

In a 100 mL round-bottomed flask, to an excess of the diamine (10-fold) in absolute ethanol (60 mL), Polyacrylonitrile (II) (1.0 g, 17.9 mmol) was added portionwise over 1 h with stirring under nitrogen. The reaction mixture was stirred for 1–2 h at room temperature and at 70 °C for 12 h. The product was filtered, washed with methanol (60 mL) and was dried in an oven under vacuum at 40 °C overnight. The following quantities were used:

2.4.1.1. Polyacrylonitrile-terminated ethylenediamine PAN–EDA (III). EDA (126 mL, 113.2 g, 1883 mmol), and PAN (II) (10 g, 179 mmol) to yield 12.2 g (57% yield). The ^{1}H NMR Spectrum showed peaks at: δ 1.21 ppm (1H, –CH$_2$-C$\underline{H}$–), δ 2.15 ppm (2H, –C$\underline{H}_2$CH–), at δ 2.04 ppm (1H, =N$\underline{H}$), δ 2.09 ppm (1H, –CN$\underline{H}$CH$_2$–), δ 2.11 ppm (2H, –



Scheme 1 Redox polymerization of acrylonitrile and synthesis of amine-terminated PANs.

N$\underline{H}_2$), δ 3.11 ppm (2H, –CNHC$\underline{H}_2$CH$_2$NH$_2$), δ 3.14 ppm (2H, –CNHCH$_2$C$\underline{H}_2$NH$_2$).

2.4.1.2. Polyacrylonitrile-terminated hexamethylenediamine PAN–HMDA (IV). HMDA (2188 g, 1883 mmol), and PAN (II) (10.0 g, 179 mmol) to yield 12.0 g (52% yield). The ^{1}H NMR Spectrum showed peaks at: δ 1.21 ppm (1H, –CH$_2$–C$\underline{H}$–), δ 2.14 ppm (2H, –C$\underline{H}_2$–CH–), δ 2.04 ppm (1H, =N$\underline{H}$), δ 2.08 ppm (1H, –C–N$\underline{H}$–CH$_2$–), δ 2.11 ppm (2H, –N$\underline{H}_2$), δ 3.14 ppm (2H, –C–NH–C$\underline{H}_2$–).

2.4.1.3. Polyacrylonitrile-terminated octamethylenediamine PAN–OMDA (V). OMDA (272 g, 1883 mmol), and PAN (II) (10 g, 179 mmol) to yield 19.8 g (54% yield). The ^{1}H NMR Spectrum showed peaks at: δ 2.15 ppm (2H, –C$\underline{H}_2$-CH–), δ 1.25 ppm (1H, –CH$_2$C$\underline{H}$–), at δ 2.04 ppm (1H, =N$\underline{H}$), δ 2.11 ppm (1H, –CN$\underline{H}$CH$_2$–), δ 2.13 ppm (2H, –N$\underline{H}_2$), δ 3.15 ppm (2H, –CNHC$\underline{H}_2$–).

2.5. Evaluation of the amino group in PAN–EDA (III)

The introduction of the amino group was evaluated as per the method previously described (Shiva et al., 2009); a stock solution of bromophenol blue (BPB) was prepared by dissolving 10 mg/mL in DMF. 500 μL of the stock solution was diluted in 50 mL DMF. PAN–EDA (III) (0.5 g, 4.42 mmol) was added to this solution and the solution was stirred for 30 min. The precipitate was filtered and washed with 20% solution of piperidine in DMF for 20 min, and then the precipitate was re-filtered. The filtrate was measured using UV–vis at 605 nm and was used to quantify the amino group.

3. Results and discussion

Chemical modifications of polymers have received much attention due to the widespread applications of the final end products. Among these applications are their uses as ion exchangers, catalyst supports and solid phase synthesis, adsorbents, sensors, and our main interest in biomedical applications such as drug delivery vehicles and antimicrobial agents. The importance of acrylonitrile polymers is due to their facile modification through the nitrile group to a wide variety of functional groups.

In our study, polyacrylonitrile (II) was prepared by free radical polymerization using initiator pair of ammonium persulfate and sodium thiosulfate as a redox initiation system (Scheme 1). New amine-terminated PANs (III–V), as functional polymers were prepared by chemical modification of PAN (II) with different diamines (Scheme 1). Generally, the reaction was carried out in absolute ethanol using excess diamine (10-fold) to avoid the formation of crosslinked product. In addition, the reaction was carried out at different time periods and different temperatures to achieve the optimum conditions for the reaction.

The prepared amine-terminated PANs were found to be insoluble in water and common organic solvents except DMSO and DMF. Moreover, the introduction of amino group onto PAN made it a suitable candidate for immobilization of drugs, antimicrobial agents and enzymes for biomedical applications. The structure of the amine-terminated PANs was confirmed by TGA, FT-IR and ^{1}H NMR spectra.

3.1. ^{1}H NMR spectra

As shown in (Fig. 1), the ^{1}H NMR Spectrum of PAN (II) did not show the characteristic peaks at δ 5.52–6.00 ppm (singlet, C$\underline{H}_2$=CH–) which confirm the polymerization process. Moreover, the introduction of the amino group was confirmed by the presence of the characteristic peaks at δ 2.04–2.15 ppm which are related to the amino group as shown in the ^{1}H NMR Spectrum of polymers (III–V).

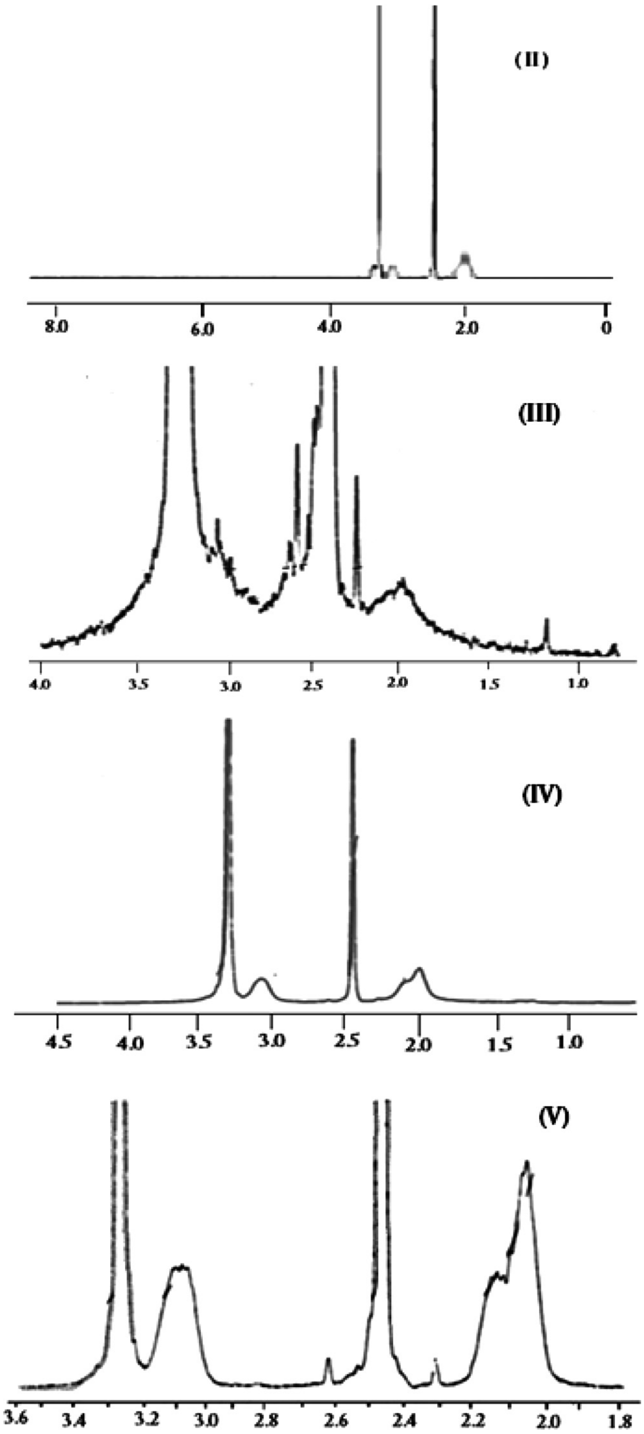


Figure 1 ^{1}H NMR spectra of polymers (II–V).

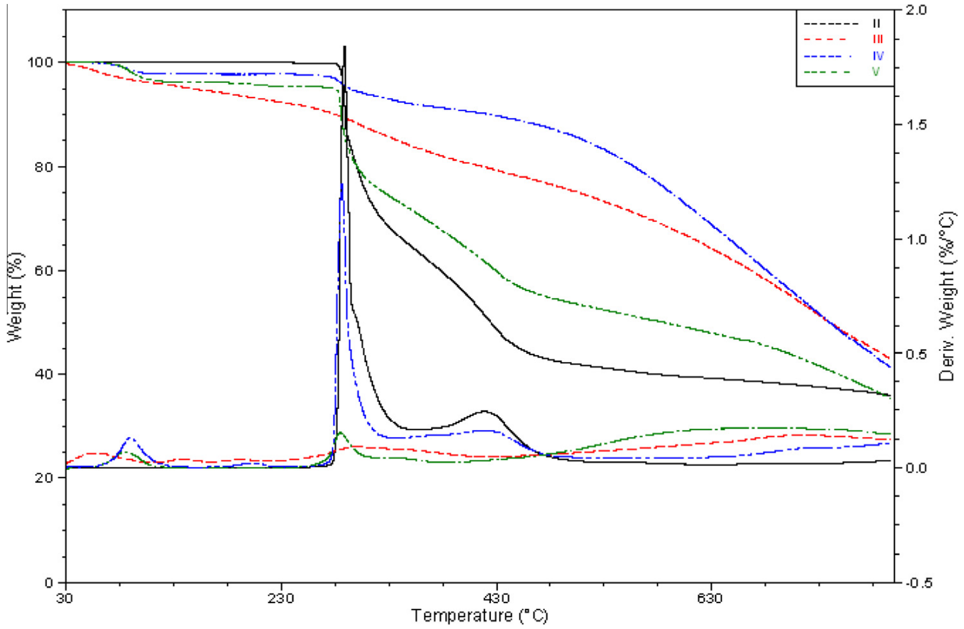


Figure 2 TGA thermograms of polymers (II–V).

Table 1 Proximate analysis (wt%) of polymers (III–V) based on thermogravimetric analysis (TGA).

Sample code	Distribution of volatile ranges (temperature range) (°C)			Residue (%) at 800 °C	T_{on} (°C)	50% Loss at (°C)
	Moisture 30–150	Grafted functional group 150–350	Remainder PAN > 350			
III[a]	1.5	14.6	34.6	49.3	272	790
IV[b]	0.7	20.0	29.8	49.5	274	791
V	3.8	24.4	36.5	35.3	282	588

[a] Grafted functional group degradation (150–335 °C).

[b] Grafted functional group degradation (150–400 °C).

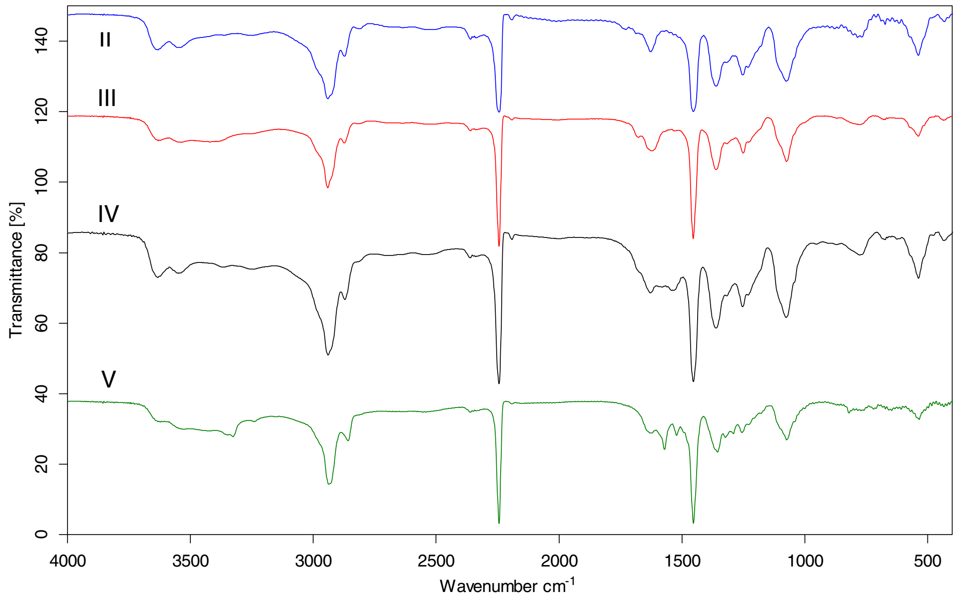


Figure 3 FT-IR spectra of amine-terminated PANs.

3.2. Thermal analysis

The thermal degradation analyses of the prepared polymers (II–V) were performed with a heating rate of 10 °C min^{-1} under nitrogen atmosphere (Fig. 2). The thermogram of PAN (II) shows three steps. However, the onset decomposition temperature for PAN (II) was 287 °C, and left a residue of 39.6% at 600 °C. The first step with a weight loss of 0.1% at 30–260 °C which may be attributed to the evolution of moisture, the second step with a weight loss of 36.6% at 260–358 °C which is attributed to the degradation of the cyclic structure and decomposition of the nitrile group and the last step represents the degradation of polyacrylonitrile chains at 358–500 °C with a weight loss of 21.2%.

Table 1 summarizes the TGA results of polymers (III–V). Generally, the thermogram of polymers (III–VI) shows a weight loss of similar pattern in three steps for all polymers. The first step ranges between room temperature and 150 °C for all polymers which may be attributed to the evolution of moisture. The second step of weight loss starts at about 150 °C and continues up to 335–400 °C due to the degradation of grafted diamine parts. The last step starts from 350 °C up to

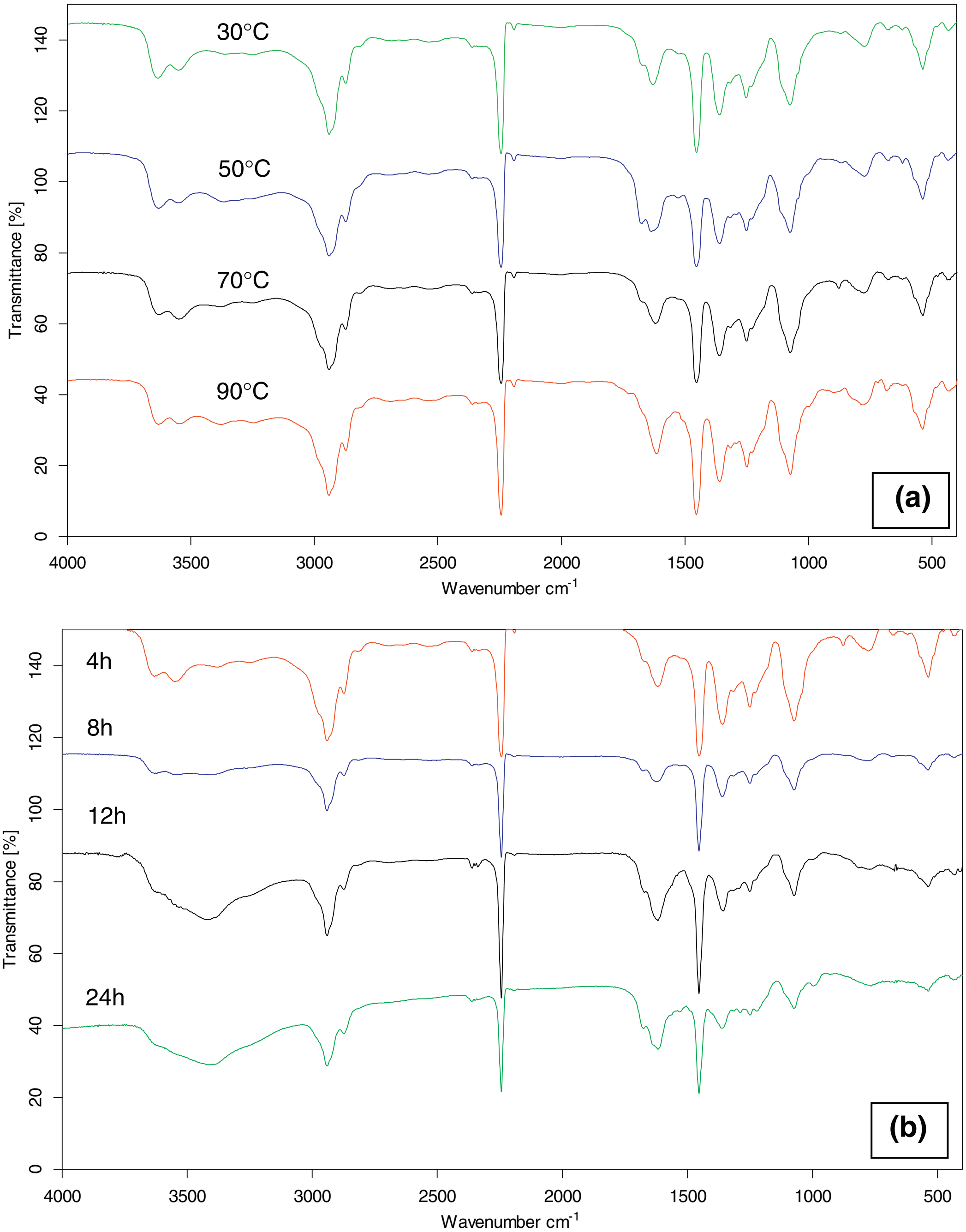


Figure 4 FT-IR spectra of PAN–ED (III); (a) at different temperatures for 4 h and (b) at different time periods for 70 °C.

over 800 °C, which may be due to the degradation of the remainder of polyacrylonitrile chains.

The data obtained in this study demonstrated slight differences in the thermal stabilities between the starting material, PAN and the amine-terminated PANs as shown in (Table 1).

3.3. FT-IR spectra

FT-IR spectroscopy was used to investigate the introduction of the functional groups onto polyacrylonitrile as presented in (Fig. 3). Characteristic sharp absorption peaks were observed at 2243, 1252 and 1075 cm^{-1} due to –CN stretching and bending vibrations, respectively and strong peaks at 2940 cm^{-1} correspond to –C–H stretching vibration and at 1361 and 1453 cm^{-1} due to –C–H in-plane deformation vibrations of CH$_2$ groups. On the other hand, the introduction of amino groups was also confirmed by FT-IR spectra. The spectra of the amine-terminated PANs (III–V) show many significant changes as well as the high decrease in the intensity of the absorption band of –CN stretching at 2243 cm^{-1} and at 1252 cm^{-1} which suggests the evidence of the introduction of amide and amino groups into the polymers as shown in (Fig. 3). In addition, a new broad band appeared around 3407, 3339 and 3350 cm^{-1}, respectively and new bands at 1629–1643, 1561–1571, and 1355–1456 cm^{-1} which are attributed to the N–H stretching vibration, demonstrating the presence of primary amine groups.

3.4. Optimization of amine-terminated PANs formation

To achieve the optimum conditions for the preparation of amine-terminated PANs (IV–VI), the reaction of PAN (II) with EDA was studied at different temperatures and different time intervals. FT-IR spectra were recorded to follow the effect of increasing temperature from 30 to 90 °C. Indeed, the obtained FT-IR spectra of the produced amine-terminated polymer showed many significant changes. On increasing temperatures, the intensity of NH stretch band that ranged from 3248–3548 cm^{-1} was slightly increased, and reached a maximum at 70 °C (Fig. 4a). On the other hand, there was observed a significant reduction of the intensity of the absorption peak of $C\equiv N$ groups of the PAN at about 2243 cm^{-1}. These results were in agreement with UV studies for the amino group content as shown in (Fig. 5a) in which we noticed the appearance of different blue color grades which confirm the presence of amino group. In addition, the introduction of the amino group was confirmed by the obtained results from the FT-IR spectra, and UV–vis spectroscopy. From our earlier results we can conclude that the optimum temperature to run the modification is 70 °C.

For the effect of time, PAN (II) was reacted with EDA at 70 °C for different time intervals that range from 4 to 24 h. The FT-IR spectra of the obtained PAN–EDA (IV) show many significant changes. As the time increases, the intensity of the absorption band of the nitrile group stretching at 2243 cm^{-1} and 1252 cm^{-1} and bending at 1075 cm^{-1} decrease. On the other hand the strong broad band at 3407 cm^{-1} corresponds to the stretching vibration of the –NH groups was also increased (Fig. 4b). In addition, the appearance of new bands at 1655, 1561, and 1392 cm^{-1} for PAN–EDA (III) suggest that the introduction of amino group onto PAN. Confirmation of the obtained results came from UV–vis studies (Fig. 5b). There was a gradual appearance of different blue color grades due to the conversion of nitrile groups to amino group in the polymeric side chains. As the time of reaction increased from 12 to 24 h, the intensity of the amino peak increased too. At the same time formation an insoluble polymer was observed most probably due to crosslinking which may take place by increasing the reaction time. In contrast, the amination reaction for only 12 h gave a soluble polymer whose FT-IR spectra showed a broad band around 3407 cm^{-1}. The last observed a result leading to rational design of the optimum condition to achieve the modification of PAN (II) with different diamines based on temperature and time factors. Finally, the optimum conditions for getting amine-terminated polyacrylonitrile can be obtained by heating the reaction mixture at 70 °C for 12 h.

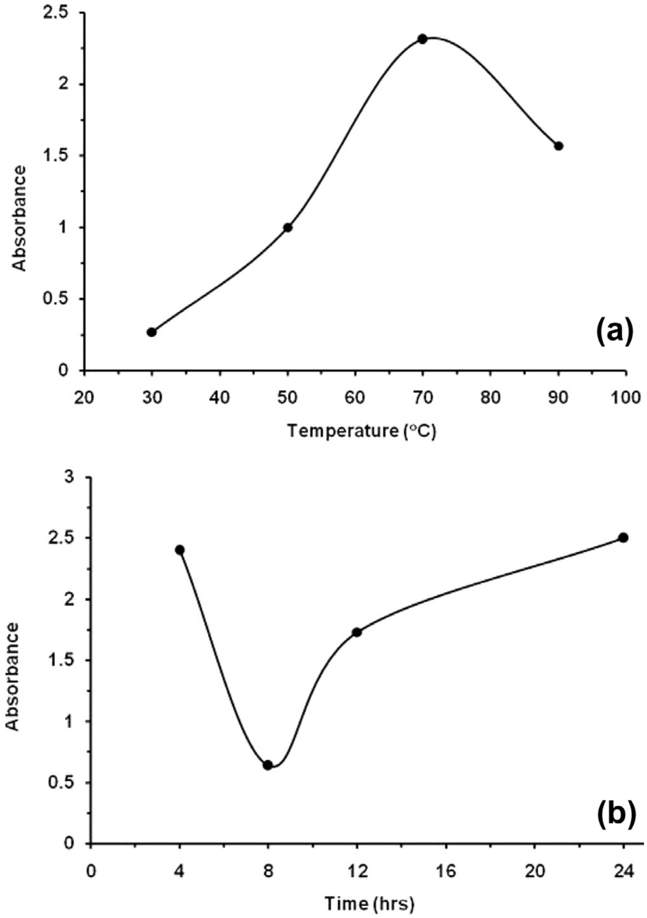


Figure 5 UV–vis Spectra for the introduction of amino group for PAN–EDA (III); (a) effect of time and (b) effect of temperature.

4. Conclusions

Amine-terminated PANs were prepared by reaction of polyacrylonitrile (PAN) with different types of diamines including ethylenediamine (EDA), hexamethylenediamine (HMDA) and octamethylenediamine (OMDA), to yield PAN–EDA, PAN–HMDA and PAN–OMDA, respectively. Chemical modification of polyacrylonitrile was carried out at different temperatures and different times to attain the optimum reaction conditions. The introduction of amino groups can be optimized at 70 °C for 12 h. The amine-terminated PANs were found to be water insoluble and have limited solubility in organic solvents. Moreover, the introduction of amino group into PAN made it a suitable candidate for immobilization of drugs, antimicrobial agents and enzymes for biomedical applications.

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