



## Preparation of polyacrylonitrile with different molecular weights and high conversion yield in aqueous phase polymerization

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### Abstract

Different molecular weights of polyacrylonitrile (PAN) homopolymers were prepared based on the process of aqueous phase precipitation polymerization of acrylonitrile. Aqueous phase precipitation polymerization system includes water as aqueous media, acrylonitrile as monomer, ammonium persulfate as initiator, and drops of HCl as the activator of polymerization process. The polymerization processes were investigated at different monomer and initiator ratios, and different pH. The results showed that molecular weight of prepared polyacrylonitrile increased up to with increasing the monomer ratio at optimized pH 2.25, and the conversion percent was decreased. However, with increasing initiator ratios the opposite trend was occurred, i.e. the molecular weight decreased and conversion percent increased. The optimized conditions for getting suitable molecular weight at high conversion (84%) were at pH 2.25, 90 g/L of monomer concentration, and 0.67 g/L of APS initiator at time 6 hr. The prepared polymers were investigated using XRD, FTIR, <sup>1</sup>H-NMR, TGA, and DSC. XRD results showed that crystallinity of the prepared polymers was decreased with increasing its molecular weight, as well as, the higher molecular weight of prepared PAN has more thermal stability than lower molecular weight.

Keywords: Polyacrylonitrile, aqueous phase precipitation polymerization, molecular weight, conversion yield.

### 1. Introduction

PAN is a well-known polymer with highly good mechanical and stability properties, due to the higher carbon content in its structure. The carbon-carbon in its backbone exhibits a higher biostability and resistance to hydrolysis, acids, alkalis and degradation. PAN is widely used in many applications such as membrane filtration, tissue engineering, high performance composite electronics and stilled a major precursor of carbon fibre (Adegbola, 2020). PAN produced as powder or granules by polymerization of acrylonitrile monomer. The most common techniques for preparation of PAN is aqueous phase precipitation polymerization, solution polymerization, and mixed solvent precipitation polymerization (Zhao, 2009). Through these above methods, the best technique is the aqueous deposition polymerization, due to some advantages than other methods. First, deionized water is the solution medium of aqueous deposition polymerization, which give a homogeneous phase of solution polymerization (Pan, 2003). Second, PAN polymers synthesized by this polymerization

method have a high molecular weight, due to the reduced probability of chain transfer coefficient of water. The higher molecular weight of PAN is desirable for new and developed spinning methods, such as dry-jet spinning to obtain the suitable spinning dope. Third, there are no extra impurities or uncomplicated computational relationships of an aqueous deposited copolymerization system (Zhao, 2009). Several research works have studied the preparation of PAN by this method, and they focused on the co-polymerization or terpolymerization of acrylonitrile with other vinyl monomers such as acrylic acid, methyl methacrylate, itaconic acid (Gupta, 1991; Bajaj, 1996; Pan, 2003), aiming to progress the hygroscopic character of PAN polymers and therefore easiness cyclization of nitrile groups to form a heterocyclic entity during thermo oxidation, as well as improve the conversion yield which cause a special high-performance PAN polymers for making a good-quality carbon fibers. But it was found that the comonomers which used in copolymerization and terpolymerization processes

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could decrease the mechanical character of the obtained polymer fibers (Zhao, 2009). Otherwise, some studies have focused on the PAN homopolymer preparation (Yang, 2011), by aqueous deposition polymerization in presence of metabisulfite as catalyst for persulfate initiator materials. However, the production yield of this methods may reach up to 90%, but with some unreacted materials remaining from the initiator or the catalysts causing some impurities of PAN polymer and changing some of its properties (Nishida, 1994), and this may need more purification steps. Russell K, et al, (Griffith, 1970) has prepared a thermoplastic and high purified PAN homopolymer with limiting conversion yield by aqueous deposition polymerization, without using any inorganic salts except water-soluble free radical polymerization initiator, at a temperature from 0 to 70° C, and the pH range of from 4.5 to 8.0.

In this work, the preparation of PAN homopolymer with different molecular weights at different conversion yield was carried out, by aqueous phase precipitation polymerization technique using water as aqueous media, acrylonitrile as monomer, ammonium persulfate as initiator, and drops of HCl as the activator of polymerization process at different monomer, and initiator ratios.

## 1. Materials and methods

### 1.1. Materials

The chemicals reagents which used in this work as following: Acrylonitrile (AN) 99% was obtained from Loba chemie, Ammonium peroxide sulphate (APS) from Chem-lab NV, Hydrochloric acid 37%, Dimethyl formamide from Biochem, and Distilled water was used to prepare all solutions. All the chemicals used as received and were of analytical grade.

### 1.2. Methods of Preparation

#### 2.2.1 Polyacrylonitrile preparation

Polymerization of AN was put into autoclavable bottle (500 ml) and stirred under a nitrogen atmosphere by APS as initiator and HCl as activator of polymerization process in aqueous media. In a batch containing different monomer ratios (82, 90, 98, 110, and 134) g/L water, at different pH (2.34, 2.24, and 2.18) and different concentrations of APS (0.1, 0.09, 0.07, 0.05, and 0.03) g/l, at 80°C for 6 h (Griffith, 1970) to obtain different molecular weights of PAN (PAN1, PAN2, PAN3, PAN4, and PAN5). The precipitated polymers were filtered, washed successively with distilled water and

acetone, and dried under vacuum at 60°C till a constant weight was obtained.

#### 2.2.2. Instrumentations and Experimental Techniques

- **Conversion:** The evidence of the copolymerization process was investigated by varied duplicate experiments. The conversion yield of prepared PAN was calculated according the following equation 1.

$$\text{Monomer conversion} = \frac{\text{Weight of polymer (g)}}{\text{Monomer feed (g)}} \times 100 \quad (1)$$

- **Molecular weight:** Viscosity average molecular weights ( $M_v$ ) of prepared polyacrylonitrile were calculated at  $(25 \pm 0.5)$  °C in oil bath based on method of Ubbelohde viscometer.

- **Fourier transform infrared (FT-IR),** In order to investigate the chemical changes that occurred during polymerization FTIR spectrophotometer (Genesis Fourier transformer FTIRTM) was used for (FTIR) analysis in Egyptian Petroleum Research Institute (EPRI). 2 mg from each samples, has been dried at 60°C overnight under vacuum and well-blended with 198 mg of KBr. 0.5 mm KBr disk of mixed powder was dried at 110°C for 24 h under vacuum, and then measured with IR spectrum (Shimadzu FTIR-4200 spectrometer) by 200 mg of KBr disk.

-  **$^1\text{H}$ NMR Spectroscopy.**  $^1\text{H}$ NMR was carried out using Varian 400MHz NMR Spectrometer in Micro analytical Unit, Faculty of Science Cairo University (MAU-FOPCU).

- **X-Ray Diffraction (XRD):** A modern PAN analytical diffractometer Xpert PRO model has been used for investigation of different forms of X-ray diffraction pattern using Nickel filtered copper radiation ( $\lambda = 1.542$  Å). The examination conditions of all diffraction patterns were at room temperature and at 40 KV & 40 mA.

- **Thermal analysis:** a Netzsch DSC 204 (Germany) was used for measuring thermal analysis character. 3–5mg weight of each sample was heated up to 700 °C with heating rate 10°C/min and cooling naturally under nitrogen atmosphere with flow rate of 60 mL/min at room temperature. After that, the traces of each sample were obtained from the second heating run.

## 2. Results and discussion

### 2.1. Measurement of molecular weight

Viscosity average molecular weights ( $M_v$ ) of prepared polyacrylonitrile were calculated at  $(25 \pm 0.5)$ °C in oil bath based on method of Ubbelohde viscometer according to the following equation (2) (Ju, 2014):

$$[\eta] = 2.83 \times 10^{-4} M_v^{0.759} \quad (2)$$

$[\eta]$  is the intrinsic viscosity and can be calculated by linear extrapolation between the concentrations of polymer and its relative viscosity obtained from Ubbelohde viscometer. Different concentrations (1, 0.7, 0.5, 0.3 and 0.1 g.L<sup>-1</sup>) from prepared polymers were used for molecular weight measurements. Table 1 shows the interesting viscosity and molecular weight average of PAN samples. As shown from this table the molecular weight of prepared PAN increases with decreasing ratio of initiator.

Table 1 shows the viscosity values, conversion yield and molecular weight values of prepared PAN samples at pH 2.25 and monomer concentration 90 g/L.

## 2.2. Effect of concentration of initiator on

Sample	Initiator (g/l)	$\eta$	Molecular weight (KDa)	Conversion (%)
PAN 1	0.22	5.74	741	74
PAN 2	0.37	4.80	580	80
PAN 3	0.52	3.94	451.56	82
PAN 4	0.67	1.87	169.12	84
PAN 5	0.74	3.04	319.8	85

### polymerization process

Figure 1 shows the relationship between the APS concentration with the molecular weight and the conversion of PAN in the precipitation polymerizations. As can be seen from this figure the conversion rate increases with increasing initiator concentration, this is because at very small concentration of APS, there are many AN uninitiated which cause decrease in the reaction rate and hence, very low conversion.

Whereas increasing the APS concentration, more radicals will form in reaction medium and consequently increase the conversion yield. However, as in the literature (Eldin, 2017; Boguslavsky, 2005) after initiator concentration reaches a certain limit, the hydrophobic polymers with short chain are very close to the polymeric radicals. Then the growth rate of micelles will not increase, so the conversion will not increase obviously.

On the other hand, the figure shows that the molecular weight is decreased with increasing APS concentration up to 0.74 g/l of APS it again increases, as it is known, in free radical polymerization, the initiator free radical species start to react with monomers to create active centers from free monomer radicals. Then these monomer radicals react with other non-radical monomers and propagate to form the molecular chain radicals and then form polymer radicals. Increasing initiator concentration initiates more radicals resulting in many propagated chains resulting in fast chain termination and then low molecular weight polymer (Tang, 2020; Duan, 2018). At certain initiator

concentration, it was noticed that the molecular weight unusually tends to increase and this may be due to the chain transfer to polymer resulting in branched polymer (Tang, 2020).

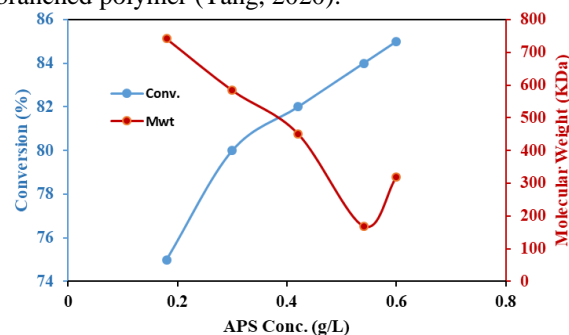


Fig 1. Effect of initiator (APS) concentration on the conversion of polymerization and molecular weight of PAN at pH 2.25, monomer concentration 90 g/L, and 6 hr.

## 2.3. Effect of monomer concentration on polymerization process

Monomer concentrations could affect both conversion yield and molecular weight of PAN polymerization, as shown in Fig 2. It is clear from this fig. that the conversion rate of PAN first increases to some extent, this is probably due to an increase of AN monomer concentration may have increased the polymerization rate (Boguslavsky, 2005), due to the precipitation rate of the radical oligomeric chains occurred rapidly, and consequently the consuming of monomer radicals in the oligomeric phase is increased (Jamil, 2015; Boguslavsky, 2005). The increasing monomer concentration causes an increase of formation of precipitated radical oligomeric chains (which are not soluble in water). These precipitated radical oligomeric chains can absorb the radicals of AN monomer, and consequently the propagation process could continue in both the oligomeric phase and the water phase, leading to an increase in polymerization rate. Otherwise, during the polymerization processes in both oligomeric phase and the water phase, the termination and the chain transfer are difficult, which resulted in higher yields (Boguslavsky, 2005; Wan, 2005). Fig2. shows also decreasing of conversion after increasing the monomer concentration than 9 g/L. The possible reason is that larger molecular volume of produced polymer chains can accumulate and resist the expansion of polymer chains and diminish the polymerization conversion (Ju, 2014). The molecular weight of prepared PAN is also strongly affected by AN monomer concentration as also shown in Fig. 2. The high molecular weight of PAN is obtained at abundant monomer concentration, this is due to the abundant concentration of monomer will activate and initiate many sites of many polymer chains, leading to formation a longer PAN

chains. On the other hand, at lower concentration of monomer, the shorter PAN chains are formed, leading to lower molecular weight (Shatat, 2017).

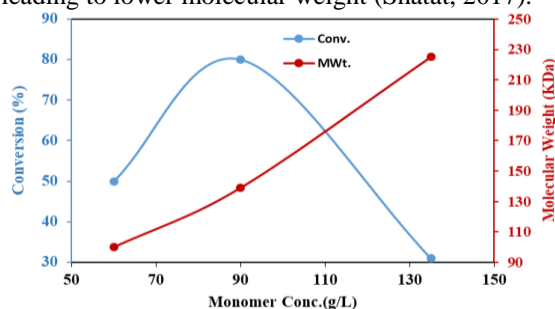


Fig 2 Effect of monomer concentrations on conversion polymerization and molecular weight.

#### 2.4. Effect of pH

The acidity of the polymerization medium affects the conversion and molecular weight of the produced polymer as shown in fig 3. From this figure, polymerization of acrylonitrile in an aqueous solution at pH 2.25 has the higher conversion (Griffith, 1970).

This is due to the partial protonization of nitrile group in the acrylonitrile monomers making it more active and the polymerization rate increased in acidic medium (pH 2.25). While at pH  $\geq 3$  the conversion is low owing to the absence of the activated protons and hence the lower activity of the monomers and then lower polymerization rate. On the other hand, when the acidity increase (pH  $\leq 2.2$ ), an excess  $H^+$  protons, may make partial hindrance to protonated monomers to react together and then the conversion decrease. The figure also shows that lower molecular weights are produced at pH rang of 2.3 - 2.2, due to presence of excess activated protonated monomers which form several propagated chains and fast termination may occur. Out of this rang of pH the length of the propagated chains may become longer, due to the lower activity of radicals monomer based on the  $H^+$  ions in the solution, and hence the molecular weight can increase.

#### 2.5. FTIR Analysis

FTIR charts of prepared polyacrylonitrile are shown in Fig.4. These figures indicate that, the different molecular weights of PAN exhibit characteristic functional groups of CN stretching sharp bands at  $2244\text{ cm}^{-1}$ . In all prepared polyacrylonitrile polymers, the bands at  $2868\text{ cm}^{-1}$  were assigned to C-H stretching whereas, the bands at  $2943\text{ cm}^{-1}$  correspond to  $CH_2$  stretching (Fochler, 1985). The peaks at 1453, 1364 and  $1249\text{ cm}^{-1}$  correspond to the vibrations different mode of C-H. The band at  $1640\text{ cm}^{-1}$  may be assigned to carbonyl group

obtained from hydrolysis of  $-C\equiv N$  group in polymerization medium (Jamil, 2012). The absorption peak at  $532\text{ cm}^{-1}$  designated to  $-C-C\equiv N$ . While the band at  $1078\text{ cm}^{-1}$  is designated to the C-H binding mode, the band at  $1249\text{ cm}^{-1}$  is assigned to the methine ( $-CH$ ) group bending mode coupled with the methylene (C-H,) groups rocking mode (Bajaj, 1996; Minagawa, 1980). From above figure, there are no effects of PAN molecular weight on the FTIR bands.

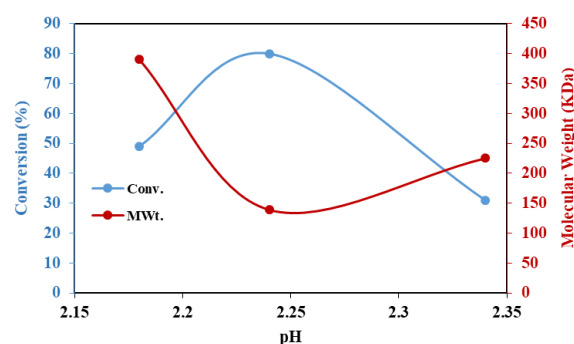


Fig 3: Effect of pH on conversion and molecular weight

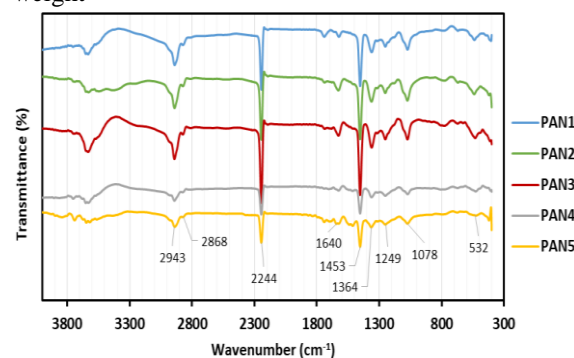


Fig.4 FTIR data of different molecular weights of PAN

#### 2.6. HNMR Analysis

Different molecular weights of PAN were analysed by  $H^1$ NMR spectroscopy for further investigation, Fig. 5 shows the  $H^1$ NMR spectroscopy for PAN1 as the higher molecular weight and PAN4 as the lower molecular weight, the signals at about 2.056 ppm refer to methylene ( $C-H_2$ ) protons and 3.14 ppm was from methine ( $CH-$ ) protons (Bai, 2019). Whereas, the strong band at 2.531 may be due to the protons of dimethyl sulfoxide- $d_6$  (Bajaj, 1996). In previous studies (Izunobi, 2011; Nguyen, 2015) it is found that the molecular weight of polymers is determined by the proton peak intensities and its area integrate. As can be seen from Fig. 5 the intensities of both methine ( $CH-$ ) and methylene ( $C-H_2$ ) protons are directly proportional with the molecular weight.



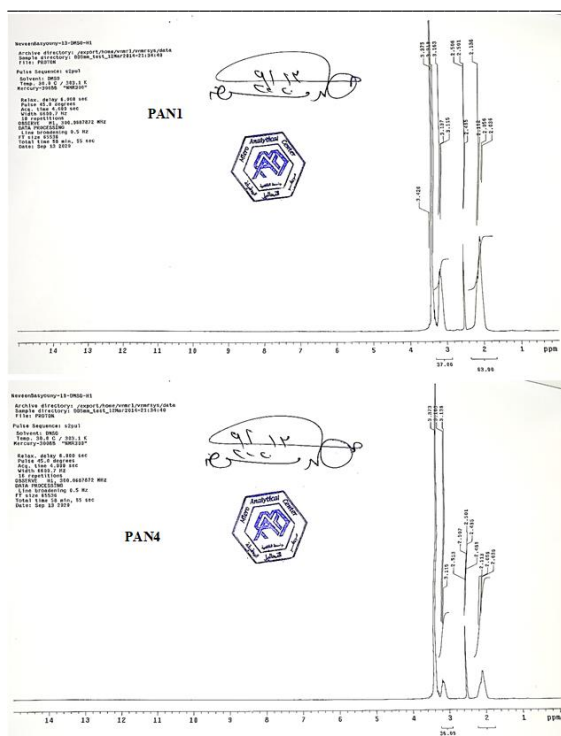


Fig. 5 <sup>1</sup>H NMR spectra of PAN1 and PAN4

**2.7. X-ray Diffraction**

X-ray diffraction (XRD) characterizations were conducted to investigate the crystallinity of different molecular weights of prepared PAN. XRD patterns show the reflection strong peaks existed around  $2\theta = 17^\circ$  and a weak one at  $29.5^\circ$  superimposed on an amorphous halo (Yin, 2012; Boguslavsky, 2005a; Boguslavsky, 2005b; Badawy, 2003) as shown in Fig 6. This figure show also that with increasing the molecular weights of prepared polymers the crystalline peaks value at  $17.12$  decrease to  $16.68$ , due to the incorporation of high molecular weight chains which prevent the interactions between intermolecular  $C\equiv N$  groups, which could decrease the PAN crystallinity (Ju, 2014).

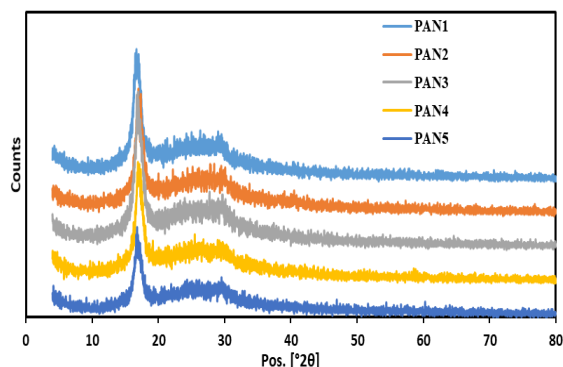


Fig. 6 XRD of different molecular weights of PAN

**2.8. Thermal analysis**

**2.8.1. TGA**

Thermogravimetric analysis (TGA) was conducted to measure the behavior of weight loss of prepared PAN with changing temperatures. Fig. 7 shows the TGA curves of different molecular weights of prepared PAN. Physical reaction such as water evaporation, and chemical reactions, such as cyclization, degradation and thermal cross-linking are resulted in heating of PAN, based on the mass and molecular weight of the polymer samples (Alarifi, 2015). TGA curves show that the mainly weight loss of all PAN samples occurred by the pyrolytic reactions at around  $280^\circ C$ . As can be seen from Fig. 7, the TGA curves of PAN show four-steps of weight loss patterns. In the first step up to about  $250^\circ C$ , there was no weight loss, due to the cyclization reaction takes place (Ouyang, 2008). The cyclization reactions of PAN polymers occurred before any mass loss at around  $200^\circ C$ , and include the formation of aromatic rings resulting from reaction of nitrile groups with other functional groups (Boulet, 2015; Xiao, 2011). At the second step (from  $250.9$  to  $282.83^\circ C$ ), shows about 20 % of weight loss for all samples, indicating that a dehydrogenation and evaporation of  $H_2$  as a chemical reaction has occurred. The onset temperature of these samples at this stage were at a range  $250^\circ C$ , which is the same in DSC thermograms as the exothermic peaks (Taheran, 2016) as shown in Fig. 9. At the third step, 25% weight loss was also observed from  $280 - 433^\circ C$  that might be due to partial vaporization of both ammonia and Hydrogen Cyanide (Ouyang, 2008). At the fourth step, from  $433 - 510^\circ C$ , the settled weight loss about 60.5% was observed, suggesting to complete vaporization of polymer chain residuals from the PAN (Alarifi, 2015). In general, TGA analysis has exhibit the influence of thermal degradation by molecular weight of PAN samples, as clear from figure 4, with decreasing the molecular weight of PAN it is could be decreasing thermal stability, this may due to the chain length of polymers.

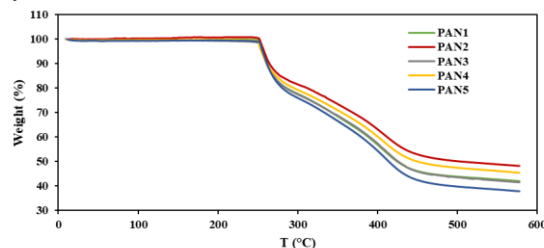


Fig. 7 TGA of different molecular weights of PAN

**2.8.2. DSC**

A differential scanning calorimetry (DSC) was applied to the thermal properties of the prepared PAN from (0-600 °C). As can be observed from Fig. 8, that the PAN polymer samples show a

broadening exothermal peaks localised around 245 °C, with onset temperature around 190 °C, after that the reaction was done around 250 °C. this is due to the cyclization processes which take place by the nucleophilic attack mechanism (free radicals mechanism) at nitrile groups, and the cyclization process continues to a next conjugated structure (Taheeran, 2016; Bhanu, 2002).

The second observed peaks of PAN samples in DSC chart, is the sharpening exothermic peaks around 280 °C, it may be due to the interfering of the free radical cyclization and various exothermic reactions such as, dehydrogenation, evaporation of NH<sub>3</sub> and HCN groups, and fragmentation of polymer chains, that can be occurred at high temperatures. The highly exothermic cyclization of nitrile groups causes the cracking of PAN polymer chains, due to the rapid heat accumulating in the samples (Alarifi, 2015; Aviles, 2002). Furthermore, it is clear from Fig 9 that the cyclization and fragmentation processes of PAN polymers are depending on its molecular weight, as increasing the molecular weight of polymer increase the temperature of cyclization and fragmentation processes, it may due to the intra and intermolecular hydrogen bonds in high molecular weight polymers chains.

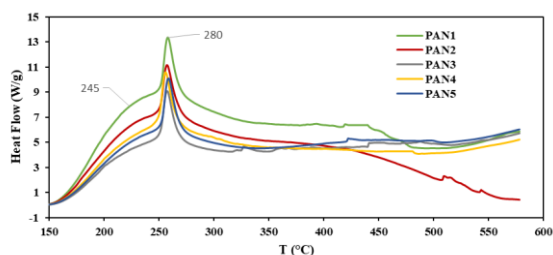


Fig. 8 DSC of different molecular weights of PAN

### Conclusion

A high purity of PAN homopolymer has been prepared with high conversion yield and different molecular weights by aqueous phase precipitation polymerization. It was found that an increase of monomer concentration increases of both conversion yield and molecular weights, due to increasing the polymerization rate. As well as, the increasing of initiator APS cause increase in conversion yield and decreasing in molecular weight of PAN. The optimum pH of this polymerization method was at 2.25 which obtained high conversion yield and favourable molecular weight. <sup>1</sup>HNMR peak intensities of prepared PAN samples are directly proportional with the molecular weight. However, XRD data exhibited decreasing in crystallinity properties with increasing molecular weight of prepared PAN. Further, thermal analysis

showed that the high molecular weight PAN is thermally more stable.

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