# CHAPTER II

THEORY

2.1 Nylon6

Nylon6 or polycaprolactam or polyamide6 (PA6) is a polymer developed by Paul Schlack at IG Farben. Nylon6 is synthesized by ring opening polymerization of caprolactam. When caprolactam is heated at about 533 K in an inert atmosphere of nitrogen for about 4-5 hours, the ring breaks and passes polymerization. During polymerization, the peptide bond within each caprolactam molecule is broken, with the active groups on each side reforming two new bonds as the monomer becomes part of the polymer backbone.
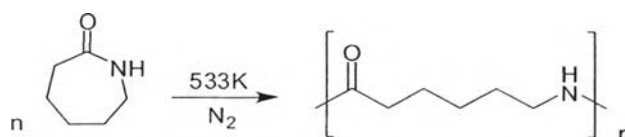
Structure of nylon6

Nylon6 fibers are possessing high tensile strength, tough, elasticity and luster. They can be highly resistant to abrasion and chemicals such as acids and alkalis. The fibers can absorb water up to 2.4%. Nylon6 is a solid (glassy) state at room temperature. Nylon fibers are highly crystalline. Crystallinity can be changed and controlled through various processing techniques.

Advantages
- Good surface
- Strength
- Inflexibility
- Chemical resistance to hydrocarbons

Disadvantages
- High water absorption
- Poor chemical resistance to strong acids and bases

2.2 Polystyrene

Polystyrene (PS) is known more than one hundred years but the nature of the real molecules has not been clarified until 1920. Staudinger described the materials of molecular structure in the early days of polymer science. About 1930 I.G. Farben, in Germany, was the first to produce foam. At the same time, the Dow Chemical company began developing their materials too. Polystyrene is a long chain hydrocarbon that alternating carbon centers are attached to phenyl groups.
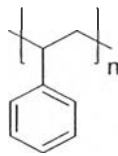
Structure of polystyrene

Polystyrene is an amorphous, glassy polymer that is generally rigid and relatively cheap. Polystyrenes have good flow properties at temperatures safely below degradation ranges, and can easily be extruded, injection molded, or compression molded. The vast quantities of polystyrene are produced in the form of heat-expandable beads containing a suitable blowing agent which ultimately results in familiar foamed polystyrene articles. Polystyrene is a solid (glassy) state at room temperature.

Advantages
- High impact resistance
- Flame retardant
- High heat resistance
- High flow

Disadvantages
- Poor solvent resistance, attacked by many chemicals
- Homopolymers are fragile
- Subject to stress and environmental cracking
- Poor thermal stability
- Flammable, but retarded grades available

2.3 Polyacrylonitrile

Polyacrylonitrile (PAN) or commonly known as acrylic is synthetic, semicrystalline organic polymer resin. It melts above 300 °C if the heating rates at 50 degrees per minute or above. Almost all polyacrylonitrile resins are copolymers to make from mixtures of monomers with acrylonitrile as the main component. The acrylonitrile repeating unit of the polymer has the following structure.
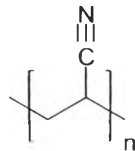
Structure of polyacrylonitrile

The appearance of polyacrylonitrile is white powder. Polyacrylonitrile fibers are the chemical substrate of high-quality carbon fiber. PAN is first thermally oxidized in air at 230 °C to form an oxidized PAN fiber and then carbonized above 1000 °C in inert atmosphere.

Advantages
- good weather resistance
- resistance to sun
- resistant to chemical reagents

Disadvantages
- not high strength
- poor fatigue resistance
- poor wear resistance

Table 2.1 The physical properties of polymers

Polymer	Chemical formula	Transition temperature[a]		Density[b] (g/mL)
		T_m	T_g	
nylon6	$(C_6H_{11}NO)_n$	228.5 °C	62.5 °C	1.084
polystyrene	$(C_8H_8)_n$	240 °C	100 °C	1.047
polyacrylonitrile	$(C_3H_3N)_n$	317 °C	85 °C	1.184

[a] T_m = melting temperature, T_g = glass transition temperature

[b] density at 25 °C

2.4 Electrospinning

2.4.1 Electrospinning process

Electrospinning is a process used for the formation of thin fibers which a charged liquid polymer solution is introduced into a very high electrostatic force. It can produce fibers with diameters range from a few nanometers to more than 1 of micrometers [31]. The obtained fibers have high surface area to volume ratio and several small pores. These fibers are interest for such application as filter media, optical sensor, electrode materials, biomedical application, pharmaceutical, protective clothing and chemical protection, etc. The electrospinning setup consists of three basic components:

- a high voltage power supply
- a spinneret such as pipette tip, a capillary with metal needle
- a collector such as a metal screen, stationary plate and rotation drum

Figure 2.1 shows two typical experimental setups for electrospinning including a vertical and a horizontal setups.

(a) (b)
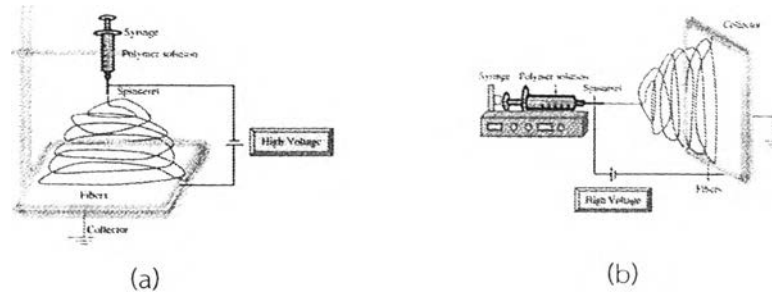
Figure 2.1 Schematics of set up of electrospinning apparatus:

(a) a typical vertical set up, (b) a typical horizontal set up [32].

In the electrospinning system, liquid polymer solution is dispensed by a needle that connected to a high voltage. The ejected polymer solution forms a continuous nanofiber when the electrical force (due to the high voltage potential of the polymer solution) overcomes the surface tension. Under applied electrical potential, the spherical pendant droplet at needle tip will change shape from semicircle to conical shape which called "Taylor's cone" [33]. If the voltage exceeds a critical value, the electrical force overcomes the surface tension and a fine charged jet is ejected. The

Taylor's cone of formation is shown in Figure 2.2. Later solution jet will be stretched until it has a smaller diameter than nanometers. After the solvent evaporates from nanofibers are left before falling on the collector.
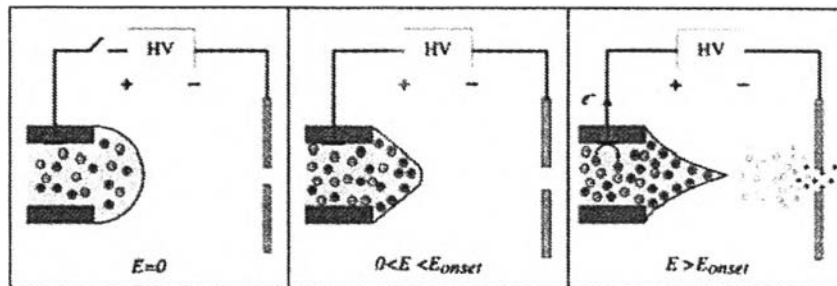

Figure 2.2 The model of polymer solution changing when electric potential increases [34].

2.4.2 Parameters of electrospinning

The main factors that affect with morphology and diameters of the electrospun fibers can be classified into two groups: material parameters and process parameters.

2.4.2.1 Material parameters

2.4.2.1.1 Solution concentration

Solution concentration, molecular weight of polymer and viscosity are correlated factors that if used high molecular weight is effect to increase in solution concentration and increase in solution viscosity. The diameter and the formation of electrospun fibers are resulted from the concentration and viscosity of solution [32]. At the high concentration, the appearance of beads can convert from globular to pivot form and larger diameters of fibers are created because the increasing of viscosity resistance within solution and the inability to uphold the solution flow at the end of the needle tip.

2.4.2.1.2 Surface tension

The important parameter of electrospinning process is surface tension. Ordinarily, the high surface tension of solution prevents the process of spinning due to an unstableness of the jet and the production of sprayed droplets

[35]. Bead formation can be induced by changing the surface tension of the solution. While the lower surface tension of solution is not always suitable for electrospinning, but the obtained electrospun fibers from this has not bead formation. Surface tension of polymer solutions changes depending on the polymer concentration.

2.4.2.1.3 Dielectric constant (Ɛ)

The dielectric constant is a constant that indicates how easy a material can be polarized by imposition of an electric field on an insulating material at any temperature. The differently of electric field is affected by solvent with different values of dielectric constant. Moreover, this parameter is effect on the morphology and diameter of electrospun fibers [36].

2.4.2.2 Process parameters

2.4.2.2.1 Applied electric potential

Applied electric potential is important parameter in the electrospinning process. At the optimum applied field can create the electrospun fibers. When increasing electric potential, the electrostatic repulsive force on the polymer jet is increased. As a result, the fiber diameter is decreased. Applying higher voltages are obtained through decreasing the distance from the tip to collector. The effects of electric potential on morphology and diameter of fiber have to be considered together with other parameters, particularly the flow rate and the distance between the needle and the collector [37].

2.4.2.2.2 Distance from tip to collector

The distance from tip to collector has an influence on the time spent in the evaporation of solvent and the strength of the electric field [38]. There are some researchers reported that the collected fibers are dried, completely stretched, and the fiber diameter is reduced when increased the distance from tip to collector. Reducing the distance is shorter and solvent evaporation time, and increases the electric field strength, which results in increase of bead formation. Therefore, the optimum distance between a tip and collector is needed for solvent evaporation.

2.4.2.2.3 Flow rate

The influence of flow rate can observably affect the velocity of the jet fluid, solvent evaporation, and morphology of the obtained fibers. An enough time for solvent evaporation with a low flow rate is an objective for electrospinning process as a result of no bead formation on fibers and the decrease in diameter of fibers [39]. In contrast, a high flow rate applied in the process of electrospinning, the resulting fiber is formed with the opposite outcome. Furthermore, the characterization of used low flow rate fibers was fine fiber.

2.5 Solid-phase extraction

Solid-phase extraction (SPE) is the most popular sample preparation method for extraction, preconcentration and cleanup of analytes with subsequent chromatographic analysis [40-42]. Compared with the traditional extraction techniques such as liquid-liquid extraction, SPE is fast, less consumption of organic solvents, good reproducibility and easy to do automation. SPE process is shown in Figure 2.3. Stationary phase can be either solid or liquid; however, if it is liquid, it has to be immobilized or absorbed on solid. Some of the components would be retained and some would be eluted. Therefore, separation between components is succeeded.
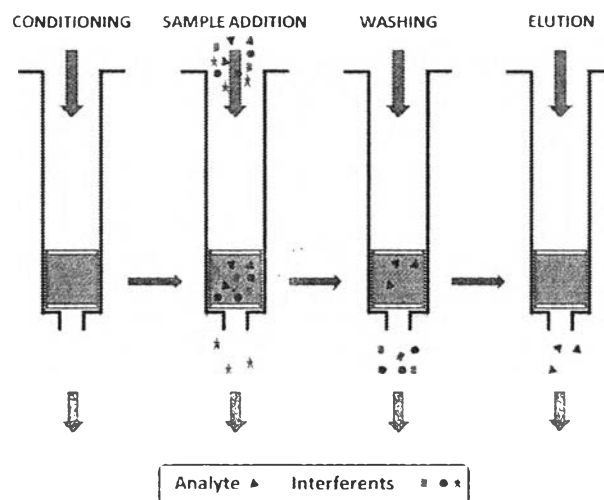

Figure 2.3 Solid phase extraction process.

The development of the SPE has progressed by focusing on the fabrication of the device. The heart of the SPE technique is the sorbent material as it has a direct influence on the selectivity, sorptive capacity and the format of the SPE device. To

optimize extraction, it is important to recognize the nature of the sorbent depends on the characteristics of physical chemistry. The most important physicochemical characteristics for optimal extraction are porosity, specific surface area and surface chemistry. In recent years, fabricated by the introduction of new sorbent and formats [43], SPE technique has been developed and applied in the determination of food, biological, drugs, pesticides and environmental, etc.

2.6 Sorption

Sorption can refer to a process that a substance (sorbate) is adsorbed or absorbed on sorbent. This process can occur at the contact surface between the two conditions, such as liquids with liquids, gas with liquids, gas with solid or solid with liquid. In the sample preparation, the term sorbent refers to the solid extracting phase, including solid-supported liquid phases upon which an analyte is retained. The difference between adsorption and absorption are described by Schwarzenbach and co-workers [44]: adsorption as meaning onto two dimensional surface and absorption meaning into a three dimensional matrix. Figure 2.4 shows analyte adsorption (analyte retained onto the adsorbent surface) and absorption (analyte retained into the bulk of the absorbent) type extraction mechanisms.
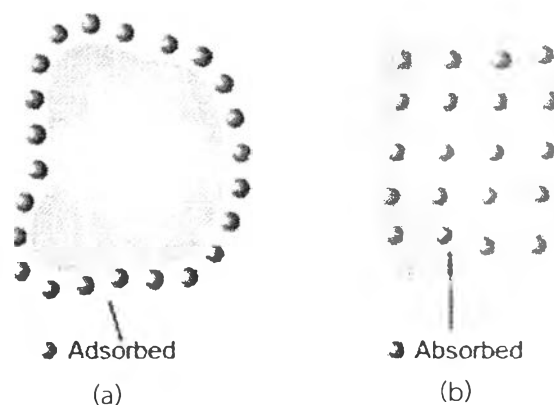

Figure 2.4 Schematic representation of (a) adsorptive and (b) absorptive extraction processes [45].

Although the sorption by using the techniques of extraction can be divided according to the absorption or adsorption processes, the two processes are not completely separated according to where they occur together. In principle, what is different is the extent of participation of the widespread extraction mechanism,

depending on the characteristics of phase extraction. Therefore, it may be difficult to distinguish the differences between the two processes [46]. So, sorption is typically used to refer to the combination of these processes. Although the scope of the mechanism of adsorption or absorption in extraction is uncertain, fundamentally, all sorption depends on the extraction technique is signifiable by the thermal partitions or distribution coefficients K, which show as the ratio of analyte concentration in the sorbent phase, $C_{sorbent}$ to that in the sample phase, C_{sample}:

$$K = \frac{C\ (sorbent)}{C\ (sample)}$$

For adsorption, surface structure (porosity and surface area) is the more important sorbent characteristic compared to chemical composition. At the same time, the chemical composition of the liquid phase is more important for the absorption.

Phase sorption of samples is basically a dynamic process in a heterogeneous system that transport of the analytes between the sorbent and the sample phase is succeeded. The process profits by a reduction in free energy until it reaches the minimum value (that is the equilibrium). The mechanism of analyte adsorption or absorption is controlled by the characteristics of interactions between the analyte and active sites of the sorbent. Thus, the selection of a sorbent depends on the binding mechanisms between the sorbent and interesting analyte.

The process of sorption analysis consists of several steps, some steps may become rate limiting in the control of the sorption of analyte. The analyte may interact with a sorbent at least four ways:

1. Through the absorption, the analyte may interact with the sorbent by entrance its three dimensional structure. Three dimensional of entry into the sorbent is an especially controlling process for solid supported liquid phases. In the process of absorption are not competitive for sites; therefore, absorbents can have a high capacity for the analyte.

2. The analyte may interact two dimensional with surface of sorbent through adsorption due to intermolecular forces [47]. Surface interactions may result in movement of solvent molecules by the analyte. In the adsorption process, analytes may competition for sites; thus, adsorbents have limited capacity. Three steps occur during the adsorption process on porous sorbents; (I) film diffusion (when the analyte through a surface film to the surface), (II) pore diffusion (when the analyte through the pores of the solid

phase), and (III) adsorptive reaction (when the analyte binds, interacts with the sorbent surface) [48].

3. The analyte is ionizable in aqueous solution, it may be an electrostatic attraction between the analyte and the charged sites on the surface of sorbent. Sorbents is especially designed to complete these types of ionic interactions are assigned to as ion exchange.

4. It is possible that the analyte and the sorbent may be chemically reactive toward such as the analyte was born covalent bond with the sorbent. This type of sorption is normally disadvantageous to analytical recovery and may lead to decreased recovery.

For porous sorbents, most of the surface area is the nanopores of the sorbent (see Figure 2.5). Nanopores of the sorbent are divided into three types; micropores (diameters smaller than 2 nm), mesopores (2 to 50 nm), and macropores (more than 50 nm) [49]. Most of the surface area is micropores and mesopores. Porous of sorbents alter in pore size, shape, asymmetry, and properties are characterized such as particle diameter, particle distribution, pore diameter, pore volume and specific surface area.

Macropore
Region
>500 Angstrom

Mesopore
Region
20-500 Angstrom

Micropore Region
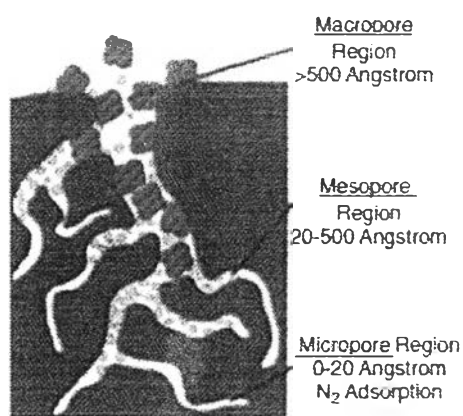0-20 Angstrom
N_2 Adsorption

Figure 2.5 Schematic representation of porous regions of a sorbent [50].

Choosing sorbent for SPE techniques is selected according to ability of a material to retain analytes selectively and rapid and complete elution. The sorption process must be reversible [51]. Moreover, SPE sorbents should have a large specific surface area as well as display stability in the sample matrix and elution solvents. Finally, a sorbent material with a good surface connect with the sample solution will be most desirable.

Poole and co-workers [52] classified SPE sorbents into three categories; (I) general purpose, (II) class specific and (III) analyte specific. A retention mechanism is the most common in SPE are based on van der Waals forces, hydrogen bonding, dipole-dipole interactions, π-π interactions and ion exchange interactions.

Choice of fabrication technique of SPE sorbent could be looked as one that produces a material that displays chemical and morphological properties that can be easy adjusted. In addition, an optimal SPE sorbent material associates the following benefits: (I) small diameter, (II) large specific surface area, (III) easy fabrication, (IV) ability to be adjusted in order to combine all sorbent functionalities, (V) ability to be adjusted in order to combine all sorbent morphologies (VI) a material that can be packed in the lower than 10 mg range without showing a backpressure limitation or low analyte recoveries.

The beginning of nanotechnology has been a significant leap forward in the research of sorbent based on sample preparation techniques as it opened up opportunities for a new class of materials that could be used in SPE applications. The main benefit of nanostructured materials is their large specific surface area that expedites the miniaturization of SPE allowing for the use of a reduced sorbent bed mass that achieves high extraction efficiency.

Although nanoparticles improved performance as sorbent material [53], they innately display some limitations. One of the main challenges is involved with their handling in packed SPE formats.

Currently, most sorption materials for SPE are in the bead shape. Typically, these beads are packed in a cartridge or column [54]. A disadvantage of the cartridge design is that due to its small cross-sectional area, sample rate are slow and the tolerance to blockage by particles and adsorbed matrix components is low. However, the intrinsic problem of all particulate media is their inability to completely fill the available space. In addition, the channeling between particles reduces the extraction efficiency and short column cannot be applied at high flow rates. Figure 2.6 shows the cartridge designs.
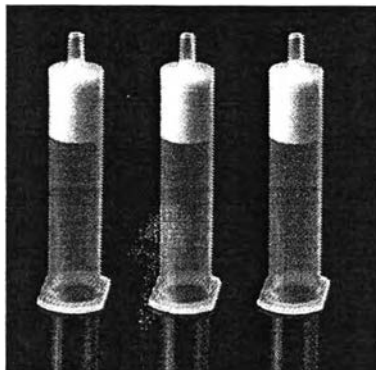
Figure 2.6 SPE cartridge format.

This has led to the development of new SPE formats such as disks with embedded small sorbent particles as shown in Figure 2.7.
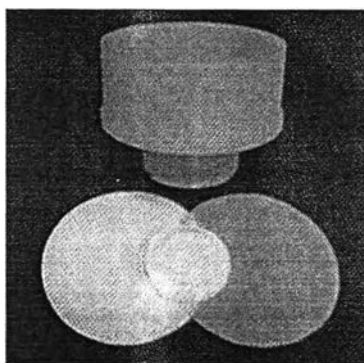
Figure 2.7 SPE disk format.

The short sample path and small particle size allows efficient trapping of analytes with a relatively high flow rate through the sorbent as compared to the cartridges [55]. The disk has many more particles and a much more tortuous path of flow, which means that there is considerably more surface area available and the kinetics of sorption is much quicker for the disk than the cartridge. SPE disk is suitable for the separation of trace analytes in large volume of samples due to the high fluid permeability and high adsorption ability. The difference lies in the particle size as shown in Figure 2.8.
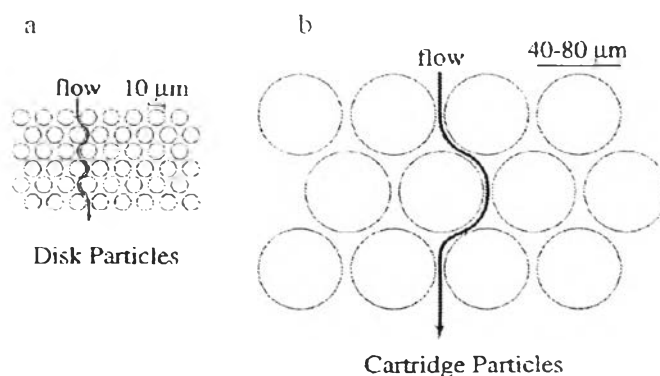
a   flow   10 μm

Disk Particles

b   flow   40-80 μm

Cartridge Particles

Figure 2.8 Schematic representation of flow paths within
(a) disk and (b) cartridge microparticle sorbent beds [56].

2.7 Analysis of aldehydes

There are many studies about extracting aldehydes using solid phase extraction. SPE is known to be a rapid and straightforward method; moreover, has been developed for derivatization and preconcentration of carbonyls in aqueous samples. Other sorbent such as C_{18} cartridge was used to extract aldehydes while the derivatization and preconcentration of the analytes take place simultaneously. The direct determination of aldehydes is complicated due to their volatility, high polarity, chemical instability and the lack chromophore in structure, leading to poor quantification. Therefore, derivatization of aldehydes with suitable reagents will provide stable products with chromophores which can be detected by chromatographic techniques. A variety of derivatizing reagents such as DNPH and PFBHA used for quantification of aldehydes by HPLC and gas chromatography (GC) analysis, respectively. DNPH derivatization is followed by HPLC and ultraviolet detection (UV). PFBHA derivatization is followed by gas chromatography and electron capture detection (GC–ECD). This method provides thermally stable and volatile oximes. The PFBHA-oxime derivatives present halogen atoms which detects by ECD detection. Although these methods provide good reproducibility, however, they are relatively less sensitive than the DNPH-HPLC-UV method.

2.7.1 Analysis of aldehydes by HPLC

High performance liquid chromatography (HPLC) is a chromatographic technique that routinely used for both quantitatively and qualitatively compounds analysis. Nevertheless, some samples have very small in amount, and using HPLC is considered as suitable because its typical column dimensions are 2.1 to 4.6 mm diameter, 30 to 250 mm length, and the columns are made with smaller sorbent particles [57]. Each analyte in the sample have different interaction with the sorbent materials, which are solid materials in the column, resulting different elution time. Moreover, one of the most popular chromatography detectors in HPLC is the UV detector and is used in this project.

Liquid chromatography is a better choice for aldehydes analysis comparing to gas chromatography. The limit of detection in water was 6 µg/L. By using GC, the detection limit is around 1 mg/L. That is the reason why many project used HPLC instead of using GC for the separation method [58]. HPLC is frequently selected for determination of aldehydes because of its excellent separation efficiency and sensitivity. However, most of aliphatic aldehydes does not have a chromophore in their structure, therefore the signal will not be able to detect by UV so it needs derivatizing agent to bind with it in order to detect by UV detector [59]. Hence, aldehyde and ketone need a derivatizing agent for UV detection.

HPLC-UV technique was used to determine the aldehydes in the mixtures. Mostly, 2,4-dinitrophenylhydrazine (DNPH) was used as a derivatizing agent which formed derivatives with aldehydes and ketones. Hence, effective determination of aldehydes involves derivatization with DNPH forming hydrazones before HPLC analysis [60].

2.7.2 Derivatization with DNPH

2,4-Dinitrophenylhydrazine (DNPH) is called as Brady's reagent.
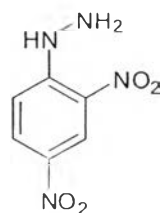
Structure of DNPH

Table 2.2 Properties of DNPH

Molecular formula	$C_6H_6N_4O_4$
Molar mass	198.14 g/mol
Appearance	Red or orange powder
Melting point	198-202 °C
Solubility in water	Slightly

DNPH is widely known as derivatizing agent for carbonyl group compounds. DNPH can be used to qualitatively detect the carbonyl functionality of a ketone or aldehyde functional group. Once carbonyl group in aldehydes or ketones is reacted with DNPH in acidic condition, the result will be the DNPH derivative (Figure 2.9) [61].
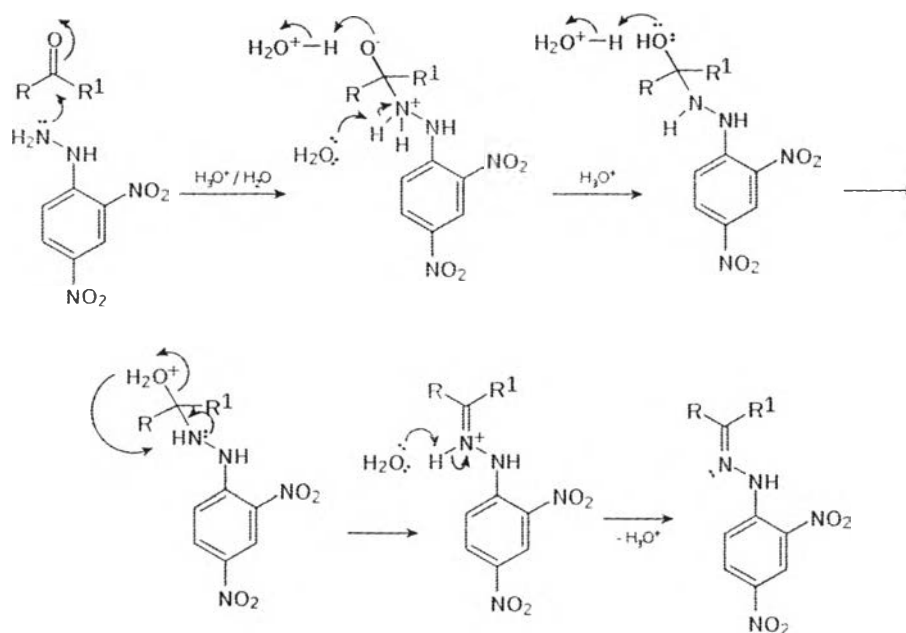

Figure 2.9 Reaction between DNPH and aldehyde/ketone.

This reaction can be described as a condensation reaction. It is an addition-elimination reaction: nucleophilic addition of the -NH$_2$ group to the c=o carbonyl group, followed by the removal of a H$_2$O molecule. Herein, DNPH is used as the derivatizing agent of aldehydes, which is the substance of interest in this work. By derivatizing aldehydes with a compound with chromophores, detecting them with UV detector would be made possible. In another word, the reaction between DNPH and aldehydes would derivatize aldehydes as well as turning them into substance that is more detectable.