SOLID STATE POLYMERIZATION AND CRYSTALLIZATION BEHAVIOR OF POLY (ETHYLENE 2,6-NAPHTHALATE)

by

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Dedicated to my parents, brother and

my lovely husband Adem

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ABSTRACT

SOLID STATE POLYMERIZATION AND CRYSTALLIZATION BEHAVIOR OF POLY (ETHYLENE 2,6-NAPHTHALATE)

Poly(ethylene 2,6-naphthalate) is a crystallizable thermoplastic produced by condensation polymerization of naphtahalene dicarboxylic acid and ethylene glycol. It has superior mechanical and physical properties compared to the well-known thermoplastic poly(ethylene terephthalate) (PET). Additionally, the resistance of PEN to chemicals, and heat make this polymer valuable for commercial uses. The production of high molecular weight PEN by melt polymerization method has many disadvantages Solid state polycondensation method is an alternative to the melt polymerization eliminates some of these disadvantages. In this study, solid state polycondensation of PEN was performed and effects of certain process parameters on polymerization rate were investigated. Isothermal crystallization study of the synthesized polymers was carried out by using differential scanning calorimetry. Isothermal crystallization kinetics of the polymers was analyzed using Avrami equation.

ÖZET

POLİ(ETİLEN 2,6-NAFTALAT)'IN KATI HAL POLİMERİZASYONU VE KRİSTALLEŞME DAVRANIŞI

Poli(etilen 2,6-naftalat), naftalin dikarboksilik asit ve etilen glikolün kondensasyon polimerleşmesi ile oluşan ve kristallenebilen bir termoplastiktir. Bu polimerin fiziksel ve mekanik özellikleri yaygın olarak bilinen poli(etilen teraftalat)'a göre daha üstündür. Ayrıca, PEN'in kimyasallara ve ısıya olan dayanıklılığı bu polimeri ticari olarak da çok değerli yapmaktadır. Bu yüzden bu polimerin birçok endüstriyel alanda kullanımı vardır. Fakat, yüksek moleküler ağırlıklı PEN'in eriyik polimerizasyon ile üretiminin birçok dezavantajı olduğundan, endüstri bu polimerden etkili bir şekilde yararlanamamaktadır. Katı hal polimerizasyonu bu dezavantajları ortadan kaldıran alternatif bir metottur. Bu çalışmada, polietilen naftalatın katı hal polikondensasyonu çalışılmış ve bazı proses parametrelerinin polimerizasyon hızına etkisi araştırılmıştır. Sentezlenen polimerlerin izotermal kristalleşme çalışması diferansiyel taramalı kalorimetri (DSC) aleti kullanılarak yapılmıştır. Polimerlerin izotermal kristalleşme kinetiği ise Avrami denklemi kullanılarak analiz edilmiştir.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

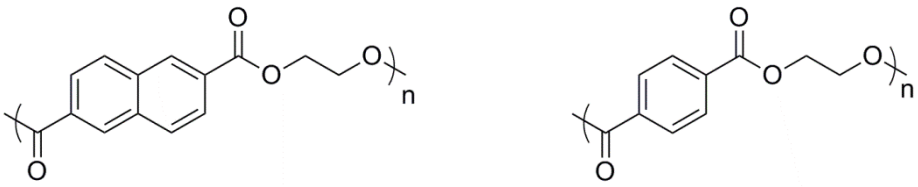
LIST OF ACRONYMS/ABBREVIATIONS

BPA-PC	Poly (bisphenol A Carbonate)
CEG	Carboxyl End Group
DEG	Diethylene Glycol
DSC	Differential Scanning Calorimetry
EG	Ethylene Glycol
ICI	Imperial Chemical Industries
IV	Intrinsic Viscosity
MGy	Milligray
Mpa	Megapascal
NDA	2,6-napthalene Dicarboxylic Acid
NDC	Dimethyl-2,6-naphthalene Dicarboxylate
PA 6	Poly (caprolactam)
PA 66	Poly (hexamethylene adipamide)
PBT	Poly (butylene terephthalate)
PET	Poly (ethylene terephthalate)
PEN	Poly (ethylene 2,6-naphthalate)
PTT	Poly (trimethylene terephthalate)
SSP	Solid State Polymerization
Tc	Crystallization Temperature
Tg	Glass Transition Temperature
Tm	Melting Temperature
Tm^O	Equilibrium Melting Temperature

1. INTRODUCTION

1.1. Poly(ethylene 2,6-naphthalate)

Polyethylene naphthalate (PEN) is a semicrystalline polyester which was first synthesized by ICI scientists in 1948 [1]. Generally, PEN is compared with polyethylene terephthalate (PET) because of their similar chemical structures. However, instead of the benzene rings in PET, PEN has napthalane rings in its main chain (Figure1.1). These two condensed aromatic rings provides more stiffness and rigidity to PEN and improves its physical and chemical properties [2]. Therefore, PEN has superior properties compared to PET and many of the other polyesters.



a. PEN b. PET

Figure 1. 1. Chemical structures of PEN (a) and PET (b).

1.2. Comparison of PEN with PET

Like PET and PEN, many of the thermoplastic polyesters which are synthesized by melt polymerization are nearly completely amorphous in nature. Table 1.1 shows some thermal data about amorphous PET and PEN. The rigidity effect of the napthalane groups on polymer backbone can be seen by comparing the glass transition temperatures of PEN and PET. Tg of the PEN is about 46 ^{o}C higher than that of the PET.

Table 1. 1. Thermal Data of PEN and PET [3].

Thermal Property	PEN	PET
Melting Point (Tm)	270 °C	260 °C
Glass Transition Temperature (Tg)	120 °C	74 °C
Crystallization Temperature (Tc)	180-220 °C	150- 190 °C
Sticking Temperature	140 °C	95 °C

Not only the thermal properties but also many other physical and chemical properties of PEN are better than PET. Table 1.2 summarizes some comparative physical and chemical data about PEN and PET.

Table 1. 2. Physical and chemical data of PEN and PET [4].

PROPERTY	PET	PEN
O_2 Permeation (cm^3 mm/ ([m^2 day atm])	2.4	0.6
Water Vapor Transmission (g mm/[m^2 dat atm])	0.7	0.2
CO_2 Permeation (cm^3 mm/ ([m^2 day atm]	12.2	2.4
Hydrolysis Resistance(h)	50	200
Tensile Strength(Mpa)	45	60
Young's Modulus (Mpa)	3900	5200
UV Absorbance at 360 nm(%)	1	17
Radiation Resistance (MGy)	2	11
Mechanical Continuous Use Temperature(°C)	105	160
Wet Shrinkage (% at 100 °C)	5	1
Dry Shrinkage (% at 150 °C)	1.3	0.6

1.3. PEN Applications

PEN has some present and potential application areas in many fields because of its pre-mentioned physical and chemical properties. The main application areas are;

- Film applications
- Packaging applications
- High performance fiber applications

In the film area, PEN films are produced by DuPont for electrical insulation, flexible printed circuitry and flexible display applications named as Teonex [5-6]. Since its oxygen and water permeation is low, PEN has some applications in food and drink packaging. Sanshain produced reusable tableware in Japan for school cafetaria uses [7]. As a high performance fiber, PEN has found application in tire cord industry. The fiber has high modulus, high heat resistance and high resilience therefore provides longer use time to the consumers [8]. Also since this fiber has high mechanical continuous use temperature and is highly durable to the friction, tire cords of racing cars are produced from PEN fibers.

1.4. Melt Polymerization of PEN

Melt polymerization is performed at a temperature above the melting point of the monomer(s). In other words, reaction takes place in a molten state. There are two common pathways for the synthesis of PEN by melt polymerization method. First one is the reaction between 2,6-napthalene dicarboxylic acid (NDA) and ethylene glycol by means of esterification reaction. And, the second is the transesterification reaction of dimethyl-2,6-naphthalene dicarboxylate (NDC) with ethylene gylcol. Figure 1.2 shows these two synthetic pathways.

The production of NDA and NDC starts by using the same starting materials, ortho xylene and butadiene. After the oxidation step in Figure 1.3, obtained product can be purified to obtain pure NDA or it can be esterified by using methanol to get NDC. However purification of NDA is a very difficult process and therefore pure NDA is expensive. Due to the above reasons, today production of most of the commercial PEN resins are performed by using NDC as the starting material [9].

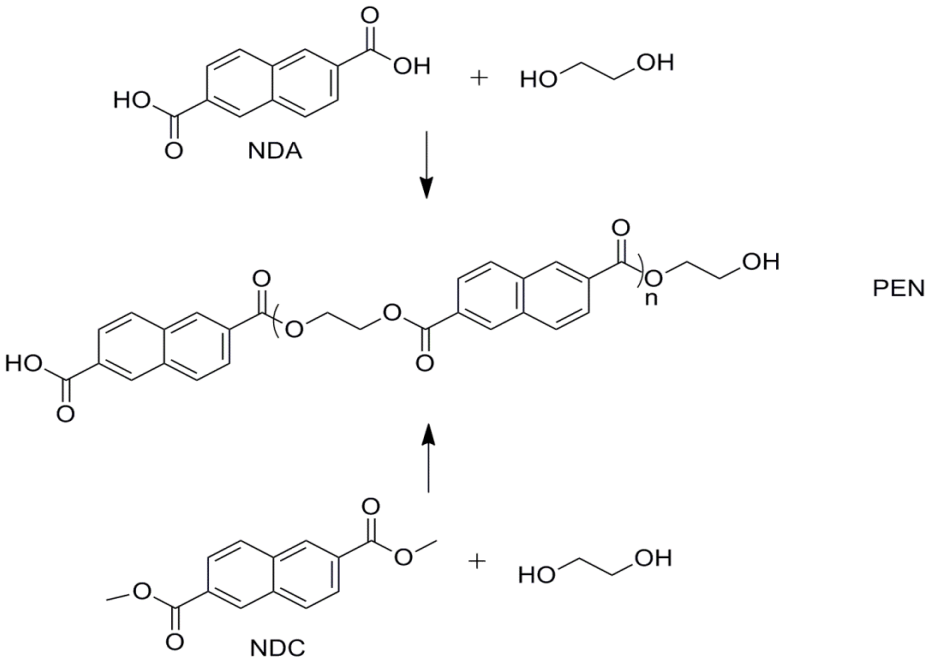


Figure 1. 2. Melt polymerization of PEN.

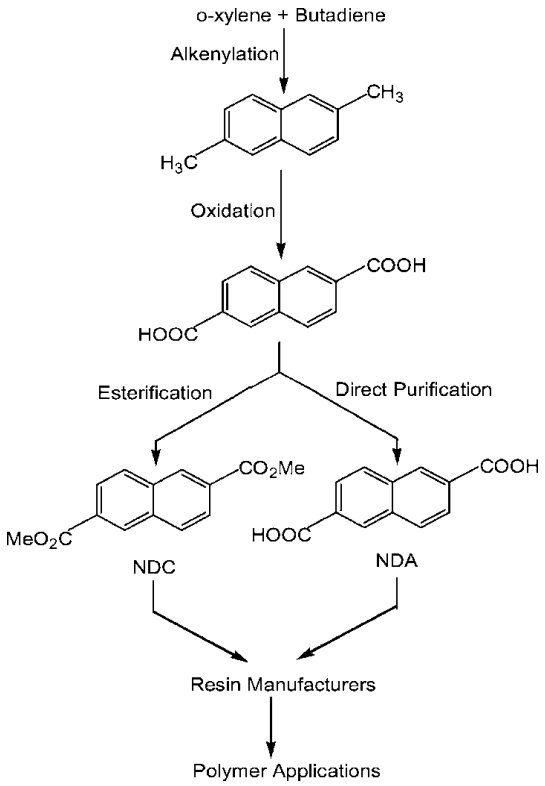


Figure 1. 3. Commercial production of PEN [10].

1.5. Problems Encountered in the Melt Polymerization of PEN

1.5.1. Degradation

The major problem of the melt polymerization of PEN is the thermal degradation. Since melt polymerizaiton occurs at temperatures higher than the melting point of the PEN, thermal degradation during production and processing of the PEN is inevitable.

Esters which have at least one β hydrogen pyrolytically decompose and they give olefins and acids [11]. PEN has many β hydrogens in its main chain and these hydrogens result in thermal degradation of PEN at higher temperatures. Figure 1.4 shows the thermal degradation of PEN .

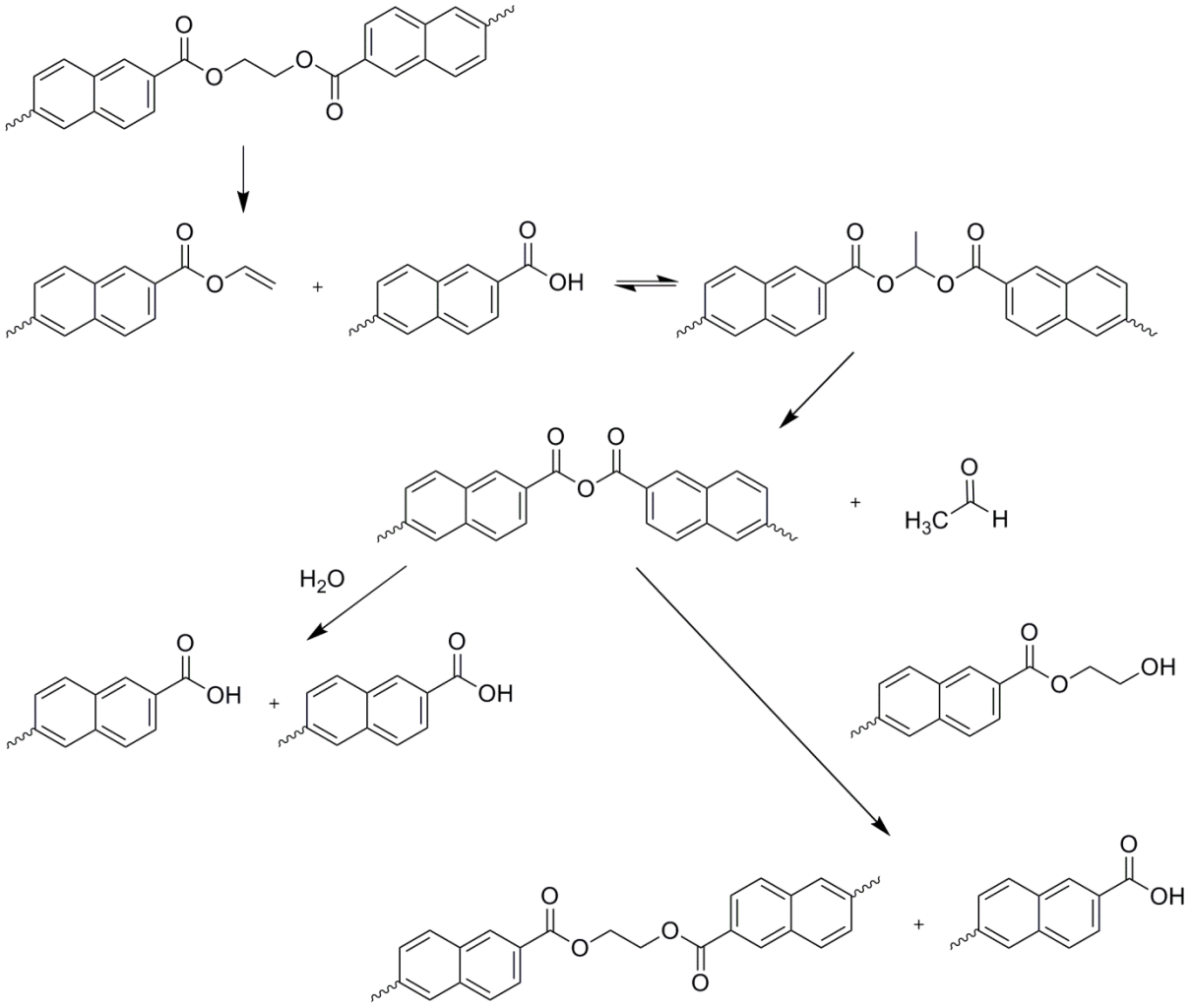


Figure 1. 4. Thermal degradation of PEN.

As it can be seen from Figure 1.4, this process produces acetaldehyde and carboxylic acids. Acetaldehyde is an undesirable compound in applications such as mineral water bottles and carbonated soft drinks because it can pass through the food package. Thermal degradation also gives rise to decrease in intrinsic viscosity (IV), increase in carboxyl end group concentration and the yellowing of the polymer. Increase in carboxyl end groups worsens the thermal and hydrolytic stability of the polymer [12].

1.5.2. Side Reactions

The main side reaction during polycondensation of PEN is the formation of diethylene glycol (DEG). In the literature there are publications that proposes different mechanisms for the formation of DEG during melt polymerizaiton of aliphatic and aromatic polyesters [13-14]. Whatever the mechanism is, diethylene glycol is included in the polymer chain as di(oxyethylene)oxy units. Presence of this compound in the polymer decreases the thermal stability and melting point of the polymer. Also whiteness of the polymer is affected by the inclusion of DEG.

1.5.3. Melt Viscosity of PEN

It is stated in the literature that melt viscosity of PEN is higher than the melt viscosity of PET at similar intrinsic viscosities [15]. Therefore, melt polymerization of PEN stops at comparatively low IV values, usually lower than 0.55 dl/g. However, for complex applications such as binding tape and tire cord, polymers which have higher IV's are needed. For example, Table 1.3 shows that at least an IV value of 0.55 dl/g is needed for textile use of PET and higher values are needed for more complicated applications and this requirement is also valid for PEN applications.

Table 1. 3. IV values of PET for different applications[16].

Uses of PET	Intrinsic Viscosity (dl/g)
Textile	0.55-0.65
Bottle	0.75-0.85
Film and Tape	0.85-1.10
Tire Cord	0.85-1.20

1.5.4. Problems Associated with the PEN Polymerization Rate

Melt polymerization of PEN continues at intrinsic viscosities up to 0.5 dl/g. At this IV, melt viscosity of the polymer is high. Since reaction medium is viscous it is difficult for chain ends to find each other and react. Also removal of the by-products will be inefficient since viscous melt will block their escape from the reaction medium.

1.6. Solid State Polymerization

Solid state polymerization is a polymerization technique in which all the reactants and the products are in the solid phase throughout the reaction. The main principle of the solid state polymerization is to heat the starting material at a temperature above its glass transition temperature but below its melting point in a *vacuo* or in an inert atmosphere. Temperature should be high enough to permit the initiation and propagation reactions which involve condensation reactions. [17].

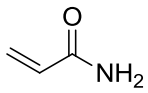
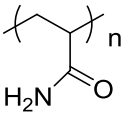
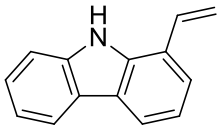
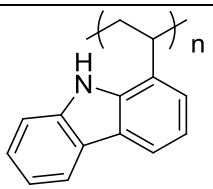
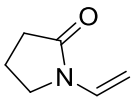
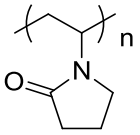
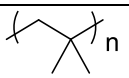
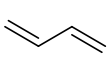
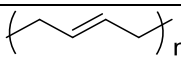
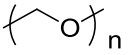
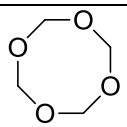
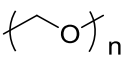
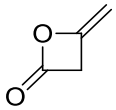
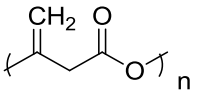
Solid state polymerization is divided in two categories according to the form of the starting material. When the starting material of the reaction is the monomer of the desired polymer, this type is called as direct solid state polymerization. However, in many of the cases starting material is not a monomer but it is a prepolymer of the desired polymer. Prepolymer can be defined as the low molecular weight version of the desired polymer, synthesized by melt or solid phase polymerization techniques [18].

Solid state polymerization is also classified by the polymerization mechanism in two parts which are solid state polyaddition and solid state polycondensation.

1.6.1. Solid State Polyaddition

Solid state polyaddition involves irradiating monomer at polymerization temperature which is below the melting point and then heating the sample for a postradiation reaction. Main advantage of the solid state polyaddition is that higher amount of active centers are formed and these are highly uniformly distributed over the sample compared to the other techniques [19]. There are many monomers which can undergo radiation induced solid phase polymerization and some of them are shown in Table 1.4.

Table 1. 4. Monomers And Their Polymer Structures Obtained by Radiation Induced SSP.

Monomer Name	Monomer Structure	Polymer Repeating Unit
Acrylamide		
Vinyl carbazole		
Vinylpyrrolidone		
Isobutene		
Butadiene		
Trioxane		
Tetraoxane		
Diketene		

1.6.2. Solid State Polycondensation

Molecular weights for condensation polymers synthesized by melt polymerization are generally low because of high melt viscosity and degradation reactions. For instance, number average molecular weight for PET which is produced by melt polymerization is about 16.000-20.000 g/mol [20]. Solid state polycondensation is a technique which is used to obtain higher molecular weight polymers that cannot be achieved in melt phase because of commercial and technical reasons.

There are many monomers or prepolymers which can be polymerized by solid state polycondensation method and the most famous ones are PET, PBT, PA 6, PA 66 and PEN. Figure 1.5 shows general reaction schemes of some condensation polymers.

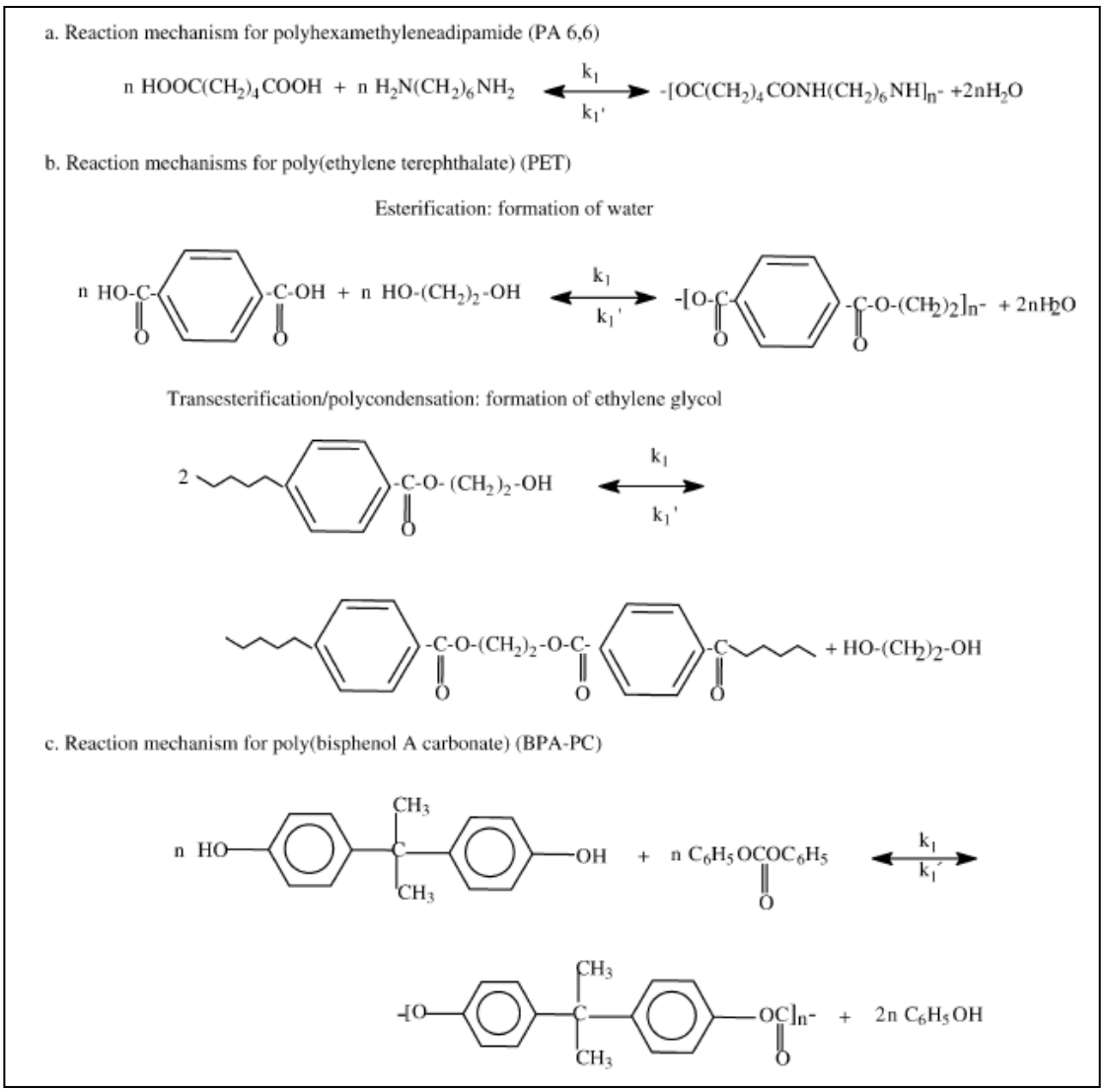


Figure 1. 5. Schematic illustration of formation of common condensation polymers [22].

In solid state polycondensation, starting material is heated in an inert atmosphere or in vacuum, at a temperature below its melting point but above its glass transition temperature and by removing the condensate. When the reaction continues material retains its solid shape and molecular weight increases. The first example of SSP in the literature is seen in a patent by Flory in 1939 [21].

1.7. Advantages of Solid State Polycondensation

In the melt polymerization method, when the reaction proceeds, molecular weight and viscosity will increase. After a point, viscosity will be high enough to hinder the stirring of the reaction medium. However, in the solid state polymerizaiton since all materials are in the solid phase (as a powder, chip , fiber etc.), there is no problem about stirring.

Melt polymerization is conducted at high temperatures and in high vacuum. However, SSP process does not require such high temperature and vacuum. Therefore investment and running costs of SSP is lower than the melt phase. Figure 1.6 shows that investment costs are five times higher for melt phase. Production costs doubles for the melt phase as it can be seen in Figure 1.7.

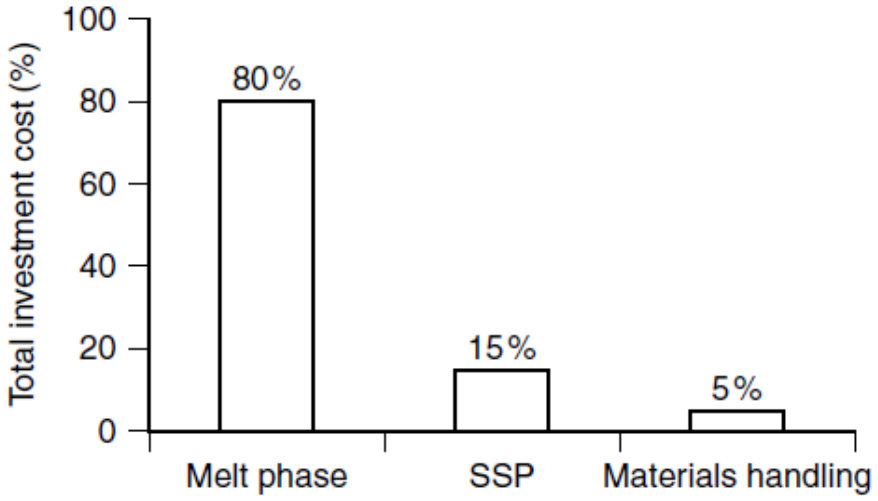


Figure 1. 6. Investment costs for a 600 t/d PET BG resin installation [12].

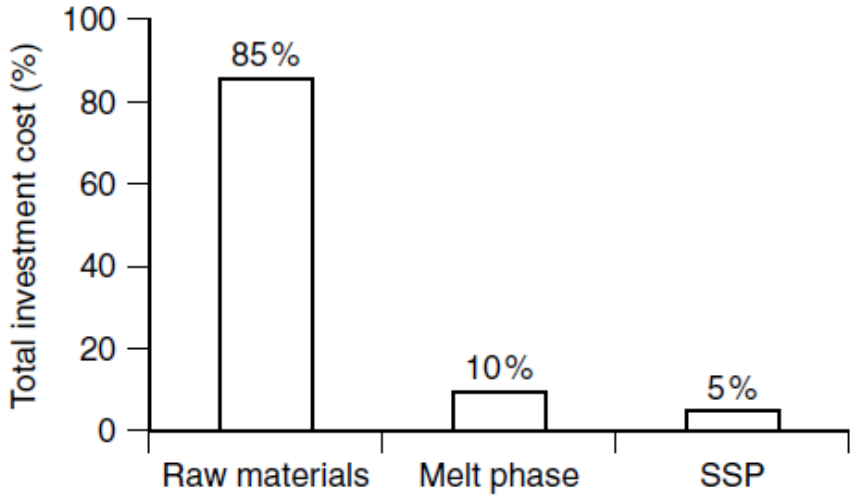


Figure 1. 7. Production costs for a 600 t/d PET BG resin installation [12].

Degradation, monomer cyclization and other side reactions are limited in the solid state polymerization because of the lower temperatures needed for the process. Therefore polymers which are obtained by SSP method shows improved properties. For example, acetaldehyde is the main degradation by-product of melt polymerization of PET and badly affects the taste of mineral water. Instead of melt polymerization, when SSP is preferred, very low acetaldehyde containing PET bottles are produced. According to the Morawetz, only linear polymers are produced in the SSP and highly oriented polymers can be prepared without mechanical drawing [23]. Also Bruck stated that compared to melt phase production, polymers obtained by SSP have better heat stability in the molten phase [24].

After melt polymerization is done, it is common to have unreacted residual monomer in the reaction medium. Therefore, it is necessary to perform an extra step to remove the monomer to be able to get pure polymer. However, such monomer removal step is not present in SSP.

SSP method give rise to increase in crystallinity and crystal perfection.

Since SSP is a solid phase process, there is no use of solvent. This makes the process more environmentally friendly.

1.8. Disadvantages of Solid State Polycondensation

The main disadvantage of solid state polymerization is its slow rate compared to the melt phase polymerization. For the solid state polymerization to proceed, chain ends should find each other, combine and react. In other words, mobility is needed. However since SSP is conducted at comparatively lower temperatures, mobility of the chain ends is very low. Furhermore, at longer reaction times, many of the functional chain ends which are close to each other will be already reacted, and the unreacted ones will be far away from each other. Since mobility will be lower at longer periods, reaction rate will also be lower.

Agglomeration of the reacting mass is also a drawback of solid state polymerization. Beaten stated in one of the patents that agglomeration of the polyamide granules occured especially at higher reaction temperatures when low molecular weight polyamides were subjected to the solid state polymerization [25].

One of the problems about SSP is the manufacturing problems of the product. Since product is in the solid phase, handling and processability of it will be difficult for the manufacturers.

1.9. Overall Rate of Solid State Polycondensation

Solid state polymerization is a complex process which involves both chemical and physical considerations. Although many researchers work on this subject, there is no general description for the kinetics of SSP. However it is generally accepted that there are four steps which contributes the overall rate of solid state polycondensation [22].

- The intrinsic kinetics of the reaction which can be defined as the collision and reaction of the polymeric end groups
- Diffusion of the functional (active) end groups in the polymeric matrix
- Interior diffusion is the diffusion of the volatile by-products from the reacting mass to the surface of the particle
- External diffusion is the diffusion of the condensate from the particle surface to the gas phase

The first two of the above steps are considered as reaction steps and the next two as diffusion steps. Depending on the process parameters, SSP can be a reaction or diffusion controlled process.

1.10. Rate Controlling Parameters of Solid State Polycondensation

There are many process parameters that affect the rate of solid state polycondensation and directly the final product properties. The most important ones are temperature, particle size, crystallinity, carboxylic end group concentration and removal of the condensate.

1.10.1. Temperature

Temperature was found as the most important parameter on the kinetic of solid state polymerization. Jabarin and Lofgren analyzed the effect of temperature on solid state polymerization of PET. Their finding is that when PET samples which have the same IV values are solid state polymerized at four different temperatures (220 ^{o}C ,230 ^{o}C ,240 ^{o}C and 250 ^{o}C), desired IV is obtained in a shorter times at higher temperatures (Figure 1.8). At higher temperatures, mobility of the end groups and diffusivity of the by-products increases and this results in increased reactivity [26].

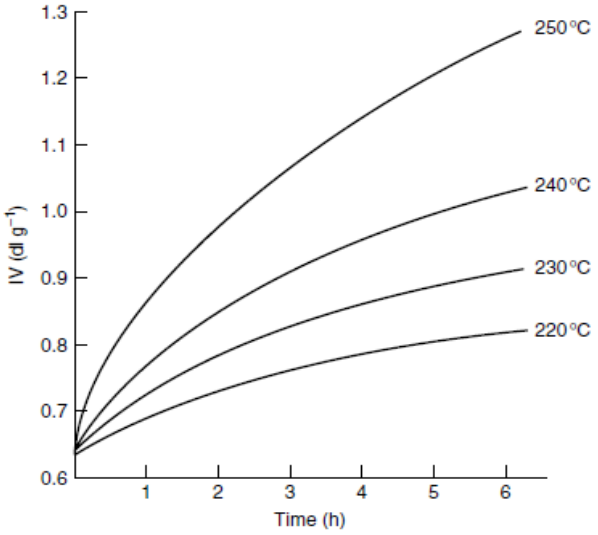


Figure 1. 8. Intrinsic viscosity as a function of time at various solid-state temperatures (under a nitrogen purge at a rate of 1 l/min) [27].

Many groups investigated the optimum temperature range for different polymers and the general agreement is that polymerization temperature should be 20 ^{o}C to 160 ^{o}C below from the melting point and the best one is 20 ^{o}C to 50 ^{o}C below of the Tm [28-29]. However, being too close to melting point may result in partial melting of the reacting mass where particle agglomeration may take place [30].

1.10.2. Particle Size

Effect of the particle size is especially important if the reaction is diffusion controlled. Internal diffusion is the diffusion of by-products from inside to outside of the polymer particle. When the particle size is smaller, diffusivity of the volatiles will be easier since diffusion path will be shortened in the interior of the polymer. Also smaller particle size means higher surface to volume ratio and easier external diffusion. Dacheng analyzed the effect of the particle size on the solid state polymerization of PET and found that smaller particle sizes give higher reaction rates [31].

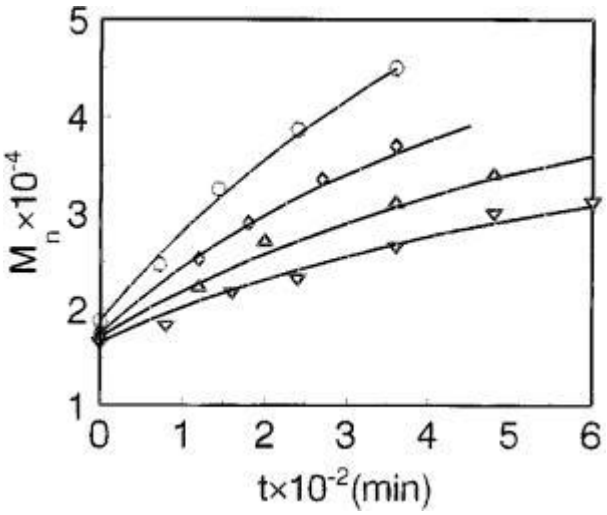


Figure 1. 9. Effect of particle size on molecular weight for PET at 235 °C.
Particle sizes: (O) R=0.1 mm; ()) R= 0.25 mm; (4) R= 0.5 mm [31].

However, there is a minumum particle size suitable for the solid state polymerization for each starting material. If the particle size is too small, agglomoration may be encountered. Duh reported a method for PEN to overcome this problem where nitrogen

was purged into the PEN before pelletizing and foamed PEN was obtained. Rate of polymerization was greatly increased by this method [32].

1.10.3. Crystallinity

According to the Duh, there are active and inactive end groups in the polymeric matrix throughout the solid state polymerization. Inactive end groups can be either chemically unfunctional groups to participate to the condensation or functional end groups but they are trapped in the crystalline parts so cannot polymerize since solid state polycondensation proceeds in the amorphous region. Therefore crystallinity of the starting prepolymer is very important for the SSP since it defines the mass fraction of the amorphous region in which reactive end groups are present [33].

Effect of crytallinity on SSP rate is dependent on whether polymerization is diffusion-controlled or reaction-controlled. In the first case, higher crystallinity decreases rate by imposing diffusional resistance. In the later case, rate of polymerization is directly proportional with the crystallinity since this increases concentration of end groups in the amorphous parts.

1.10.4. Carboxylic End Group

The effect of carboxylic end group of the prepolymer depends on the resistivity of by-product diffusion and this resistivity is directly related with the particle size and flow rate of the inert gas. If particle size is small and the flow rate is high, by- product is eliminated easily and polymerization becomes reaction controlled. In this case polymerization rate increases with decreasing carboxylic end group of prepolymer (Figure 1.10). However if polymerization is diffusion controlled, there is an optimum carboxylic end ratio for each starting material. There are two main reactions in SSP which are esterification and transesterification. Diffusion resistivity makes faster the esterification reaction which produces water as a by-product compared to the ethylene glycol in the transesterification. Since water has a higher diffusion coefficient, its removal is easier and therefore SSP needs a specific carboxylic to hydroxyl end group ratio [34].

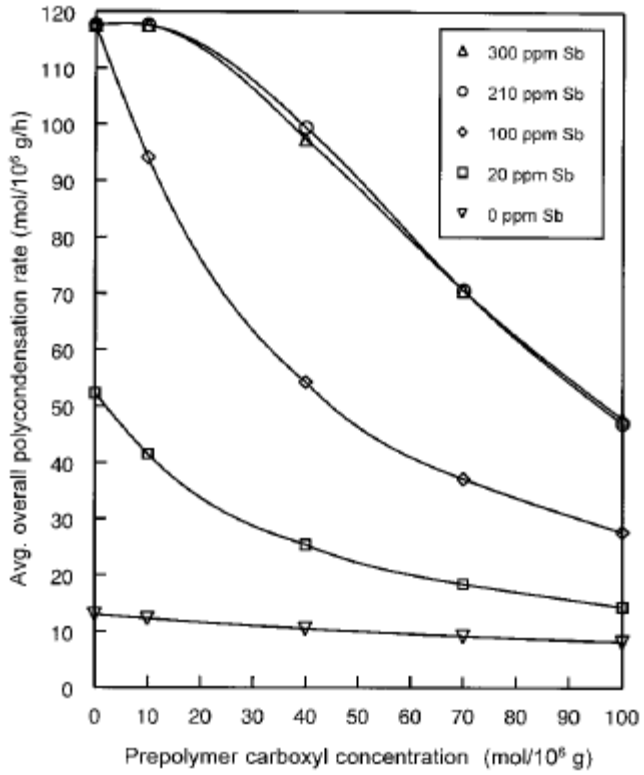


Figure 1. 10. Effect of carboxylic end group on SSP rate of PET [34].

1.10.5. Removal of the Condensate

Solid state polycondensation is a reversible reaction, therefore removing the by-products is important to shift the reaction towards the product. Also SSP needs oxygen free atmosphere to avoid oxidation reaction which causes the polymer degradation and coloration. Therefore, SSP is conducted either in a vacuum or in an inert atmosphere. Vacuum is generally applied in small scale production. In large capacity productions, risk of oxygen rushing, so oxidation and coloration increases [35].

Use of inert gas is commonly used in SSP processes in both industrial and academic area, and the most frequently used one is the nitrogen gas. Nitrogen gas removes the oxygen and volatile by-products from the reaction medium and also provides homogenous heating of the reacting mass if it is preheated [36].

1.11. Crystallization of Polymers

Polymers are large molecules which have tangled chains and strong intermolecular forces. Crystallization of polymers is a process associated with the orientation of these long chains from a disordered state. According to amount of these alignments, polymers are classified into three categories. Polymers can be amorphous, crystalline and semicrystalline. In the amourphous polymers, polymer chains cannot pack well to form crystal structure and therefore polymer is composed of randomly coiled and entangled chains. In the crystalline polymers, all chains are highly oriented and packed. Semicrystalline polymers contains both crystal and amorphous regions. Crystal portions are called as lamellae and amorphous parts are found in between these lamellaes. There are some parts in the semicrystalline polymers that connect the amorphous and crystalline parts called as tie molecules [37].

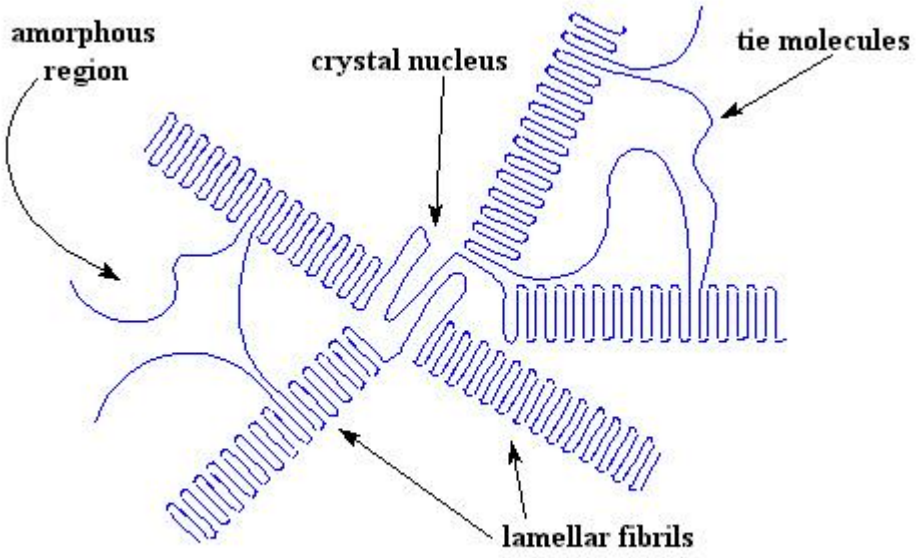


Figure 1. 11. A semicrystalline polymer [38].

Polymers can be crystallized by different methods such as

- Crystallization (solidification) from melt
- Crystallization from solution
- Crystallization by streching

- Confined Crystallization [39].

1.11.1. Crystallization From Melt

In this method, a polymer is heated above its melting point and after total melting it is cooled to a temperature below its melting point. Crystallization in this method follows two steps, first one is the nucleation in which nuclei that are in critical size and amounts are produced. Second one is the crystal growth in which the produced nuclei provide template for the incoming crystallites to grow and form spherulites (Figure 1.12) [40].

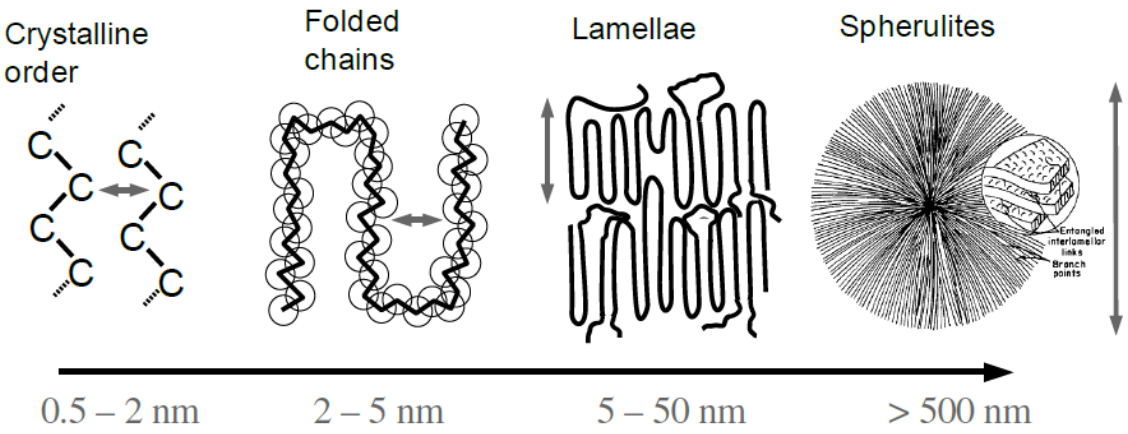


Figure 1. 12. Schematic illustration of crystallization steps [41].

Figure 1.13 shows the steps that occur during crystallization with time. Induction step is the same as nucleation step. In the primary crystallization, crystal growth is fast and sphere like structures (spherulites) are formed. Secondary crystallization is also a crystal growth step however, it is very slow compared to primary crystallization and the formed crystals are not spherulites, instead they are the impingement of present spherulites [42].

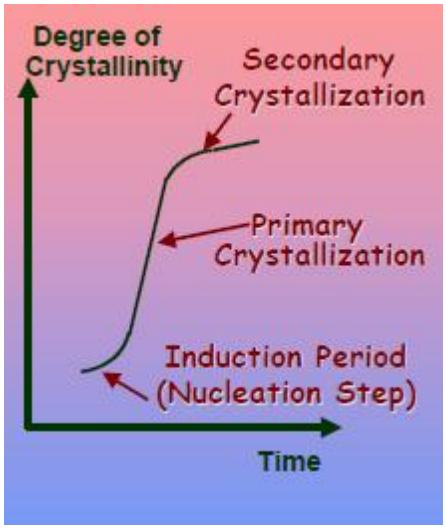


Figure 1. 13. Occurence of crystallization steps with time [41].

1.11.2. Isothermal Melt Crystallization

Isothermal melt crystallization is a sub-class of crystallization from the melt process. This procedure is performed by using differential scanning calorimetry. In this method a polymer is heated 20 to 30 ^{o}C above its melting point, then rapidly cooled to the predetermined isothermal crystallization temperature which is above its glass transition temperature but below its melting point. Sample is kept at this temperature for a while for complete crystallization [43].

Isothermal crystallization behaviour of polymers is generally analyzed by Avrami equation. The general form of the Avrami equation is:

$1-X(t) = \exp(-kt^{n})$,

where X(t) is the relative crystallinity of the polymer at different times, k is the rate constant of the crystallization and n is the Avrami exponent which describes the nucleation mechanism and form of the crystal growth [44]. Relative crystallinity is calculated by the following equation in which numerator is the amount of generated enthalpy at time t, and the denominator is the time at infinity [45].

$$X(t) = \int_0^t \left(\frac{dH}{dt}\right) dt \; / \; \int_0^\infty \left(\frac{dH}{dt}\right) dt$$

Physical and chemical properties of semicrystalline polymers are related to the microstructure. And this microstructure is determined by the degree of crystallinity and crystallization rate. Isothermal melt crystallization process and Avrami analysis provides a way to examine the parameters for obtaining products that have desired properties and morphologies.

2. AIM OF THE STUDY

The first aim of the study was to synthesize poly (ethylene 2,6 naphthalate)s with different molecular weights by solid state polycondensation method. As starting materials lower molecular weight amorphous PEN's were used. Polymerization temperature and initial intrinsic viscosity were selected as parameters to investigate their effects on solid state polymerization. Experiments under inert gas flow and under vacuum as means to remove condensate were carried out to determine which method resulted in higher polymerization rate.

As a secondary goal, isothermal crystallization studies of synthesized PEN's have been performed by using differential scanning calorimetry. Change in degree of crystallinity of polymers with time were determined at different temperatures since degree of crystallinity affect many important physical and mechanical properties of PEN. Avrami equation was selected to analyze the isothermal crystallization rate, crystal growth and crystallization mechanism of the polymers. Finally, a thermodynamic parameter and equilibrium melting point of polymers were determined by using Hoffman-Weeks plot.

3. RESULTS AND DISCUSSIONS

In this study, solid state polymerization of poly (ethylene 2,6-naphthalate) was performed. Prepolymer forms of the PEN with two different initial intrinsic viscosities were used. Prepolymers were put in a vacuum oven at 120^{O}C for 24 hours prior to the polymerizations. This process is known as the devolatilization step. In this step, the volatiles which come from the melt polymerization of the prepolymer and trapped inside the polymer such as water, acetaldehyde and low molecular weight chains are removed from the prepolymer. When this step is omitted, prepolymer chips puffed of during the crystallization step. This phenomenon is called as "pop-corning of polymers" in the literature [46]. After the devolatalization step, crystallization step was done. Polymer chips were subjected to 190 ^{O}C for 1 hour by passing inert gas or applying vacuum to gain some crystallinity before the solid state polymerization. Finally prepolymers were heated to the polymerization temperature and samples were taken from the reaction medium periodically for intrinsic viscosity and carboxyl end group analyses.

3.1. Effect of Temperature on SSP of PEN

To study the effect of temperature on solid state polymerization of PEN, firstly low intrinsic viscosity amorphous PEN was used. Solid state polymerization was performed at four different temperatures T1, T2, T3 and T4 ^{O}C under vacuum. Samples from the reaction medium were taken after the crystallization step and 4 and 8 hours of SSP. Results are shown in Figure 3.1. As it can be seen from the figure, intrinsic viscosity increases with time at a given polymerization temperature. Also, as the SSP temperature increases, rate of polymerization increases. IV values of polymers after one hour were nearly same at all the temperatures and slightly higher than the initial IV values. This shows that during the crystallization step at 190 ^{O}C, there is no an obvious polymerization.

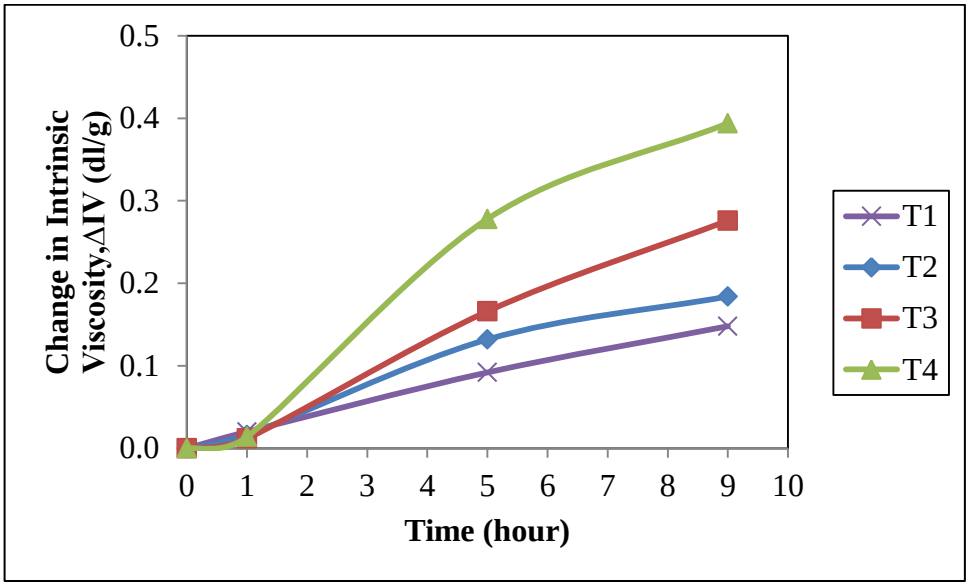


Figure 3. 1. Change in intrinsic viscosity *vs* time graph for PEN at different temperatures.

Solid state polycondensation of PEN proceeds at the chain ends by the reaction of –OH and –COOH groups. Therefore, it is expected that as the reaction continues, short chains will react and combine to form longer chains and the amount of chains will be lesser with time. This means that carboxyl end group of the medium should decrease with time. Figure 3.2 shows that at all temperatures, carboxyl end group (CEG) concentration decreases with time. The leveling of CEG concentration is very fast at T4.

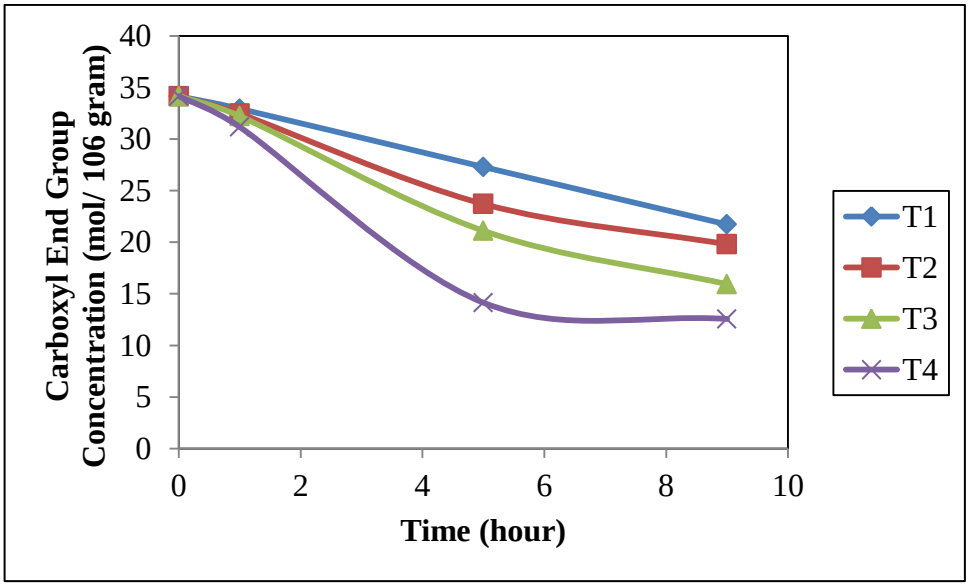


Figure 3. 2. CEG concentration *vs* time graph for PEN at different temperatures.

3.2. Effect of Initial IV on SSP of PEN

To study the effect of initial intrinsic viscosity on the final polymer IV and SSP, two PEN prepolymers with different intrinsic viscosities (low and high intrinsic viscosities) but similar particle size and dimension were used. Prepolymers were subjected to solid state polycondensation at both T3 and T4 under vacuum. Samples were taken from the reaction medium after the crystallization step and at 4th and 8th hours of the polymerization.

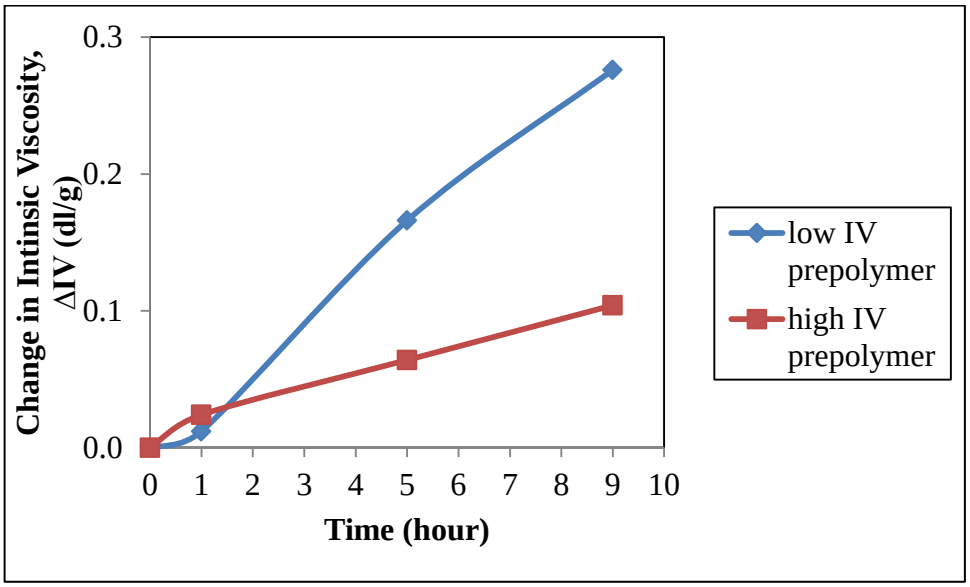


Figure 3. 3. Change in intrinsic viscosity *vs* time graph of PEN's at T3.

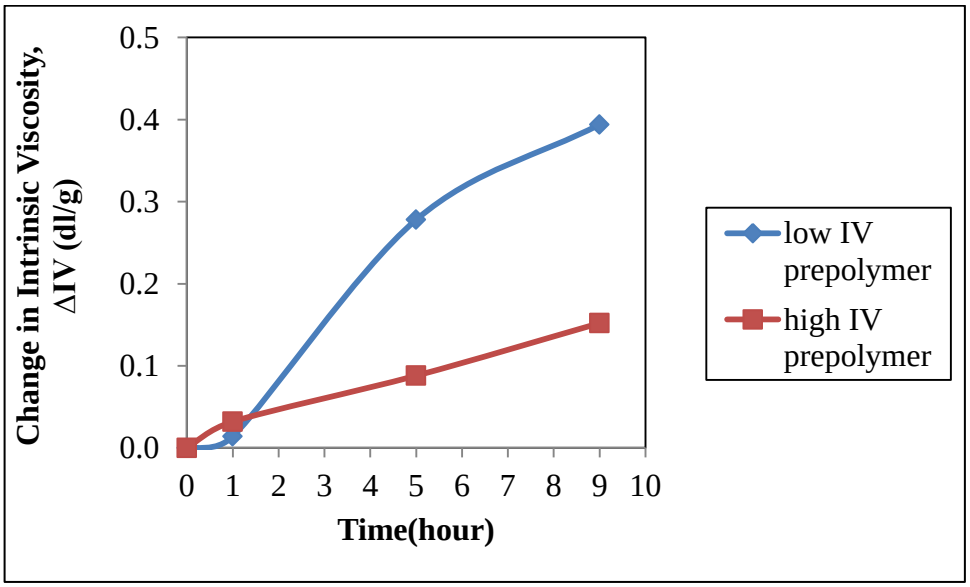


Figure 3. 4. Change in intrinsic viscosity *vs* time graph of PEN's at T4.

According to the Figure 3.3 and 3.4, as the initial IV of the PEN prepolymer increases, rate of polymerization decreases. For the low molecular weight PEN, it is easier to reach the desired IV in a shorter time at each temperature. These findings conflict with one of the literature paper [33]. Duh states that as the initial IV of the prepolymer increases, rate of polymerization increases for SSP of polytrimethylene terephthalate (PTT) and other polyesters. It is claimed that higher initial IV means longer chains and for the longer chains it is not easy to trap them in the crystalline region. So there are more available chains and chain ends in the amorphous region to be polymerized [33]. However, our present findings seem to indicate that the lower end group concentration decreases the probability of the chains to combine and react. Therefore higher initial IV, decreases the rate of solid state polycondensation.

3.3. Effect of Nitrogen Flow and High Vacuum

Since SSP of PEN is a condensation reaction it is crucial to remove the condensate from the reaction medium to shift the reaction to the product side. In this study either nitrogen sweep or high vacuum was used for the purpose and their effects on final IV values were determined. For the nitrogen flow experiment, nitrogen gas was passed through the reaction medium during the whole reaction period. For the vacuum experiments, high vacuum (1.0 mbar) was applied. Results are shown in Figure 3.5.

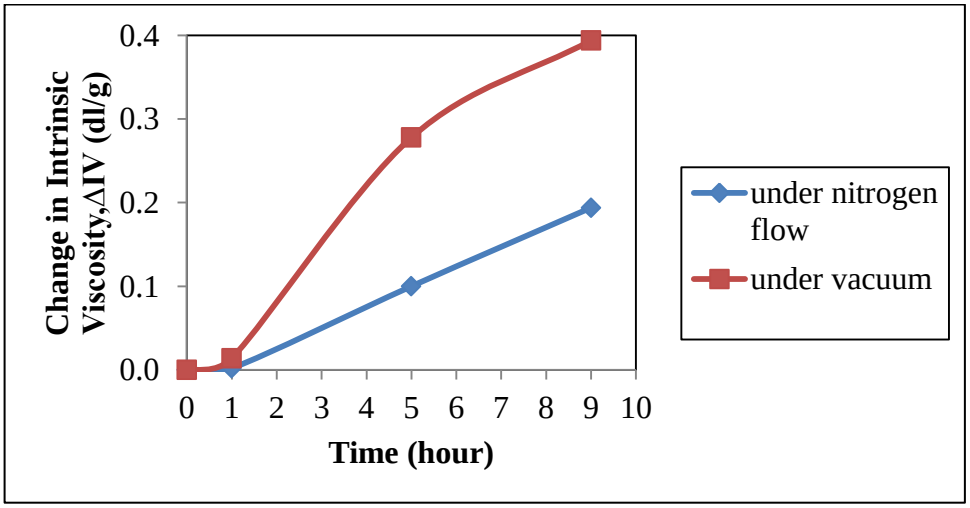


Figure 3. 5. Change in intrinsic viscosity *vs* time graph of PEN at T4.

These results show that under identical conditions (similar IV, shape, dimension, amount and temperature), rate of SSP of PEN is higher under vacuum than under nitrogen flow.

3.4. Thermal Characterization of Amorphous PEN

The thermal behaviour of amorphous PEN was investigated by using differential scanning calorimetry (DSC). Glass transition temperature, cold crsytallization temperature and melting temperature of the polymer were obtained with a scanning rate of 10 ^{O}C/min.

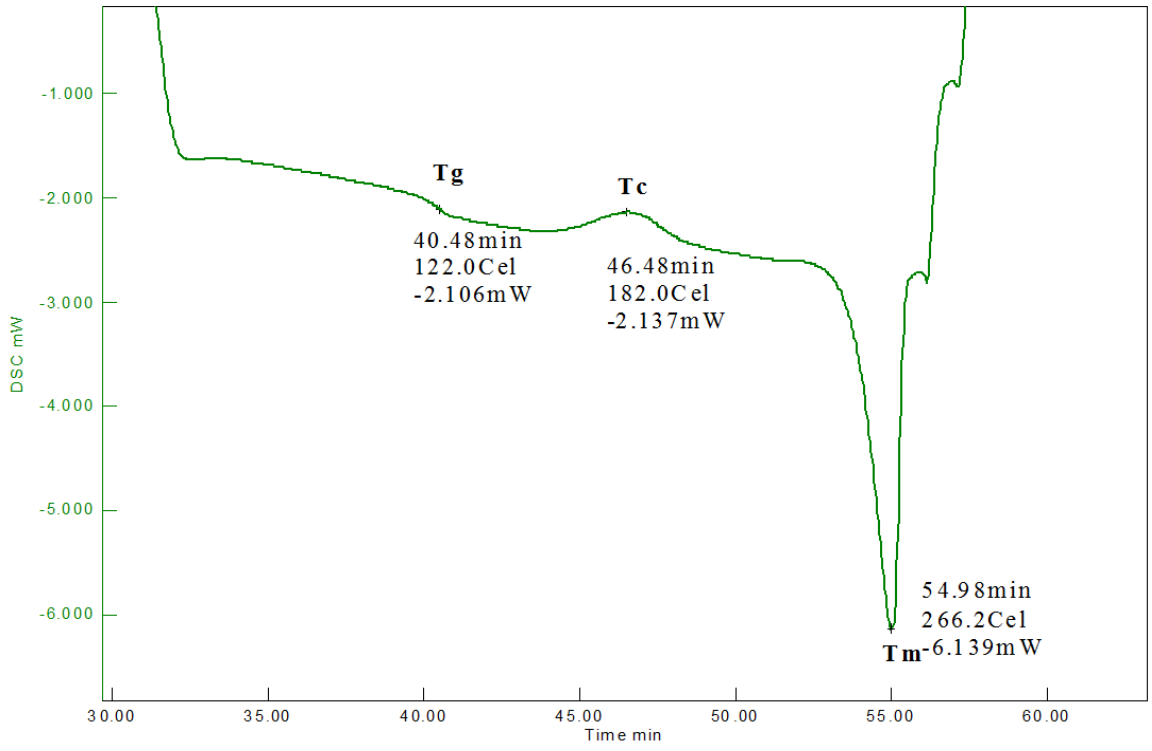


Figure 3. 6. DSC thermogram of the amorphous PEN.

Amorphous PEN shows a glass transition peak (Tg) at 122 ^{O}C, a crystallization peak (Tc) at 182^{O}C and a melting peak (Tm) at 266.2 ^{O}C (Figure 3.6). It should be noted that this data were collected in EXSTAR SII 7020 DSC, which is arranged to display exothermic transition peaks in a upward direction and endothermic transition peaks in a downward direction.

3.5. Isothermal Melt Crystallization Study of Amorphous PEN

Isothermal melt crystallization of amorphous PEN was performed at T10, T9, T8, T7, T6 and T5 ^{O}C respectively. PEN samples were heated up to 300 ^{O}C with a heating rate of 20 ^{O}C/min, the samples were then kept at this temperature for 3 min for complete melting, and then rapidly cooled to the crystallization temperature at a cooling rate of 100 ^{O}C/min. The DSC thermogram of the process is shown in Figure 3.7.

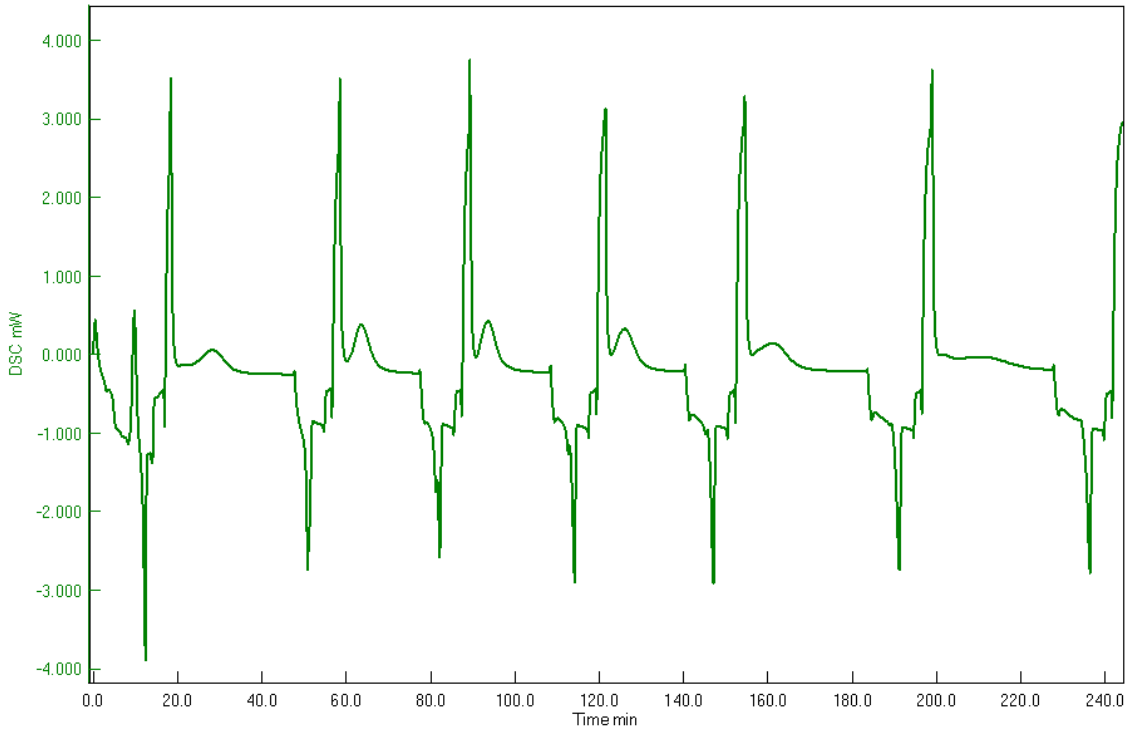


Figure 3. 7. DSC thermogram of isothermal melt crystallization of amorphous PEN.

Relative crystallinity (Xt) is the ratio of the crystallinity at time t to the crystallinity as the time goes to infinity. Relative crystallinities of the polymers were calculated by the following equation:

$$X(t)= \int_0^t \left(\frac{dH}{dt}\right) dt \; / \int_0^\infty \left(\frac{dH}{dt}\right) dt$$

This calculation was done by integrating the crystallization exotherms in Figure 3.7. Data of percent crystallinity at a given time was obtained by using software program of the DSC instrument. Then the percent crystallinity was transformed to the relative crystallinity. Results are shown in Figure 3.8. Sigmoidal shaped isothermal crystallization

is obtained in the plot. Relative crystallinity *versus* time graph is very informative to determine the percent crystallinity at a given time. Since many important properties of polymers such as brittleness, modulus, high working temperature, dimensional stability etc. are controlled by the degree of crystallinity of the polymer, determining the target degree of crystallinity is critical in obtaining polymers with desired physical and mechanical properties.

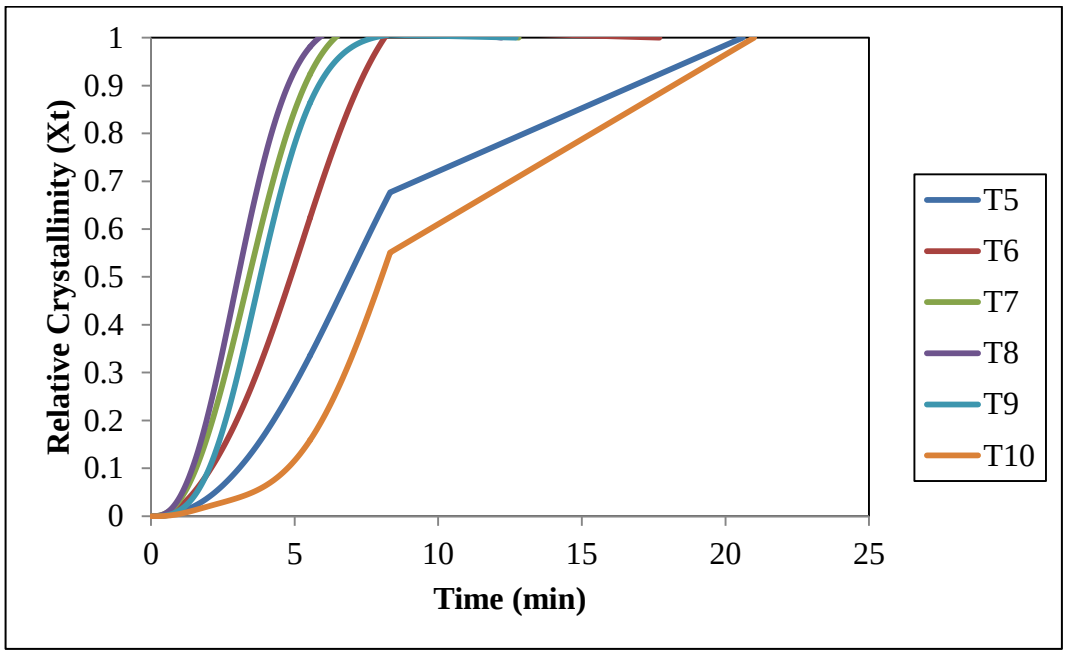


Figure 3. 8. Relative crystallinity *vs* time graph for amorphous PEN.

From the plot in Figure 3.8, times to reach 50% of crystallinity for each temperature were calculated. This is known as the half-time of crystallization, $t_{1/2}$ (Figure 3.9).

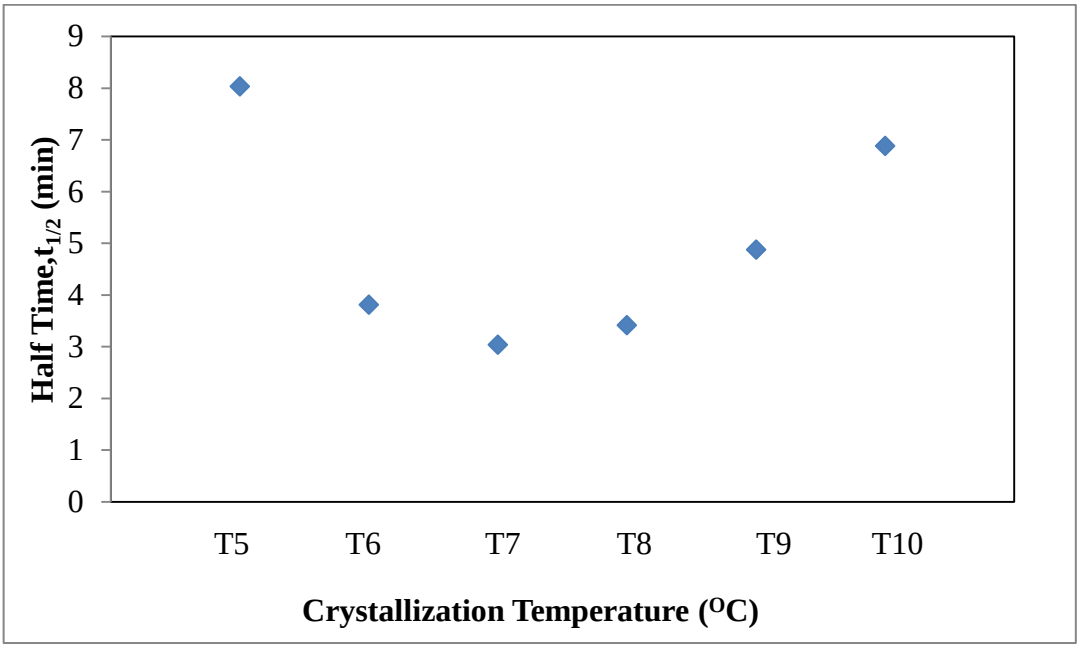


Figure 3. 9. Half-time of crystallization *vs* crystallization temperature for amorphous PEN.

From Figure 3.9, it can be said that crystallization of the amorphous PEN is fastest at temperatures T7, T8 and T9, and it slows down at temperatures higher than T9 and lower than T7.

Avrami equation is used to analyze the crystallization behavior of the polymers:

$$\ln(-\ln(1-Xt)) = n \ln t + \ln k$$

Xt is the relative crystallinity, k is the rate constant of crystallization which contains both crystal nucleation and growth and n is the Avrami exponent. Figure 3.10 shows the Avrami plot for the amorphous PEN. Slope of the lines gives the Avrami exponent and intercept of the lines provides rate constant "k". The Avrami analysis was done to analyze primary crystallization kinetics of the polymer.

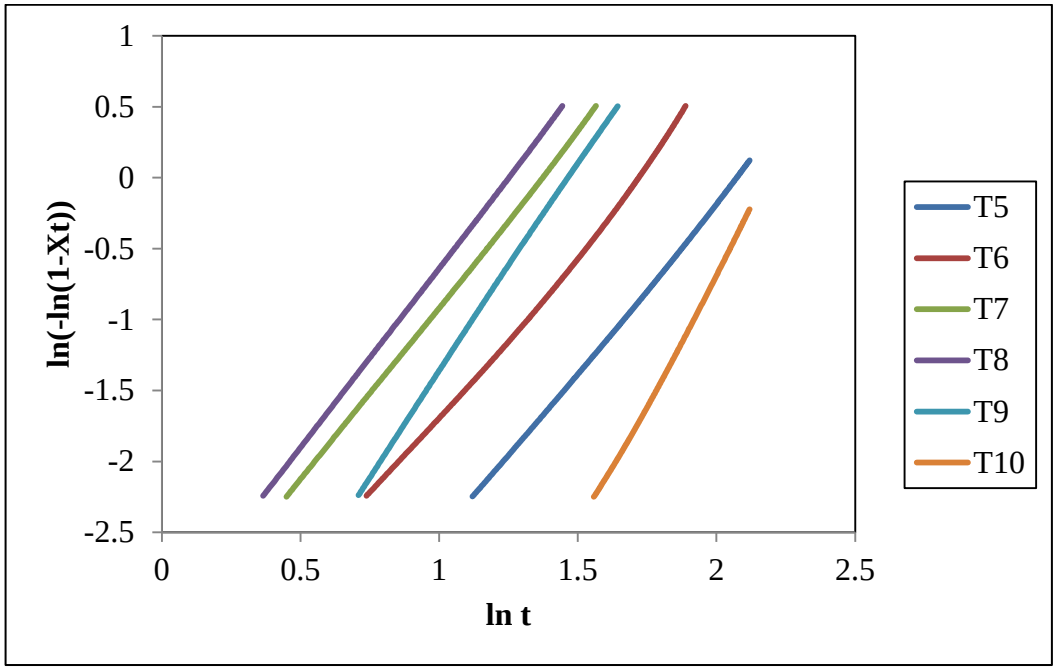


Figure 3. 10. Avrami analysis of amorphous PEN.

When Avrami plot was drawn, Xt values that are in the range of 0.1-0.8 were used. Time to reach Xt=0.1 is called as the induction time in which primary nuclei is formed. After Xt=0.8 crystal impingement occurs, and growth rate of the crystals decrease because of secondary crystallization. Table 3.1 summarizes the kinetic parameters of amorphous PEN. Most of the Avrami exponent (n) values are close to 3 which indicates sphere like crystal growth and athermal nucleation. Also, an inverse correlation between $t_{1/2}$ and k values was found.

Table 3. 1. Isothermal Melt Crystallization Kinetic Parameters for Amorphous PEN.

Tc (^{O}C)	**$t_{1/2}$** (min)	**n**	**k** (min^{-n})	**$\Delta H\infty$** (mJ/mg)
T10	8.0333	3.652	0.0037	17.9
T9	3.8083	2.933	0.0136	24.1
T8	3.0334	2.538	0.0418	22.1
T7	3.4167	2.452	0.0346	19.5
T6	4.8750	2.378	0.0167	14.7
T5	6.8834	2.371	0.0072	6.29

3.6. Isothermal Melt Crystallization Study of Solid State Polymerized PEN

In this isothermal crystallization study, a semicrystalline PEN was used. This sample was obtained by solid state polymerization of the amorphous PEN at T2 under vacuum in 8 hours. Isothermal melt crystallization method applied to this sample was the same as the method previously described above. Sample was melted at 300 ^{O}C for 3 minutes, then immediately cooled to the crystallization temperatures T10, T9, T8, T7, T6 and T5 (T10> T9> T8> T7> T6> T5) respectively. DSC thermogram of the process is given in Figure 3.11. The DSC thermograms of both amorphous and solid state polymerized PEN, crystallization peaks at T10 and T5 do not have the typical bell shaped crystallization curves (Figure 3.7-3.11). This finding emphasizes the importance of selecting the right crystallization temperature. If Tc is high (closer to Tm), forming nucleating sites for crystallization becomes difficult. And for lower Tc's, closer to the glass transition temperature, viscosity of the polymer will be high and crystallization will be difficult. In both cases, required time for complete crystallization goes to infinity. Therefore Tc should be selected in the range between Tg and Tm but not too close to either of them.

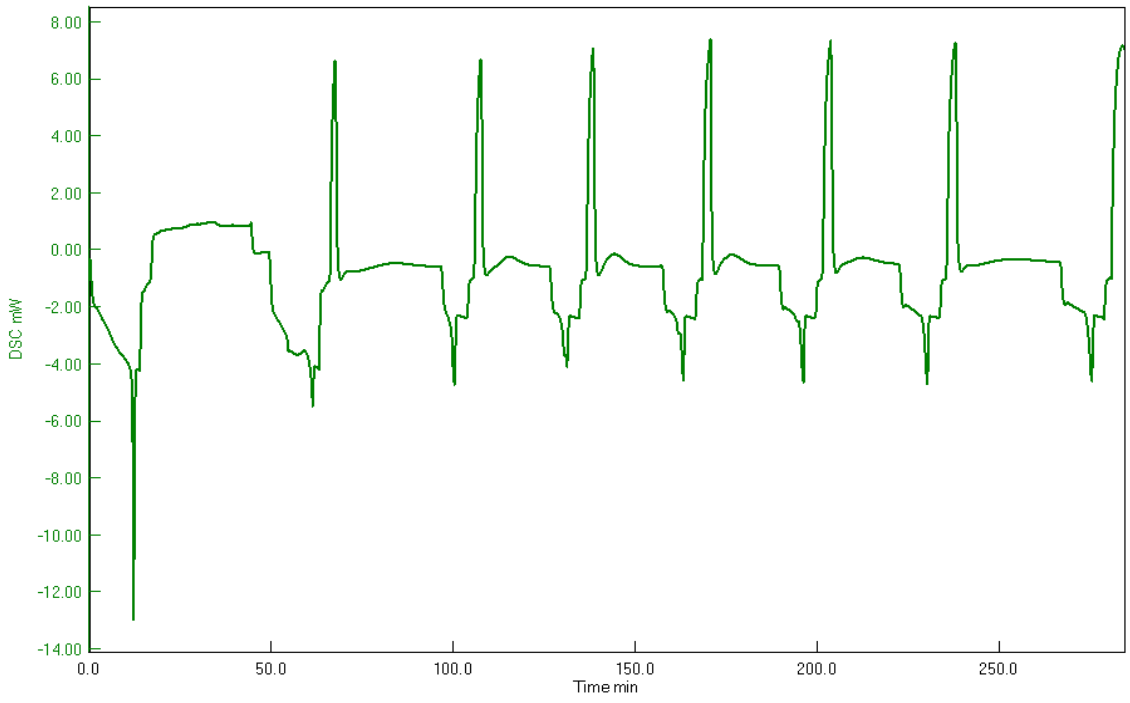


Figure 3. 11. DSC thermogram of the solid state polymerized PEN.

Relative crystallinity *vs* time graph for solid state polymerized PEN has also a sigmoidal shape and effect of temperature on Xt is similar with the amorphous PEN (Figure 3.12).

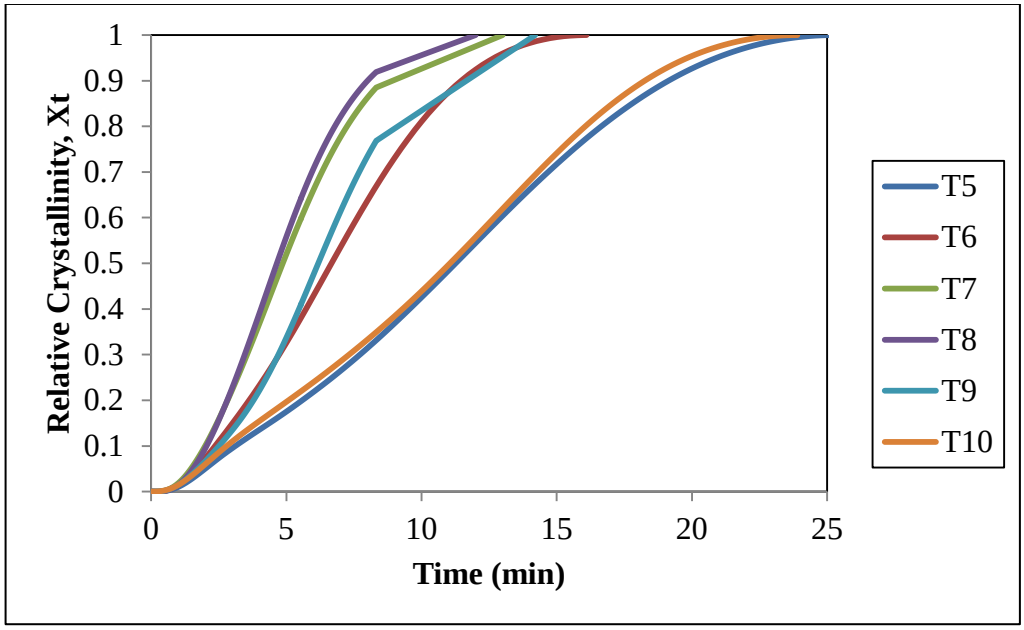


Figure 3. 12. Relative crystallinity *vs* time graph for solid state polymerized PEN.

Trend of half time of crystallization with crystallization temperature for solid state polymerized PEN is again similar with the amorphous PEN. However for all temperatures, $t_{1/2}$ is 1 to 5 minutes higher for the solid state polymerized PEN (Figure 3.13). Because solid state polymerized PEN has higher molecular weight, rate of crystallization for this polymer should be slower since it is difficult to crystallize the longer chains. And since higher half-time means slower rate of crystallization, the findings seem reasonable.

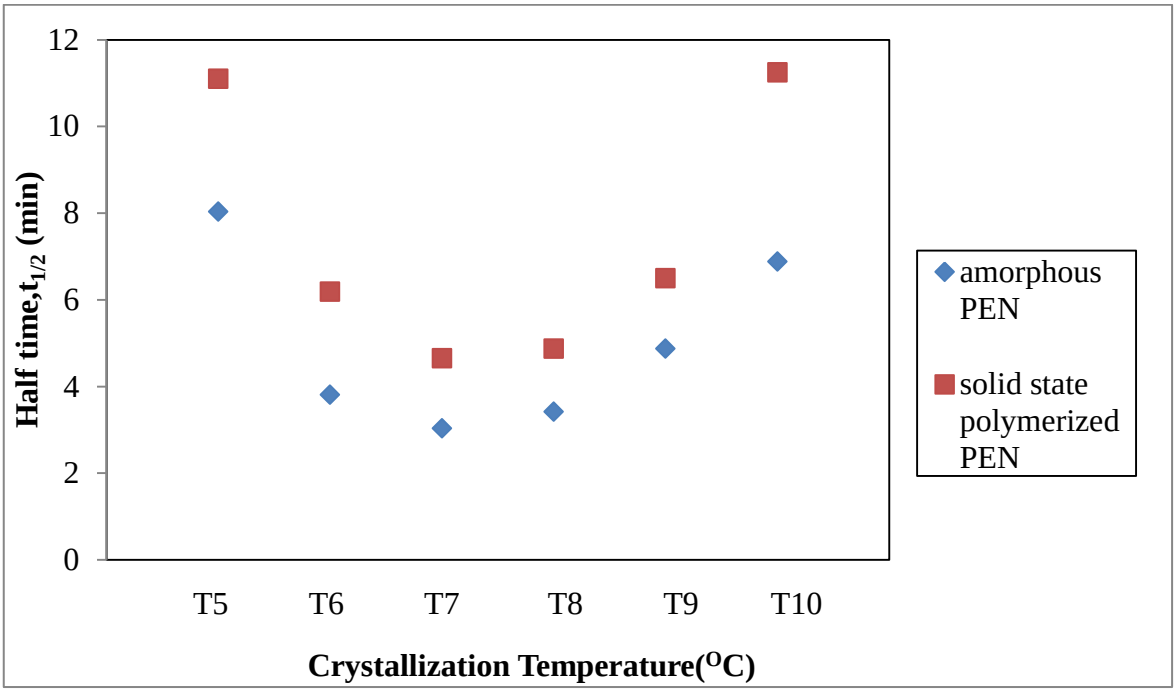


Figure 3. 13. Comparison of half-time of crystallization for amorphous and solid state polymerized PEN at different Tc values.

Avrami analysis of solid state polymerized PEN is also consistent with the amorphous PEN (Figure 3.14). Besides having lower rate of crystallization, Avrami exponent (n) values of the solid state polymerized PEN is also lower especially at T5 and T10 (Table 3.2).

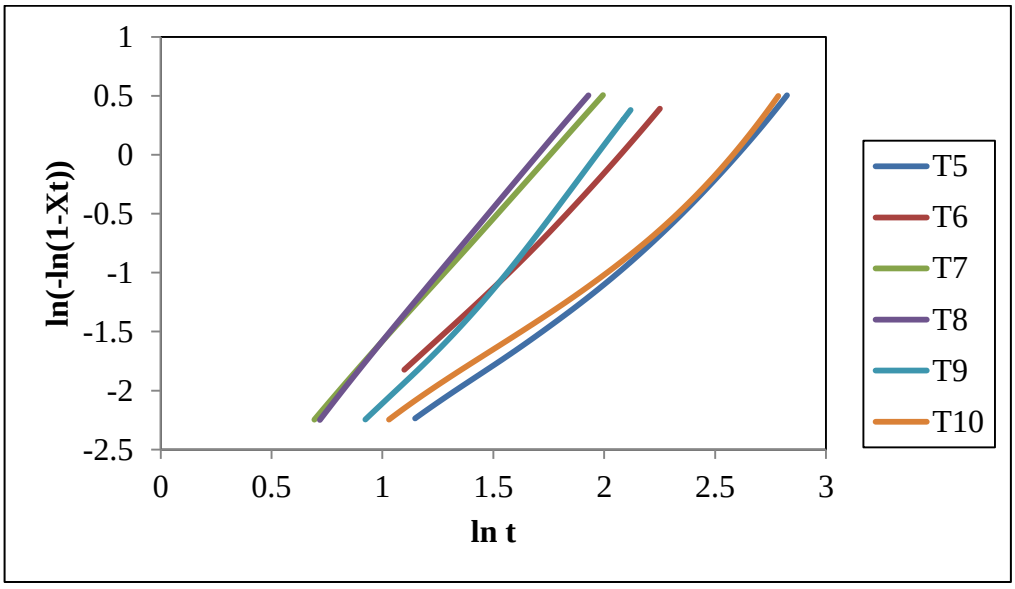


Figure 3. 14. Avrami analysis of solid state polymerized PEN.

Table 3. 2. Isothermal Melt Crystallization Kinetic Parameters for Solid State polymerized PEN.

Tc (°C)	$t_{1/2}$ (min)	**n**	**k** (min^{-n})	$\Delta H\infty$ (mJ/mg)
T10	11.1000	1.932	0.0180	52.9
T9	6.1840	2.633	0.0114	40.2
T8	4.6500	2.579	0.0215	40.5
T7	4.8750	2.468	0.0294	40.5
T6	6.5000	2.076	0.0193	40.7
T5	11.2500	2.001	0.0131	46.5

3.7. Isothermal Melt Crystallization of PEN Melted at Different Temperatures

When isothermal melt crystallization procedure is done, polymers are first melted at a predetermined temperature, then cooled to the crystallization temperature. Throughout this study, we choose this melting temperature as 300 °C. However, in this part of the study, we investigated the effect of this melting temperature on crystallization rate and Avrami parameters. Isothermal crystallization temperature was selected as T9, since DSC thermograms shows good Tc peak at this temperature. As a melting point T11, T12, T13 and T14 °C were chosen. Figure 3.15 shows the effect of change in melting condition on crystallization rate. As the temperature in which polymers were melted increases, rate of crystallization decrease. The reason is that as the temperature increases, number of self-nuclei will decreases, therefore it will take longer to nucleate and crystallize [47].

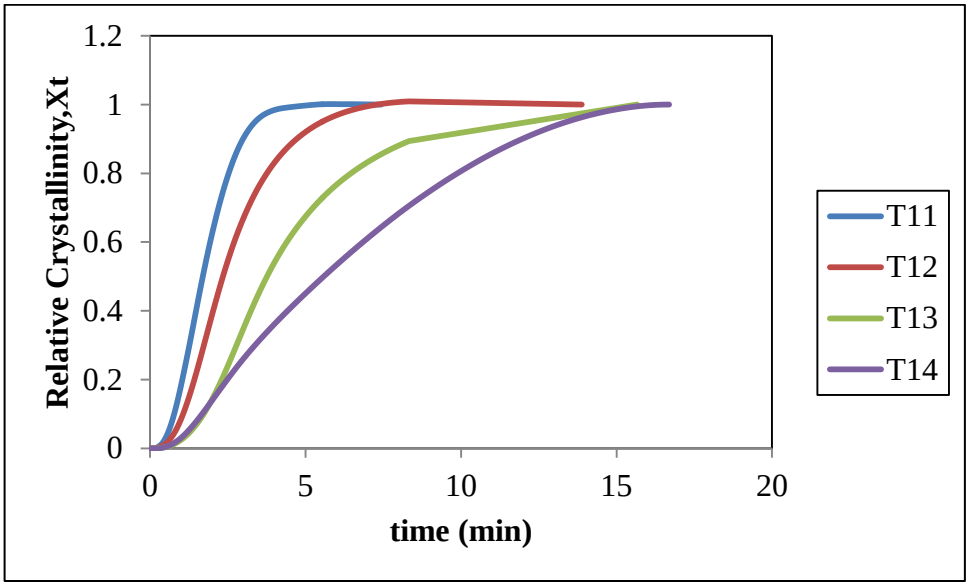


Figure 3. 15. Relative crystallinity *vs* time graph for PEN at T9 after melted at different temperatures.

Avrami plot for the process is also consistent with the above findings (Figure 3.16).

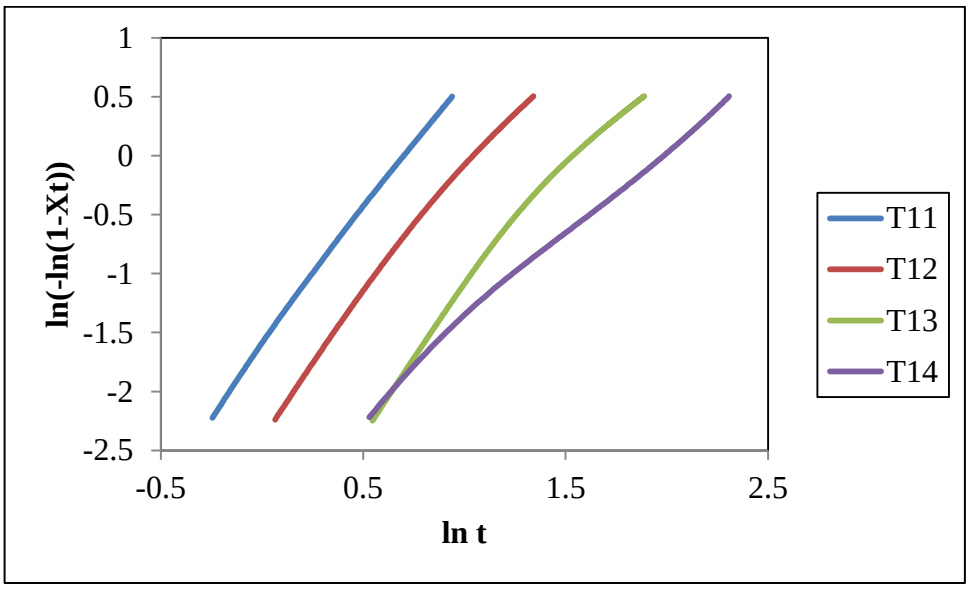


Figure 3. 16. Avrami analysis of PEN at T9 after melted at different temperatures.

3.8. Melting Behavior and Equilibrium Melting Point of PEN

3.8.1. Melting Behaviour of PEN

Figure 3.7 in Section 3.5 shows the melting points of the amorphous PEN after crystallization at different temperatures. Melting peaks are the sharp downward (endothermic) peaks in the figure. However melting peaks are not clear in that thermogram. Figure 3.17 shows the zoomed version of the thermogram corresponding to the crystallization at T9. It is clear in this figure that there are two melting points one at 254.6 ^{O}C and the other at 265.1 ^{O}C.

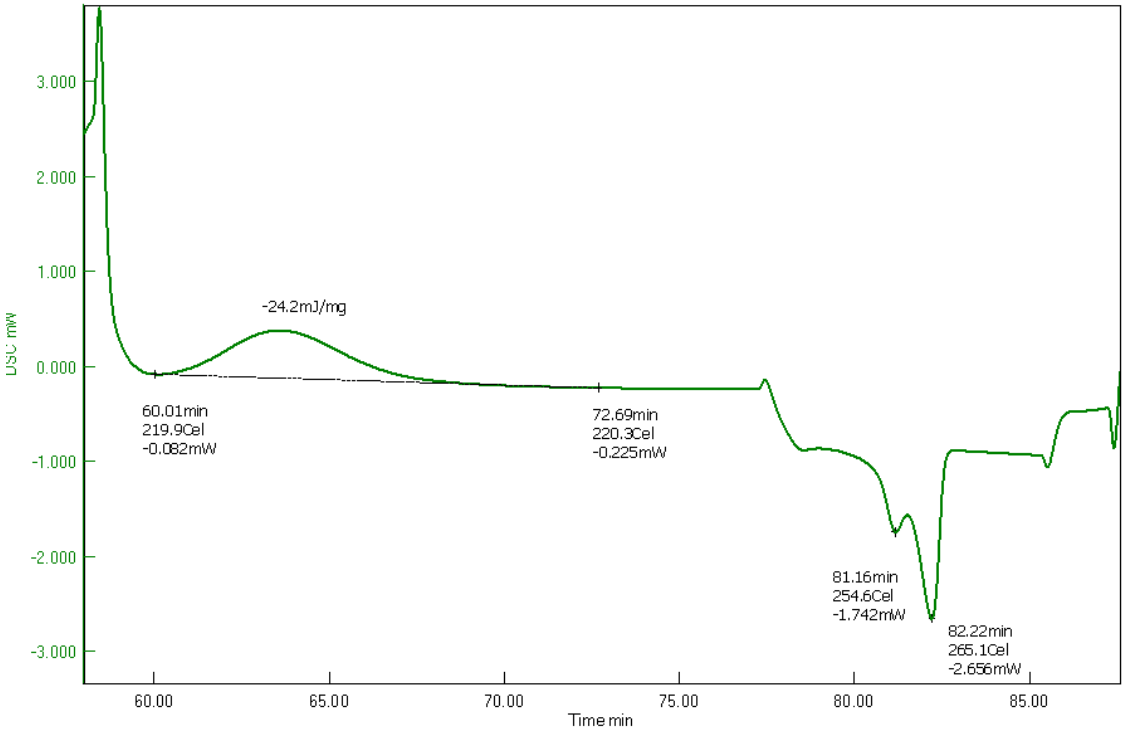


Figure 3. 17. DSC thermogram for crystallization of amorphous PEN at T9.

This double melting peak is not present only at T9 but also at nearly all Tc's for both amorphous and solid state polymerized PEN (Table 3.3). It should be important to determine which peak is the actual melting peak that results from the melting of primary crystallites that were formed at isothermal crystallization temperature. When correlation between isothermal crystallization temperature and melting points at both left and right side is investigated, it is shown that as the Tc increases melting point at the left hand side also increases but the changes in the right melting peak is negligible. It is nearly constant

for all Tc's. In the literature, multiple melting peak case is also present for PET [48]. In the DSC thermogram of PET, there are 3 melting peaks. Similar to our case the peak at the extreme right remains constant for all Tc's. Deshpande stated that this peak stem from the melting of the perfected crystallites which were produced by the recrystallization during the heating [48]. We also found that at temperatures T10 and higher, right melting peak disappeared which shows that recrystallization is not favored at higher temperatures.

Table 3. 3. Melting peaks of PEN after isothermal crystallization from different temperatures(^{O}C).

	Amorphous PEN		**Solid State Polymerized PEN**	
Tc	**Tm (left)**	**Tm(right)**	**Tm (left)**	**Tm(right)**
T10	259.3	not determined	261.1	not determined
T9	254.8	265.1	256.2	263.9
T8	250.2	264.8	251.2	264.2
T7	245.7	264.5	247.4	264.2
T6	241.9	264.0	243.5	263.9
T5	237.9	264.0	240.6	263.4

3.8.2. Equilibrium Melting Point of PEN

Rate of crystallization of polymers is dependent on the degree of supercooling which is found by the following equation.

$$\Delta T = Tm^{O} - Tc$$

In this equation ΔT stands for the degree of supercooling and Tm^{O} is the equilibrium melting point of the polymer. To understand the effect of temperature on crystallization rate, we should determine these two variables. Tm^{O} is defined as the melting point of the infinitely thick crystals and is a very important thermodynamic parameter to understand the driving force for the polymer to crystallize. Tm^{O} is found by extrapolating Tm *versus* Tc graph according to the Hoffman-Weeks linear extrapolation. After determining equilibrium melting point, degree of super cooling is calculated by the above equation.

For this part of the project two solid state polymerized PEN samples were selected. First one was obtained by solid state polymerization of amorphous PEN at T4 under vacuum in 4 hours and the second one is in 8 hours. Intrinsic viscosity values were 0,866 and 0,982 dl/g respectively. For this study, isothermal crystallization temperatures were

selected as T9a, T9, T9b and T9c since it was shown that around T9 crystallization peaks were better. Hoffman-Weeks plots for these two PEN were drawn (Figure 3.18-3.19). Equilibrium melting points for the polymers is the intersection point of the Tc=Tm graph and extrapolated line. Equilibrium melting point of the PEN which has the lower IV is 281.74 ^{O}C and for the high IV PEN it is 288.84 ^{O}C. It is shown that as the molecular weight increases Tm^{O} value of the polymers also increases.

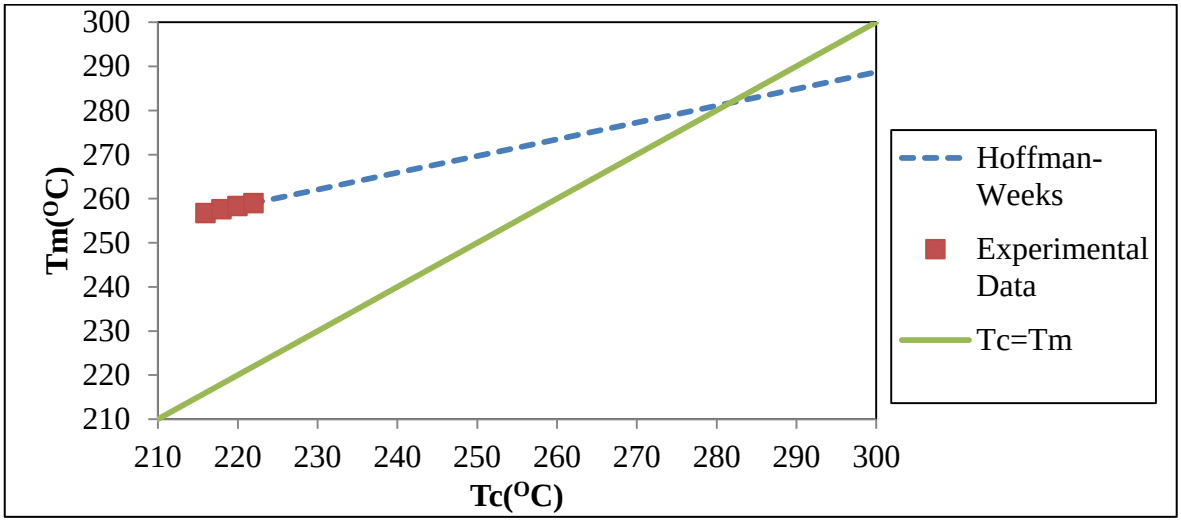


Figure 3. 18. Hoffman-Weeks plot for PEN with IV of 0.866 dl/g.

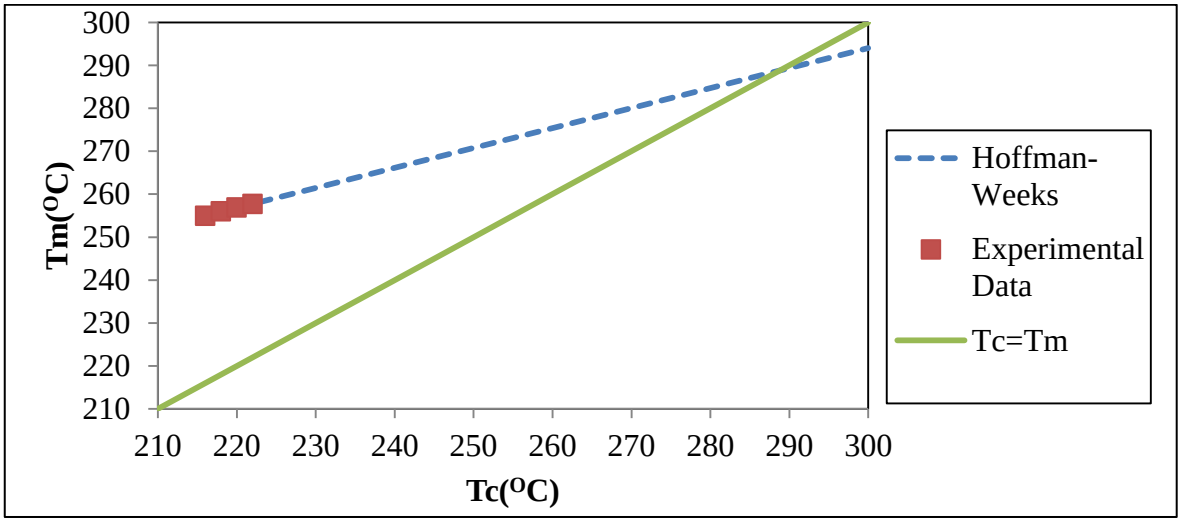


Figure 3. 19. Hoffman-Weeks plot for PEN with IV of 0.982 dl/g.

4. EXPERIMENTAL

4.1. Synthesis of PEN by Solid State Polymerization Under Nitrogen Flow

Amorphous PEN chips which have been synthesized in our laboratory by melt polymerization method were used as a starting material in the experiments. Amorphous PEN was waited at vacuum oven at 120^{O}C for 24 hours prior to synthesis. This step was done to remove volatiles from the samples and named as devolatalization step. Then polymers were transferred to the reactor which was pre-heated to 190 ^{O}C by using J-KEM Gemini 230 heat controller and they were waited here for 1 hour under nitrogen flow to gain some crystallinity before the polymerization. After crystallization step, temperature was raised to the polymerization temperature (T1, T2, T3 and T4 such that T4>T3>T2>T1) and polymerization continued for 8 hours.

For each experiment, about 30 grams of PEN was used. 10 grams of samples were taken away from the reactor after crystallization, 4 and 8 hours polymerization steps. These samples were used for intrinsic viscosity and carboxyl end group analysis. Nitrogen flow was continued throughout the reaction. However, flow rate of the nitrogen gas was increased when samples were taken to prevent oxygen intake to the reaction zone.

For the experiments which were run under nitrogen, a special two necked cylindrical flask reactor fitted with a reflux condenser was used. Reactor was composed of a glassware column and a porous filter for distributing the gas and supporting the sample. Reactor was designed so that nitrogen is pre-heated before entering the polymerization zone. This is achieved by inserting a spiral glass tube which is coiled up around the cylindrical reactor. Nitrogen gas passes through this glass tube which is also in the oil bath, and heated. So when it enters the reaction medium from bottom of the reactor, it will have approximately same temperature with the prepolymer particles.

4.2. Synthesis of PEN by Solid State Polymerization Under Vacuum

The devolatalization step for the under vacuum experiments is same with the under nitrogen experiment. For the crystallization and polymerization steps nitrogen gas was not

used for condensate removal. Instead, vacuum was applied to the reactor by using Vacuubrand CVC3000 vacuum controller. Pressure was adjusted to 1 mbar for all the experiments.

Reactions were carried in two necked round bottom flask fitted with a reflux condenser. When samples were taken for the IV and CEG analysis, nitrogen gas was passed through the reactor. If sample meets with oxygen before nitrogen, degradation due to oxidation and yellowing happens.

4.3. Intrinsic Viscosity Analysis

Intrinsic viscosity analyses of the PEN samples were done by using ASTM D5225 procedure.

4.4. Carboxyl End Group Analysis

Carboxyl end group concentration analyses of the PEN samples were done by using ASTM D7409 procedure.

4.5. Isothermal Crystallization Study

Isothermal crystallization studies of the samples were done by using EXSTAR SII DSC 7020 instrument. Instrument is interfaced to a computer to monitor the change in rate of heat evolution with time. DSC is calibrated with high purity metals; indium, tin, lead and stearic acid. Nitrogen atmosphere was used for all experiments. Samples which are 5-10 mg were put in aluminum pans and an empty aluminum pan was used as a reference.

For the isothermal melt crystallization studies, polymers were melted at 300^{O}C with a scanning rate of 20 ^{O}C/ min for 3 minutes, and then rapidly cooled to the predetermined isothermal crystallization temperature with a rate of 100 ^{O}C/min. Polymers were waited for 30 minutes at isothermal crystallization temperature for complete crystallization and stable baseline. After each isothermal crystallization step, polymers were heated to 300 ^{O}C with a rate of 10 ^{O}C/min to determine the melting point of the crystallites that were formed at that Tc.

Isothermal melt crystallization of PEN was also performed at T9 after melted at T14, T13, T12 and T11 (T14>T13>T12>T11) for 30 minutes.

5. CONCLUSION

Molecular weight of polyesters which are synthesized by only the melt polymerization is low for high performance applications. Solid state polycondensation is a method to increase molecular weight of polyesters. In the present study, solid state polycondensation of PEN prepolymers was studied. Polymerizations were done at temperatures T1, T2, T3 and T4. Among these temperatures, polymerization was found to be fastest at T4 and as the temperature decreased, the rate of polymerization also decreased. Also it was found that polymerization which was done under vacuum was faster than the one done under the nitrogen flow. Therefore the vacuum process seems to be more effective to remove volatile by-products. Another finding about SSP of PEN is that as the initial intrinsic viscosity of the PEN prepolymer increases, polymerization rate decreases due to the limited mobility of the chain ends and lower concentration of end groups.

Isothermal melt crystallization studies of amorphous and synthesized PEN were done. Relative crystallinity of the polymers at time “t” was determined at different temperatures. Crystallization of PEN is found to be fastest at T8 and it slows down at higher and lower temperatures. Avrami kinetic analysis for the isothermal melt crystallization of amorphous PEN gives Avrami exponent of “n” in the range of 2.3 to 3.0 which shows athermal nucleation with sphere like crystallites. Avrami exponent for solid state polymerized PEN is somewhat lower and in the range of 2.0 to 2.6. For the isothermal analysis, the effect of the temperature at which polymers are melted were investigated and the result show that polymers which are melted at higher temperatures crystallize slowly at T9.

Finally, melting behavior of crystallized PEN was investigated. Two melting peaks for crystallites were observed in DSC and the left peak is considered results from the melting of crystallites which are formed at that crystallization temperature. The right melting peak is not changing with Tc so it may be stem from the melting of crystallites that are formed during recrystallization.

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