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ABSTRACT

PROCESS-STRUCTURE-PROPERTY RELATIONSHIP OF A MESOGENIC BIOERODIBLE POLYARYLATE

by Seung Uk Yoo

Polymeric biomaterials are artificially synthesized polymers designed for in-vivo use. The material must be characterized and should satisfy the requirements suitable in human bodies.

For the proper characterization of materials, it is essential to apply specific processes, analyze thermal and mechanical properties, and understand the process effect and the morphology. Thermal analysis is one of the most sophisticated and well developed techniques for polymer characterization. Turi [1] has explained about the thermal characterization of polymeric materials. Jaffe et al [2], in the chapters of characterization of fibers and films, emphasized the effect of the process history of a polymer to the end-use by thermal analysis.

The polymer used for this study is a Kohn polymer which is a bioerodible, desaminotyrosyl-based polyarylate combinatorial library synthesized by Kohn and coworkers [3-5]. The polymer has two substitutable sites in the main chain and the branch.

The kohn polymer library is established by the change of the number of methylene groups in the two sites. Accordingly, various Kohn polymers can be produced, and several polymers were selected from the library and spun to fiber forms as a use of bioerodible scaffolds for anterior cruxes ligament repair [6]. In this study, the focus is on

the poly (DT 12, 10). It was selected because of the stability of its orientation [6, 7]. The abbreviation, DT, represents Desamino Tyrosil, and the numbers indicate number of methylene groups in the side chain and the main chain respectively.

Spinning, drawing, and annealing processes were applied to the fiber, and then analyzed by Thermomechanical Analysis (TMA) Differential Scanning Calorimetry (DSC) for figuring out the influence of processes on the properties. Polarized Light Microscopy (PLM) and X-ray diffraction were used to determine the structure. As a result, it was found that all the processes developed the properties effectively. One of the major findings was that the polyarylate fiber exhibited a highly negative coefficient of thermal expansion, and the optical micrograph, which showed a liquid crystal pattern, confirmed that the poly (DT 12, 10) possesses a layered liquid crystal structure regarded as a smectic phase.

PROCESS-STRUCTURE-PROPERTY RELATIONSHIP OF A MESOGENIC BIOERODIBLE POLYARYLATE

by

Seung Uk Yoo

A Thesis Submitted to the Faculty of New Jersey Institute of Technology In Partial Fulfillment of the Requirements for the Degree of Master of Science in Materials Science and Engineering

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APPROVAL PAGE

PROCESS-STRUCTURE-PROPERTY RELATIONSHIP OF A MESOGENIC BIOERODIBLE POLYARYLATE

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First,

I would like thank my Lord

who has always guided me in my life,

who gives me strength and inspiration in my work,

and who answers my prayers.

This thesis is dedicated to my beloved parents, Yoo Hong-Sik and Lee Hyun-Jung, and

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CHAPTER 1

INTRODUCTION

Professor J. Kohn [3] has established a new family of polymeric biomaterial, the desaminotyrosine-based (DT) polyarylate combinatorial polymer library. The Kohn polymer consists of a diacid component and a diphenol component. The polymer has a side chain in the diphenol component region. There are two substitutional sites: one in the backbone chain and one in the side chain.

The combinatorial library is constructed by the combination of the number of methylene groups in the two substitutional sites. The polymer compositions are referred to as poly (DT R, Y), in which R is the number of methylene groups in the side chain and Y is the number of methylene groups in the backbone chain. Since there is a backbone amide linkage in the DT monomer, these polymers may be referred to as polyarylates or alternating polyester amides (Figure 3.1).

Several polymers were chosen from the library for study. The analysis of the selected polymers was performed by Jaffe et al. [6, 7, 8]. The results of thermal analysis and biorelevant characterization have indicated that the polyarylate compositions with short side chains and short aliphatic groups in the backbone chain have a relatively high glass transition temperature, strong water plasticization effects, and undesirable water shrinkage.

In contrast, the polymers which have high values of R and Y exhibit low glass transition temperatures, but possess long-range order, which is a globally oriented structure. These polymers are characterized by very low moisture absorbance and no absorbable water shrinkage at 37°C. The long-range order can be easily found in poly

(DT 12, 10) as shown in the X-ray diffraction.

In this study, the poly (DT 12, 10), which possesses the long-range order, is investigated. Fiber spinning, drawing, and annealing processes are applied to this polymer, and analyzed by Differential Scanning Calorimetry (DSC), Thermomechanical Analysis (TMA), X-ray diffraction, and Polarized Light Microscopy (PLM).

The purposes of this investigation are to understand the effect of processings on the properties and the structure of the resulting fibers and films, and to use these results to determine the origin and nature of the long-range order that the poly (DT 12, 10) possesses.

CHAPTER 2

BACKGROUND

2.1 Liquid Crystals

Liquid crystal is described as a state of aggregation that is in an intermediate order between the crystalline solid and the isotropic liquid [9]. Liquid crystal phase possesses both the solid state and the liquid state. It flows like a liquid but the optical property of the phase differs from the flow direction. In addition, the properties are similar to a crystal. The directions of molecular axes, which compose the material, are in the medium state between the crystalline solid phase and the isotropic liquid phase. The liquid crystal phase, which possesses these kinds of properties, is also called mesomorphic phase or mesophase.

From an optical point of view, as mentioned above, liquid crystal has anisotropic characteristics. Even though the fluidity is like a liquid, the different optical properties as the flow directions are like a crystal. Some materials that exhibit this character in a certain temperature range are called thermotropic liquid crystals, and others which show orders induced by solvents are called lyotropic liquid crystals. The former, thermotropic liquid crystal, is related to electronic devices, and the latter is connected with biological or body tissues.

In 1888, the phenomenon of a liquid crystal phase was first observed by an Austrian botanist, Friedrich Reinitzer [10, 11]. He was interested in cholesterol and its biological function in plants and found the new phase of matter during his research. When he was heating the cholesteryl benzoate, he observed that it melted at 145.5°C to a cloudy

liquid phase and changed to a transparent liquid phase at 178.5°C. He observed birefringence and colors from the matter. The change of the phase was reversible when the liquid was cooled down.

O. Lehmann [10], a German physicist, using polarized light microscope, confirmed that there were optical anisotropic properties and suggested the term "liquid crystal" for the materials, which have both the liquid mobilities and optical anisotropic properties. Another German scientist, D. Vorlander [10, 11], contributed to the study of liquid crystal chemistry. He synthesized many liquid crystals and found more than 250 until 1920. The research about liquid crystals evolved during the 1920s. There were special symposia about liquid crystals in 1933 [12]. Because there was no development of applications for liquid crystals, the researchers thought that all major curiosities were solved and the research interest decreased until the 1950s. However, after the 1960s, many applications using liquid crystals were invented (ex: liquid crystal thermography) and the study was activated again. There are more than 10 thousand liquid crystal compositions known.

Liquid crystalline phases can be found in a material which has a linear or planar molecular structure, and they are classified by the conformation of the molecular orientation. George Friedel [10, 11], a French scientist, suggested three types of liquid crystals based on optical observation: nematic, cholesteric and smectic liquid crystals.

2.1.1 Nematic Phase Liquid Crystal

"Nematic" comes from a Greek prefix "nemato", which means threadlike. It is the most

common type of phases, which are observed in liquid crystals. Mesogens, (a mesogen stands for a rod-like molecule, which play a major role in the behavior of a liquid crystal phase), are aligned to threadlike shape and they are oriented in the same direction (Figure 2.1). In other words, the director (n), the direction of the orientation, of all the mesogens is same at least locally. Nematic phase has an orientational order but there was no positional order.



Figure 2.1 Molecular orientation of nematic phase.

2.1.2 Cholesteric Phase Liquid Crystal

Because this phase was first observed in cholesterol derivatives, it is called the cholesteric phase. Cholesteric phase liquid crystal are similar to a nematic phase. When the asymmetric molecules are mixed in a nematic phase material or a liquid crystal is composed of chiral molecules, the molecular axes are twisted and form a cholesteric phase. Therefore, they are also known as Chiral nematics or twisted nematics.

The cholesteric phase has a layer structure like a smectic phase, but the array of mesogens in each layer is same to that of nematic phase. The axes of mesogens are parallel to the layer axes. However, they are twisted in each layer and the directors of the twisted mesogens form a helical structure when it is observed perpendicular to the layer axes. The length of that the director make 360° turn is called a pitch and the range is about 0.3μ m. Figure 2.2 shows molecular orientation of cholesteric phase of each layer in $\frac{1}{4}$ pitch.



Figure 2.2 Molecular orientation of cholesteric phase.

2.1.3 Smectic Phase Liquid Crystal

The word "smectic" means soap in Greek ("smegma") because smectic phase was first found in a thick soap solution. The smectic phase has a lot of variants according to the conformational array of the mesogens. The characteristic of this phase is that the mesogens have orientational order like a nematic phase but they form a layer structure (Figure 2.3).



Figure 2.3 Molecular orientation of smectic phase.

Many smectic phases were identified and thay are defined using the alphabets, A, B, C, etc, in the order in which they were discovered [13]. There are two general phases of smectic phases. They are smectic A and smectic C phases. In a smectic A phase, the axes of mesogens are perpendicular to the layer but there is no positional order in a layer. Smectic B phase has layered structure and has an order in a layer. In smectic C phase, the director is tilted from the position perpendicular to the layer.

2.2 Liquid Crystalline Polymers

Polymers, which have characteristics of liquid crystals, are called liquid crystalline polymers. They exhibit analogous properties to small molecule liquid crystals [14]. Having rod-like molecule part, which is called mesogen, in a polymer chain, is critical for a polymer to have liquid crystal properties.



Figure 2.4 Liquid Crystalline Polymers : (a) Main chain LCP; (b) Side chain LCP; (c) Main chain-Side chain LCP.

There are two approaches, which determine the types of liquid crystalline polymers [14, 15]. The determination of types depend on the position of mesogens in polymer chains. The first one is main chain liquid crystalline polymer. The mesogens are located in the main chain and usually they are connected with a flexible polymer chain, which is called a spacer, but some main chain liquid crystalline polymers don't have spacers and mesogens are directly combined each other. The other one is side chain liquid crystalline polymer, which has mesogens in the side chain. The flexible spacers connect between the mesogen and the backbone chain. The main chain - side chain liquid crystalline polymer is a conjoined structure of both main chain and side chain liquid crystalline polymers (Figure 2.4).

2.2.1 Main Chain Liquid Crystalline Polymers

As a first class, the main chain polymer liquid crystal is a polymer liquid crystal, which has mesogens in its main polymer chain. Two classes of main chain liquid crystalline polymers exist [14, 15]. One is that mesogens in the main polymer chains are connected with flexible groups, spacers, which have a role of binding mesogens linearly. The other is that there are no spacers in backbone chain. Monomer of the polymer has two or more aromatic rings and methyl group does not exist in it.

Simple main chain liquid crystalline polymers often show crystal meltings at higher temperature than the temperature where the polymer is degrading. For controlling the liquid crystal phase in a proper condition and temperature for processings, it is necessary to lower the melting temperature. Several methods can be used for the purpose.

Because the reason of having high melting temperatures is the good orientation of

chains and large molecular interaction between them, they can be decreased by copolymerization for reducing the interaction or by giving random orientation.

2.2.2 Side Chain Liquid Crystalline Polymers

The structure of side chain liquid crystalline polymers is that the mesogens are located at side chains in a branched polymer [14, 15].

The property of main chains, backbone chains, of the side chain liquid crystalline polymers is critical to show the behavior of liquid crystal because if the backbone chain is very stiff, the glass transition temperature and the melting temperature will be high. Then, it is difficult to observe the liquid crystal behavior from the polymer. By giving flexibility to the backbone chain, the glass transition temperature can be decreased. It can be achieved when the aliphatic chain is imported to the backbone chain.

The mesogen is composed of several aromatic rings and usually attached in the end of the side chain and the spacers are connecting mesogens to the backbone chain. Because of the mobility of mesogens connected by the spacers, the length of spacers plays an important role in the side chain liquid crystalline polymers forming liquid crystal phases.

2.3 Process-Structure-Property Relationships of Polyarylates

The polymeric biomaterial, desaminotyrosyl-based polyarylate combinatorial library, has been studied by Jaffe et al. [6]. The investigation was executed by multilateral analysis as a purpose of finding out the process-structure-property relationships. The earlier study performed by Kohn [3] indicated that the polyarylate, which has short side chain and short aliphatic group in a main chain, exhibits high glass transition temperature, and the long main and side chain polyarylate has low glass transition temperature relatively.

Considering the variation of glass transition temperature of the polyarylates, the polymer compositions, poly (DT 2, 2), poly (DT 2, 4), poly (DT 8, 8), and poly (DT 12, 10) were chosen and produced as fiber forms.

From the investigation with the fibers, it was confirmed that longer aliphatic group in a backbone chain make the polyarylate fiber more flexible and showed lower glass transition temperature. However, drastic shrinkage under body conditions (wet and 37°C) was found with fibers spun from short side chain polymer with small aliphatic group, poly (DT 2, 2). From the wet shrinkage test, it was indicated that the drawing effect, improved orientation of the polymer chains in the fiber, caused the increase of wet shrinkage. And when compared the wet fiber with the dry fiber (undrawn fibers), it was shown that the wet condition given to the fiber induced the decrease of the glass transition temperature.

In the result of the poly (DT 12, 10) fiber, the exothermic peak regarded as crystallization was observed in cooling cycle in a DSC experiment. Surprisingly, other polymer fibers did not show the peak at the same cooling rate. The X-ray diffraction pattern of poly (DT 12, 10) and poly (DT 8, 8) exhibited a systematic, long-range order polymer while poly (DT 2, 4) showed amorphous, liquid like patterns. The exhibited X-ray diffraction pattern in poly (DT 12, 10) showed similarity to smectic phase liquid crystal pattern, which has layered structure. The results strongly indicated that the structure of poly (DT 12, 10) fiber possesses long- range order or mesogenic phase. Prof.

Jaffe described the structure as that of a condis (conformationally disordered) crystal.

Jaffe et al. [8] continued the study about the long-range order of this polymeric material. It was observed that the relatively strong hydrogen bonds between amide groups exist in long-range order polymers, and weak hydrogen bonds lie between amorphous polymers. The investigation to establish whether strong hydrogen bonds the major key to establishing the long-range order is underway.

2.4 Coefficient of Thermal Expansion (CTE)

The coefficient of thermal expansion is defined as the fractional dimension change per unit increase in temperature. When the dimensional change is focused on the linear expansion or shrinkage, the coefficient of thermal expansion stands for linear coefficient of thermal expansion (α), and if the volume change is a main issue, it means volume coefficient of thermal expansion (β or α_v). Generally, the change of longitudinal dimension is considered for CTE. For simple exchange of linear and volume CTE, assuming dimensionally isotropic material, β is defined as 3α .

When the material is heated, the atoms of the material absorb the energy and they are in motion. As a result, most of the materials expand and show positive dimensional change. However, some materials exhibit negative CTE. Several highly oriented polymers show negative coefficient of thermal expansion, and some metallic compounds also exhibit negative value of it. It has been well studied about the negative CTE for inorganic or non-polymeric materials. Many inorganic materials which have negative CTE were found and the theoretical concept of the reason for negative CTE is well established [16, 17], moreover, the general formula of compositions is produced [18]. However, the study about negative CTE of polymers is rare, and only a few highly oriented polymers have negative value of CTE [19, 20].

For inorganic materials, Evans et al. [18] found the general formula of $A_2(MO_4)_3$ for the compounds showing negative CTE, and suggested the requirement of having negative CTE. The alphabets A and M stand for $3+ \sim 6+$ cationic metal atoms. For example, $Sc_2(WO_4)_3$ exhibit negative CTE because of the vibration of the oxygen atom binding two M atoms. Evans et al. [18] suggested that the transverse vibration of the oxygen atom between two M atoms caused the diminution of the M-M distance. The CTE value of these types of inorganic materials is variant. The material $Sc_2(WO_4)_3$ has $\alpha =$ - $2.2 \times 10^{-6} \text{ K}^{-1}$, and $Zr(WO_4)_2$ has $\alpha = -8.7 \times 10^{-6} \text{ K}^{-1}$.

Polymeric materials have relatively higher value of CTE than other materials. The normal range of α is 50 ~ 100 × 10⁻⁶ K⁻¹ for polymeric materials. Some highly oriented polymers, UHMWPE and aromatic polyamides for examples, show negative CTE. Bruno et al. [19], in the study of negative CTE with the ideal model of orthorhombic polyethylene, concluded that the negative CTE is a result of vibrations of the polymer elements perpendicular to the chain axis accompanied with the transverse expansion. Lacks et al. [20] investigated about the relationship of thermal expansion and thermal effect to aromatic polyamides, and suggested that one of the factors of causing negative CTE could be the elastic response to the thermal stresses perpendicular to the chain axis, which is related to the change in entropy with strain and the heat capacity.

CHAPTER 3

EXPERIMENTAL

3.1 Materials

The polymers investigated in this study were polyarylates described by Professor Joachim Kohn [7]. The basic chemical structure of the polymer is described below (Figure 3.1). Polymer compositions are referred to as poly (DT R, Y). R and Y in the Figure 3.1 represent the number of substituted methylene groups, and the abbreviation DT represents 'Desaminotyrosinetyrosyl-based'. The poly (DT 12, 10), which is a major polymer for this study, stands for a shorthand for the polymer where $R : -(CH_2)_{11}-CH_3$ and $Y : -(CH_2)_{10}-$.



Figure 3.1 Basic chemical structure of desanino tyrosil polymers.

The polymer was supplied by Advanced Material Design (AMD). The number average molecular weight and the weight average molecular weight of thE polymer were 69,000 g/mol and 130,000 g/mol, respectively.

3.2 Processing

For determining the processing effect on the properties, 140µm as-spun fiber was drawn to 100µm fiber at room temperature with drum type fiber drawing equipment. Then, to further investigate the control of thermo-mechanical properties, all fiber samples were annealed at different temperature for different periods. Before processing, the material was first heated in a vacuum oven at 100°C for one hour as a purpose of removing any residual moisture. Figure 3.2 shows a schematic chart of the processing.



Figure 3.2 Schematic process diagram.

3.2.1 Film

A 1mm thick metal plate with a 130mm diameter circle cut out from the middle of the plate was constructed to fit between the plates of a heated press. The pre-dried polymer was put in the middle of the punctured space and both sides were covered with Kapton (thin polyimide film made by Dupont) for the easy separation of the film from a press.

The prepared material set was put in a Carver press. It was pressed with light pressure until the polymer was somewhat spread, and the Carver press was heated to 130°C until the polymer shape was fixed to a film form. The temperature was measured with a thermocouple. The pressed film was cooled down to room temperature.

3.2.2 Spinning and Drawing

The flow rate of the polymer was measured in a melt index to decide the appropriate temperature for the spinning. The pre-dried polymer was heated at a specified temperature (130°C, 140°C, and 150°C) in a barrel and a standard weight (5.1kg, 5.1kg, and 2.16kg at each temperature) is applied to a piston, which extrudes the polymer through a hole of die. The weight of polymer extruded out through the orifice was measured with time. According to the melt flow rate, the temperature for the spinning was found between 130°C and 140°C.

The melt spinning was performed with a James plunger fed micro-melt spinning machine. The barrel was installed in the spinning machine with a screen and 762 μ m diameter-hole die (spinneret). The plunger speed was constant as 2.5 rpm, and the fibers were spun to different diameters by changing take-up speed. Fiber with diameters between 140 μ m and 45 μ m were produced. In this study, 140 μ m fiber was used for the

experimentation because of the ease of handling and observation of processes.

The drawing process was applied to the as-spun fiber at room temperature using the difference of drum speed. Fibers were hung over two drums and the two independent drums rotated with different velocity. The draw ratio was 2.71, which is expressed as a ratio of the drum rotation speed (R2/R1). The first drum speed (R2) was 3.2 rpm and the second drum speed (R1) was 1.18rpm. Young's modulus of both fibers were measured with Thermomechanical Analyzer (TMA). The sample was kept isothermal at room temperature, 27°C, and the experiment was executed with the ramp force of 0.1N/min to 1.0N/min. The modulus of as-spun fiber was 0.82GPa, and the drawn fiber showed 1.88GPa of Young's modulus.

3.2.3 Annealing

The annealing temperature was chosen by the result of thermomechanical analysis (TMA) data. Paying regard to degradation during the annealing process, the temperature range employed was 40°C and 55°C for 140µm fiber and 100µm fiber. Each temperature was determined from the apparent softening temperature from the TMA result of each fibers. For discerning the effect of annealing time, one-hour annealing time as a short period, and 24-hour annealing time as a long period was used. After the samples were annealed under each condition described above, they were cooled down room temperature and thermal analysis was performed.

To determine the appropriate condition of fibers during the annealing process, TMA test was performed with fibers annealed under two conditions; freely relaxed, and both ends fixed. As there were no significant differences in properties, the annealing process was done under free to shrink fiber condition. The lack of difference between constrained and unconstrained fibers is indicative of a global mesogenic structure.

The temperature of an oven was first set, and then left empty for the oven to equilibrate. A certain length of the fiber was taken from a spool and placed in an aluminum dish without entanglement. The process condition followed Figure 3.2.

3.3 Characterization

The characterization of the polymer was executed by thermogravimetric analysis (TGA), thermomechanical analysis (TMA), differential scanning calorimetry (DSC), X-Ray spectrometry, and polarized light microscopy (PLM).

3.3.1 Thermogravimetric Analysis (TGA)

As a first step, the measurement of water take-up of the polymer was performed with a thermogravimetric analyzer (TA instruments Q50) to measure absorbed moisture in the material. Thermogravimetric analysis, TGA, measures the change of weight of a material as a function of temperature or time.

The experimental condition was that the temperature increased to 150°C with heating rate of 10°C/min, and kept isothermal condition for 30 minutes. The weight change (%) was observed as a function of process time and temperature change. From the result, it was found that this material did not absorb significant moisture (0.0035% or less of weight reduction before degradation).

3.3.2 Thermomechanical Analysis (TMA)

Thermo mechanical measurement was carried out on a thermo mechanical analyzer (TA Instruments 2940). Thermomechanical analysis, TMA, measures the dimensional change of a material as a function of time, temperature, and applied load. For the observation of dimensional change during the increase of temperature, the fiber samples were heated from -60°C to 120°C.

Approximately 15mm of fiber sample was first taken and held it with two stainless steel clamps using alignment fixture. The sample is placed in a stage which is a part of the furnace assembly. The furnace is closed and the experiment condition is set with computer software. The temperature range was -60°C to 120°C as mentioned above, heating rate was 5°C/min and the applied load was 0.05N.

The applied load has the role of giving tension to the sample fiber during the experiment, so the result showed smooth curve. When the applied force was very low (ex: 0.001N), the result graph showed a high level of noise. The length of the fiber sample was measured by the thermomechanical analyzer with a probe/stage assembly for fiber samples, and the liquid nitrogen (N_2) was poured in the coolant reservoir located on top of the furnace to reach the initial temperature. The liquid nitrogen was added several times in the experiment.

3.3.3 Differential Scanning Calorimetry (DSC)

Thermal measurements of the prepared polymer film and fiber were carried out on a differential scanning calorimetry (TA instruments Q 100). Differential scanning calorymetry (DSC) measures the changes in specific heat of a material as a function of

temperature, and time. The samples were analyzed under three cycles, heating, cooling, and reheating. The collected data showed the initial transition temperature, melting temperature, crystallization temperature, and the properties influenced by processes. The heating rate and cooling rate was fixed to 10°C /min, and 5°C /min through all the experiments to allow accurate comparison of data.

The sample was heated from -40°C with heating rate of 10°C /min to 140°C. In the pre-test of DSC with this polymer, no peaks were found after 100°C, and the fiber was broken around 100°C in TMA result. Therefore, the temperature range was fitted to allow parallel observation with TMA result. The cooling cycle was continuously performed after the first heating cycle under flowing nitrogen gas. Second heating cycle was also processed with same rate of first cycle in same temperature range.

3.3.4 X-RAY Diffraction

Wide angle X-ray scattering (WAXS) experiment on the as-spun fiber was performed by Dr. Jing Wu [7]. Cu-K α radiation with a wavelength of λ - 1.54Å was used in the experiment, and the distance between the sample and detector was 60mm. The diffraction pattern was recorded using a Siemens Hi-Star X-ray area detector.

3.3.5 Polarized Light Microscopy (PLM)

Liquid crystal textures of the polymer and the phase transition morphology were observed with an ZEISS polarized light microscope equipped with M23 35mm manual camera. The 0.5×0.5 cm, and about $0.15 \sim 0.20$ mm thick, polymer film sample was slightly pressed at room temperature with glass slides.

For the observation of the pattern of the film, the sample was put on a new slide glass. After $1 \sim 2$ drops of mounting fluid (Type B) was added it was covered with cover glass. The observation was executed at room temperature between crossed polars, and the total magnification of the of the microscope was ×400 (×40 for objective, and ×10 for eyepieces).

For non-isothermal experiments, a Mettler FP 82HT hot stage was installed between the objectives and the stage of the microscope. The pressed film was heated in the hot stage from 25°C to 100°C with 5°C /min of increasing rate. After heating process, it was cooled down to room temperature. The cooling rate was also 5°C /min. The phase change was observed with the total magnification of ×63 (×6.3 for objective, and ×10 for eyepieces) because of the small working distance in high magnification. The patterns observed through the microscope was recorded by M23 manual camera which was installed on top of the optical microscope.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Thermal Analysis – Effect of Drawing

As a general method to modify fiber properties, especially to enhance the fiber orientation and improve mechanical properties, the drawing process was applied to the poly (DT 12, 10) fiber. The effect of the process was observed with thermomechanical analysis, and differential scanning calorimetry.

4.1.1 TMA Result of As-spun Fiber and Drawn Fiber

The effect of drawing process on the mechanical properties was observed by TMA (Figure 4.1). The apparent softening temperature, the temperature where the dimensional change starts to increase, was 43°C and the slope between the apparent softening temperature and the breaking point was steep when compared to the behavior of the drawn fiber.

In the TMA result of 100µm drawn fiber, it was observed that the drawing process influenced the fiber structure and modified the thermo mechanical properties. The apparent softening temperature increased to 59.32°C. When compared with as-spun fiber, the slope between the softening point and breaking point was decreased (Figure 4.2). The creep modulus, observed for eight minutes from the apparent softening temperature, of drawn fiber was increased compared with as-spun fiber (from 210MPa to 360MPa).

Even though the apparent softening temperature can be changed by the applied load, the increase of the apparent softening temperature shows the development of orientation of the polymer chains, and the change of the slope tells that the internal

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Figure 4.1 TMA result of 140µm as-spun fiber.



Figure 4.2 TMA result of 100µm drawn fiber.

molecular structure of the fiber is somewhat stabilized by the drawing process. In other words, the yielding and necking process period was shortened by the drawing process. Young's modulus of as spun fiber and drawn fiber was 0.82GPa and 1.88GPa. The obvious drawing effect was observed from the result.

It was found that the coefficient of thermal expansion (CTE) of poly (DT 12, 10) fiber is highly negative, and the negative value of CTE also increased. Usually, materials have positive CTE, and polymers have CTE in the range of $50 \sim 100 \times 10^{-6} \text{ K}^{-1}$. Some highly oriented linear polymers or aromatic polyamides have negative CTE. However, the value is very low (ex: -5 X 10⁻⁶ K⁻¹) [18, 19]. This is one of the most remarkable characteristics of this polymer and will be treated in more detail in chapter 5.

4.1.2 DSC Result of As-spun Fiber and Drawn Fiber

The TMA results indicated that the apparent softening temperature increases and the slope of the yield region decreases with drawing. Processing effects were also found through DSC experiments (Figure 4.3).

During the first heating, four endothermic peaks were observed in both fibers. The initial transition temperature of as-spun fiber started at 33°C before forming small sharp peak around 45°C. A second strong, sharp exothermic peak was observed around 58°C and followed by two small, broad endothermic peaks. For the drawn fiber, the initial transition temperature was observed around 34.5°C, and the curve gradually conjoined with the first endothermic peak. The strong and sharp peak appeared at 63.73°C, and followed by small peak around 74°C, the last peak was observed at 95.15°C.

As shown in the graph, all the peaks in red dotted line (140µm-as-spun fiber) were



Figure 4.3 DSC Result of 140µm as-spun fiber (red-dotted line) and 100µm drawn fiber (blue-solid line).

shifted to higher temperature (peaks in blue solid line, 100µm-drawn fiber) except for the first endothermic peak. The energy absorbed during the first heating was calculated by the integration of the area made by curves and it was about 30.37 J/g for the as-spun fiber and 32.05 J/g for the drawn fiber. This result also shows the increased structural perfection after the process. It was observed that the last two broad endothermic peaks were developed, grown and had more obvious shapes.

From the TMA and DSC results, the change of the fiber structure and the change of the properties accompanied by the structure change were observed. As a morphological point of view, it is expected that the polymer chains have better orientation with regard to the fiber axis, higher perfection, and perhaps stronger interaction forces between molecules of polymer chains as a function of the drawing process.

4.2 Thermal Analysis – Effect of Annealing

Annealing, thermal treatment at an elevated temperature for a certain time, was performed both as-spun fiber and drawn fiber. The effect of the process was observed with thermomechamical analysis, and differential scanning calorimetry.

4.2.1 TMA Result of Annealed Fibers

The annealed fibers were analyzed by TMA and DSC, and the change of thermal properties as a function of each condition was observed. In TMA results, the apparent softening temperature shifted to the higher temperature as the annealing time and temperature was increased.

Fiber	Annealing Condition	Apparent Softening Temperature
	Original	42.82 °c
	40°C for 1hour	48.08 °C
As-spun Fiber (D:140µm)	40°C for 24 hours	52.38 °C
	55°C for 1hour	64.46 °C
	55°C for 24 hours	69.75 °C

Table 4.1 Apparent Softening Temperature Change (As-spun Fiber)

 Table 4.2
 Apparent Softening Temperature Change (Drawn Fiber)

Fiber	Annealing Condition	Apparent Softening Temperature
	Original	59.32 °C
As-spun Fiber (D:100µm)	55°C for 1hour	67.29°C
	55°C for 24 hours	71.20°C



Figure. 4.4 The change of apparent softening temperature as annealing conditions.

Table 4.1 shows the change of the apparent softening temperature of as-spun fiber after annealing process. The apparent softening temperature of as-spun fiber was increased about 5°C after annealing at 40°C for one hour; after 24 hours of annealing time at same temperature, it was increased 9°C. As a result of annealing process at 55°C, the fiber showed increase of the apparent softening temperature. From the normal response under the annealing process at higher than 42.82°C, it was found that the effect of annealing is not dependent on the apparent softening temperature.

In the first heating cycle in DSC result of unannealed fibers, the temperature where the major endothermic peak appeared is expected to be the major phase transition point of the fiber. Therefore, it is expected that this point is where the maximum structure formation is occurring and the effective limit of the annealing temperature would be the point where the major peak appeared.

The drawn fiber was annealed at 55°C for different time periods. Because the apparent softening temperature of the unannealed drawn fiber was higher than that of asspun fiber annealed at 40°C for 24 hours, the annealing process at 40°C for the drawn fiber was not performed. The result exhibited a similar response to the annealing of the undrawn fiber. The apparent softening temperature increased more than 7°C after one hour annealing process and about 11°C increased after 24 hours of annealing period (Table 4.2). Figure 4.4 shows the change of the apparent softening point as different annealing condition for as-spun fiber and drawn fiber at a glance.

4.2.2 DSC Result of Annealed Fibers

The DSC results of each fiber annealed under different conditions showed three to five

endothermic peaks in the first heating cycle. Generally, the first phase transition occurred between 30°C and 50°C. It was common that there was a strong, sharp endothermic main peak among small peaks and followed by two weak, broad peaks in first heating cycle. The second cycle, the first cooling process after the first heating, and the third cycle, second heating cycle, of all fibers annealed under different condition showed same behavior by DSC.

During the first cooling, only one strong, and sharp exothermic peak was observed around 42°C when it was cooled down with 5°C/min after being heated to 120°C. In the second heating, three endothermic peaks, one strong peak, and two broad peaks, were observed. The strong endothermic peak was observed between 55°C and 60°C, and two broad weak endothermic peaks were observed around 68°C and 88°C.

The curves obtained in the second heating cycle showed similar form in the last three peaks, to those observed in the first heating cycle. Figure 4.5 is DSC result of three cycles (first heating, cooling, and second heating) of the as-spun fiber. The curves shown in the first cooling and second heating cycles were always observed at same position with same shape whether the fiber was drawn or annealed. It indicates that only the curve from first heating cycle reflects the effect of process history.

The first heating cycle removed all process history and the fiber returned to its undrawn, unannealed state. The second cycle, the cooling cycle, caused the crystallization or reordering of polymer chains, and the thermal characteristics of material so ordered were reflected in the second heating cycle. It can be expected that the strong, sharp main endothermic peak and two small, broad peaks followed by the main peak found both in the first heating and second heating cycle indicate that an intrinsicly ordered molecular structure and molecular interaction forces exist in poly (DT 12, 10).



Figure 4.5 Three cycles of DSC result (140µm as-spun fiber).

The DSC curve for 140µm as-spun fiber, showed that the first transition was observed around 33°C and the second endothermic peak appeared at 45.5°C. The third peak, the strong and sharp peak, was observed at 58.3°C, and two weak, broad peaks were observed at around 71°C and at 88.90°C. With the 100µm drawn fiber, the first transition started around 34°C and the first endothermic peak appeared at 42.64°C. The next peak observed was the strong, sharp peak that is appeared at 63.73°C. Two weak peaks appeared at 74.87°C and 95.15°C. The shift of peaks shown in these two results indicates the obvious drawing effect of the fiber. The peaks of as-spun fiber shifted to higher temperature after drawing process. It tells that the initial structure of the fiber was improved, and it is probable that their orientation, molecular interactions, and secondary bonds (van der waals force, hydrogen bond, etc.) between polymer molecules were increased by the process.

As the apparent softening temperature increased in the TMA results, the DSC results also showed the shift of the main endothermic peak to high temperature. It shows the clear evidence that the process gives rise to reordering of polymer chains to a more perfect ordered structure in the fiber. Considering the molecular structure of the repeat unit of this polymer, which has two aromatic rings and an amide group between the rings, it can be expected that the planar aromatic rings in one chain are overlapped to those of another chains to form π -bonds and thus pack better with each other. It is likely that the molecular chains to have much more interaction between them and that the hydrogen bonds between amide groups were increased.

The DSC result of annealed fibers shows similar response to that of drawn fibers. From the similarities of two results, it turned out that the thermal and mechanical properties of the fiber could be influenced by both drawing and annealing process.

Comparing the result of the annealed fiber with that of original as-spun fiber, the peaks shifted to higher temperature as was observed in drawn fiber. However, the shift occurred in a certain temperature range. For 140µm as-spun fiber, there was no significant shift of peaks under the 40°C temperature with 24 hours of annealing. But, when the fiber was annealed at 55°C for one hour, the main peak, the strong and sharp endothermic peak, shifted to a higher temperature. When the annealing time increased, the location of the main peak also moved up to higher temperature. The 100µm drawn fiber showed an analogous result.

The difference in annealing behavior between the drawn fiber and as-spun fiber is that the effective annealing condition range to move the main peak to higher temperature for the drawn fiber was more intense than that of the as-spun fiber. While the shift of main peak of as-spun fiber happened after it was annealed for one hour, drawn fiber showed the main peak shift only when it was annealed for 24 hours at 55°C.

The TMA result showed that the apparent softening temperature of as-spun fiber annealed at 40°C for 24 hours was still much lower than that of original drawn fiber. Both TMA and DSC results are corresponding with each other.

The reason that there was a difference in effective annealing conditions between as-spun fiber and drawn fiber can be explained as follow. The molecular orientation and perfection of the 100µm fiber was somewhat developed already by the drawing process, and the molecular structure could not be changed by the mild condition because the applied energy (heat and time) was less than that required energy to reform and improve the structure. Figure 4.6 shows the movement of the main endothermic peaks under



Figure 4.6 Main endothermic peak change as different annealing condition.



Figure 4.7 DSC cooling cycle of 140µm as-spun fiber at different cooling rates.

different annealing conditions. It was found that the crystallization during the second cycle, the cooling process, in DSC was time dependent on the cooling rate. As mentioned earlier, the cooling rate was fixed at 5°C/min to give uniform experimental conditions, and the strong and sharp exothermic peak appeared at same temperature range, around 42°C. However, when the cooling rate was reduced to 1°C/min, the crystallization peak appeared at higher temperature. As was expected, the peak appeared at lower temperature when the cooling rate was increased to 10°C/min. As the cooling rate reduced, crystallization time decreased. (Figure 4.7).

Comparing the DSC curves with the TMA results, relationships between the two results were found. Some specific points in the DSC curves appear to correspond to the apparent softening point and the maximum of the slight curve between apparent softening point and breaking point. The obvious relationship between TMA and DSC result could be observed in 140µm as-spun fiber.

According to TMA and DSC data of 140µm as-spun fiber showed in the Figure 4.8, the temperature where the positive dimensional change starts before the apparent softening temperature (point A) accords with the start point of a phase transition in DSC result (point A'). The temperature that the maximum of the slight curve between apparent softening point and breaking point in TMA graph (point B) matches the temperature between the strong and sharp main peak and the next small peak, the end-neck point of the main endothermic peak, in DSC curve (point B').

The highest temperature weak endothermic peak, which appeared in all DSC curves (point C), correlates with the temperature range of concave region in TMA curve, which indicates the onset of catastrophic fiber failure (point C'). These correspondences



Figure 4.8 TMA and DSC data of 140µm as-spun fiber.

were observed in all the DSC results of the as-spun fiber annealed under different condition. It shows that the progress of dimensional extension, softening and the fiber breaking are parallel to the changes in fiber intermolecular order.

The process of fiber breaking can be divided into three regions. At first, at the initial transition temperature, the temperature where the polymer chains begin to creep, and second, there is a sudden and big dimensional change occurred at the point where the main endothermic peak appears. In other words, by losing the highly oriented molecular structure or breaking long-range ordered regions, an irreversible yielding process has occurred. Finally, the fiber breaks after the weakening of the molecular interaction forces as indicated by two small and broad endothermic peaks. The TMA curves of drawn fiber show some difference compared with the curves of as-spun fiber, but the same general correspondences with DSC results occur.

After 40°C annealing, creep occurred more gradually and when the fiber was annealed at high temperature, the slope between softening point and breaking point was reduced. One of the surprising changes in these TMA results was in the slope of the creep between softening point and breaking point. In addition to the increase in the apparent softening temperature, the concave region in TMA curve for the as-spun fiber, which has its origin in the yielding and necking in the stress-strain curve of typical polymers, has changed to a straight line. After the drawn fiber was annealed at high temperature (55°C), the region of creep decreased and the period from the onset of creep to the fiber breaking point shortened (Figure 4.9). It is the evidence that this is due to increased fiber stiffness.

Even though most of TMA results and DSC results show parallel patterns for each condition, the drawn fiber annealed at 55°C for 24hours shows a different DSC



Figure 4.9 The slope change as different processes (red-dot : as-spun fiber; blue-solid : drawn fiber annealed at 40°C; green-dash dot : drawn fiber annealed at 55°C).

result. The strong, main endothermic peak and the next broad peak have apparently combined in sharp endothermic peak. It is anticipated that, in this case, the molecular interaction between chains has increased leading to a more perfect long-range ordered structure.

4.3 Phase Analysis

To analyze the phase nature of this polymer, fiber and film samples were observed in a polarized light microscope, fitted with a hot stage.

Initially, an unoriented film was observed at room temperature. No texture was found in the sample in the observation. The sample was then, observed as a function of temperature on a hot stage. The temperature increased from 25°C to 100°C with 5°C/min rate. The translucent sample became transparent around 75°C and there was no birefringence. Some interference colors appeared at the edge of the sample and around scratches in the film surface, but these effects were not the original phase of the sample.

After the film sample was stretched, it was observed on the hot stage. During the observation without temperature change, the stretched poly (DT 12, 10) film appeared white and opaque. And when the temperature was increased, the birefringence was observed. The film showed various color change as temperature increased to 70°C. Then, the film was slightly pressed and observed. A smectic texture pattern was now evident in the sample. The micrographs showed layered textures similar to a smectic liquid crystal pattern (Figure 4.10).

The phase transitions of a pressed film sample were observed with the hot stage (Figure 4.11). The textures were a reduced scale of the texture shown in Figure 4.10 because

of the lower magnification. As shown in the Figure 4.11, there was no significant pattern change in the fiber until 45°C and mostly red and green colors were observed.

However, from 50°C, the optical pattern started to change. At 55°C, thin lines, distorted ellipses and other shapes shown in the pattern expanded. Very colorful shapes appeared and the pattern blurred and simplified, with the red color in the upper part of the picture fading at 60°C. All the original color patterns disappeared and yellow, dark-red, and green colors were dominant at 65°C. Finally, at 70°C, only black and white textures were remained. It looked like that all the colorful paints were removed from the film. Above 75°C, all the texture disappeared and the melt appeared isotropic.

Fiber samples were also observed between crossed polars. They were similar to that of stretched film in appearance. Observation with the hot stage showed the change of color started from the inside of the edge around 40°C, and was spread to the middle of the fiber. The color change continued until 70°C and then, the fiber became transparent. The pressed fiber showed similar patterns to that of the pressed film.

To understand the relationship between the phase transitions and thermal properties, the pressed film was analyzed with DSC and the results were compared to the optical microscopy results. For the DSC analysis of the pressed film sample, the heating and cooling rates were set at 5°C/min. It is the same rate to the hot stage observation. In this result, only three peaks were observed. The first is a strong, sharp endothermic peak that appeared around 55°C, others are two broad, small peaks appeared at 68°C and 85°C, respectively.

Comparing with DSC result, the temperatures where the remarkable phase transition occurred in optical microscopy matches to the points of inflection in the DSC.





Figure 4.10 Optical micrographs showing texture patterns (different parts in a same film sample).



(a) 25°C

(b) 30°C



 $(e) 45^{\circ}C$

Figure 4.11 Optical micrographs showing texture pattern changes as temperature increases (from room temperature to 75°C). (Continued)



(g) 55°C





(i) 65°C





(k) 75°C

Figure 4.11 Optical micrographs showing texture pattern changes as temperature increases (from room temperature to 75°C).



Figure 4.12 DSC result of a pressed film.

The point where the pattern change started (50°C) corresponds to the onset temperature of the first strong, main endothermic DSC peak and the temperature of the main peak (55°C) matches to the temperature where the first noticeable change was observed microscopically. At 60°C, where most of the optical color pattern disappears, the endothermic main peak ends. The point that the colored textures are all gone and black and white texture was observed corresponds to the first small, broad endothermic DSC peak (70°C). Figure 4.12 shows the DSC result of a pressed film.

These results suggest that the anisotropic long-range ordered structure in the poly (DT 12, 10) is gradually losing orientation and the isotropization occurs at around 70°C. This corresponds to where the first broad peak appears and the birefringence disappeared.

There were no significant differences between the DSC results of pressed film and non-pressed film. However, some differences in DSC results between fibers and films were found. In the DSC curve of a film, there were only three peaks observed. There was the strong main peak, and the two broad and weak higher temperature endothermic peaks, all of which are also found in second DSC heating cycle. However, in most of DSC results of fibers, one or two peaks at lower temperature before the main peak were observed by DSC. These low temperature peaks disappeared in the second heating cycle indicates that the low temperature peaks is the process effect of either the axial tension or the annealing.

CHAPTER 5

CONCLUSION

5.1 Process Effect on Properties of the Material

The influence of the spinning process to the properties has been described in the earlier study executed by Jaffe et al. [6, 7]. Through thermal analysis of the poly (DT 12, 10) presented in this study, it has been shown that the improvement of thermal and mechanical properties can be induced and controlled by the processing.

Horizontally, the softening temperature and endothermic peaks of as-spun fiber shifted to higher temperature by the drawing process, and vertically, for both as-spun fiber and drawn fiber, the same responses were observed after annealing process under variant conditions. From the results of the experiments, it is obviously disclosed that all the processes applied to the polymeric biomaterial, spinning, drawing, and annealing, are relevant to the development of the properties.

5.2 Phase Structure

Jaffe et. al.[6] suggested, from the X-ray diffraction pattern of poly (DT 12, 10) fiber (Figure 5.1) combined with the transition at low temperatures, that the poly (DT 12, 10) possesses a highly layered mesogenic structure, which is similar to that of a smectic or discotic liquid crystal [21].

The texture pattern of sheared poly (DT 12, 10) film in this study observed through the polarized light microscope strongly support that the poly (DT 12, 10) has long-range ordered structure and possesses smectic liquid crystal phase. It has not been exactly defined as to how the molecular chains are aligned, what the major factors for constructing the structure are, and why the smectic phase observed after fresh shearing of a sample.

However, considering the monomer structure which has two aromatic rings and an amide group between them, it is reasonable to expect that the diphenol component section forms mesogen, rod-like molecule structure, and the secondary bonds, hydrogen bonds as an example, exist between amide groups in the chain binds the rod-like molecules together to cause orientationally ordered, layered structure.

Lukac [22] explained, based on Monte Carlo simulation [23], that the mixture of ellipsoids and spheres, which are models for molecule shapes, are demixing in a layered structure by the compression using computer simulation. Even though this simulation is simplified model and does not explain the real mechanism of forming layered structure in the poly (DT 12, 10), it supports to interpret the occurrence of smectic pattern in the pressed poly (DT 12, 10) film after shearing.



Figure 5.1 X-ray diffraction pattern of Poly(DT 12,10) fiber.

5.3 Analysis of Highly Negative CTE

In the TMA results, a highly negative coefficient of thermal expansion (CTE) of poly (DT 12, 10) fiber was observed. Some high modulus polymers, aromatic polyamides and densely packed, highly oriented linear polymers, also exhibit negative CTE.

It has been suggested that the major effect to cause negative CTE is the transverse vibrations of the chain molecules and the elastic response to the thermal stresses [19, 20]. However, the negative CTE values of these polymers are very low comparing with poly (DT 12, 10).

For example, as-spun fiber of poly (12, 10) possesses $\alpha = -47.27 \times 10^{-6} \text{ K}^{-1}$ while a typical aromatic polyamide, poly para-phenylene terephthalamide (PPTA), has α = - 5.5 X 10⁻⁶ K⁻¹. This big difference implies that there would be other factors to cause the highly negative CTE of poly (DT 12, 10) beside the above two effects. Considering the polymer structure of poly (DT 12, 10), the major reason to maximize the negative CTE value would be the long aliphatic chains in the backbone chain and the side chain.

It is expected that the poly (DT 12, 10) may possesses rigid rod-like molecules followed by long methylene groups in the backbone, which can be easily entangled and random coil form, and there is a long aliphatic group in the side chain. For polymers, specific volume is increasing as temperature increase because polymer chains are cooperatively rotating, vibrating, and stretching by heat.

Therefore, somewhat lineally aligned polymer chains by process would be entangled and randomly coiled making many void spaces between them, which cause the shrinkage of fiber axial dimension with increasing specific volume until the temperature goes to the softening point. As a hypothesis, reason for the highly negative CTE can be long aliphatic group (methylene groups) connected to a mesogen in backbone chain and as a side chain, and their coordinate movement.

5.4 Analysis of the Molecular Structure

It has been observed that, among the selected polymers for the research and made fiber form, poly (DT 2, 2), and poly (DT 2, 4), exhibited amorphous properties while poly (DT 8, 8), and poly (DT 12, 10) showed mesogenic structure and properties. The long-range ordered structure was found in polymers, which have long aliphatic chains.

The fact that the strong hydrogen bonds exist between amide groups in the longrange ordered polymers has been found [8]. In addition, hypothesis that the π -bonds created between overlapped aromatic rings of the polymer chains was formed with the strong support of the TMA and DSC results of the poly (DT 12, 10) fiber in this study. In view of the results so far achieved, it is expected that the dominant molecular interaction forces which are globally being scattered in the polymer structure bind the polymer chains closely and caused the long-range ordered structure of the poly (DT 12, 10) fiber.

FUTURE WORK

Through this investigation, the remarkable property, distinguished from other materials, was found. The highly negative value of CTE is very rare in known materials, especially in polymers.

The author will continue to define the major chemical origin causing highly negative CTE and the long-range order of poly DT polyarylate, and hopes to assess the impact combining the specific characteristics of poly (DT 12, 10) in biomedical applications. Establishment of standards for biorelevant characterization of polymeric biomaterials is also desired.

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