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Thomas F. McCarthy
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THE SYNTHESIS, CHARACTERIZATION AND MECHANICAL TESTING OF NOVEL LIQUID CRYSTALLINE POLY(ESTER-AMIDE)S AND THEIR BLENDS WITH NYLON-6,6

A Dissertation Presented
by
THOMAS F. MCCARTHY

Submitted to the Graduate School of the University of Massachusetts in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

February 1993

Department of Polymer Science and Engineering
THE SYNTHESIS, CHARACTERIZATION AND MECHANICAL TESTING OF NOVEL LIQUID CRYSTALLINE POLY(ESTER-AMIDE)S AND THEIR BLENDS WITH NYLON-6,6

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ABSTRACT

THE SYNTHESIS, CHARACTERIZATION AND MECHANICAL TESTING OF NOVEL LIQUID CRYSTALLINE POLY(ESTER-AMIDE)S AND THEIR BLENDS WITH NYLON-6,6

FEBRUARY 1993

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The principal objective of this research was to prepare an LCP/nylon-6,6 blend having enhanced tensile properties relative to nylon-6,6. It was hoped that amide-containing LCPs having a flexible spacer groups would have either good interfacial adhesion or partial miscibility with nylon-6,6.

Rigid-rod polyamides containing a biphenol mesogenic unit did not exhibit a LC phase. Polymers having a mesogenic group consisting of three \( \theta \)-substituted aromatic units and a flexible spacer were, however, shown to form the nematic phase. The thermotropic LCPs were prepared in high molecular weight by the solution polycondensation of various \( N,N' \)-trimethysilyl-\( N,N' \)-dimethylpolyalkylenediames and terephthaloylbis(4-oxybenzoyl chloride). The polymers contained \( N \)-methylimino groups in order to reduce interchain hydrogen bonding, such that a LC phase could form below the onset of polymer degradation. The loss in interchain hydrogen bonds may, however, yield polymers having a compromise in mechanical properties.

The LC poly(ester-amide)s showed maxima in the loss tangent by dynamic mechanical thermal analysis from 67°C to 116°C, depending on the
flexible spacer length, which were probably glass transition temperatures. Nylon-6,6/LCP solution cast films were shown to be partially miscible, as indicated by the perturbation of the mechanical relaxations associated with the pure LCP. The poly(ester-amide)s were melt-extruded with nylon-6,6 using various melt-processing temperatures. Each of the "as spun" nylon-6,6/LCP melt-extruded blends were shown to be compatible by DMTA. However, in some cases, phase separation occurred during post drawing.

The tensile properties of the pure LC poly(ester-amide)s were shown to be significantly less than all-aromatic LCPs such as Vectra®. Blends containing LCPs having long flexible spacer units showed no improvement in tensile properties relative to nylon-6,6, while modest improvement was observed for blends containing an LCP having shorter six methylene flexible spacer units when melt-extruded at 275°C. Blends containing an LC poly(ester-amide) having a short six methylene flexible spacer unit showed a considerable improvement in tensile modulus when melt-extruded at 300°C, but a reduction in tensile strength. The significant enhancement in tensile modulus is attributed to molecular interchange reactions.
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CHAPTER 1

AN INTRODUCTION TO LIQUID CRYSTALLINE POLYMERS

Introduction

Unlike small molecules, polymers consist of many repeat units linked together by bonds which may have significant freedom of rotation. Those small molecules and polymers which have relatively unhindered barriers to rotation have an organization from end to end whose trajectory can be described as random\(^1\). Liquid crystals, both polymeric and small molecules, can be distinguished from other molecules in that they are limited in the ways they can arrange themselves in a concentrated solution or in the molten state. A liquid crystal often consists of a rigid unit which has a high length to width ratio in which there are fewer conformations the polymer chain can adopt. These rigid segments might consist of biphenyl or naphthalene groups, for example, and are referred to as mesogenic units or mesogenic blocks. Due to excluded volume effects, the stiff aromatic units align themselves in a parallel arrangement. The liquid crystalline state is regarded as having molecular order intermediate between the highly ordered crystalline state and the disorder of the liquid state.

The molecular characteristic which primarily determines a polymer's tendency to form the liquid crystalline state is the asymmetry of its shape. The rigid segment of a liquid crystal can be envisioned as a long cylinder having an axial ratio of three or greater\(^2\). In a polymeric liquid crystal these cylinders may be directly linked together or may be separated by a flexible spacer unit. Polymers in which the rigid segment is located along the backbone are
referred to as main-chain liquid crystals. Side-chain liquid crystals are those in which the rigid segment is a type of branch extending from the main-chain of the polymer.

Of some debate is the influence of intermolecular forces on the formation of the liquid crystalline state. Two conflicting theories exist concerning the role of intermolecular attractive forces. Maier and Saupe have emphasized the role of anisotropic intermolecular forces which have been suggested to stabilize the liquid crystalline phase\(^3-4\). The London forces along the p-phenylene group, for example, are polarized such that they are much stronger along the chain axis than in any of the transverse directions. This favors the stacking of aromatic units on top of each other\(^2\). However, Onsager concluded that the excluded volume associated with long thin rods is sufficient to cause the formation of an anisotropic state depending on the concentration of the rigid-rod component\(^5\). In this regard, it has been shown by Kantor, et. al. that all-hydrocarbon polymers containing only weak dispersion forces form liquid crystalline domains in the absence of strong intermolecular forces\(^6-7\). These results suggest that strong intermolecular forces such as hydrogen bonds or dipole-dipole interactions are not necessary for the formation of the liquid crystalline state. A delicate balance exists between the stabilization and destabilization of the LC phase. As the strength of intermolecular forces increases, the stability of the crystalline state may be favored at the expense of the LC phase.

The least ordered liquid crystalline state is the nematic phase. A schematic representation of the organization of a nematic phase is illustrated in Figure 1.1(a). A nematic phase can be described by a parallel array of polymer chains having no periodic spacing of the repeat units along the length of the polymer backbone.
Figure 1.1. Schematic illustration of a liquid crystalline melt. (a) Nematic mesophase. (b) Smectic mesophase.

The smectic phase can be distinguished from the nematic phase by the long range order present in smectic domains. A schematic representation of a smectic phase is shown in Figure 1.1(b). The smectic phase is characterized by periodicity both between the parallel chains and along the repeat units of the polymer backbone. The arrangement of the polymer chains in a smectic phase may additionally have the three dimensional organization typical of a crystalline solid. In the smectic B phase, for example, the polymer chains are packed in a highly ordered hexagonal arrangement within the LC domains.

Those polymers which form liquid crystalline domains in solution are commonly referred to as lyotropic LCPs, and should be distinguished from the thermotropic liquid crystalline polymers, TLCPs, which form liquid crystalline domains in the melt. A well known example of a lyotropic liquid crystalline polymer is the polyaramide, poly(p-phenyleneterephthalamide), PPTA. PPTA forms has nematic LC order when processed from concentrated sulfuric acid or
N-methyl-2-pyrrolidinone solutions. PPTA is recognized as an ultra-high strength, high modulus polymer. Although PPTA is the most well known lyotropic LCP, other polymers which are commonly extruded from anisotropic solutions include polybenzamide, PBA, and poly(2-phenylene-2,6-benzobisthiazole), PBZT.

**Synthesis of Amide-Containing LCPs**

**Literature Review**

The synthesis of amide-containing LCPs presents a challenge. One well known characteristic of polyamides is the high level of hydrogen bonding which occurs between adjacent polyamide chains. Studies on linear aliphatic polyamides have shown that nearly all of the N-H groups are hydrogen bound at room temperature. Nylon-6,6 and nylon-6 are essentially all aliphatic polymers, yet have melting temperatures of 265°C and 225°C respectively. Spectra®, by contrast, is ultra-high molecular weight polyethylene, which is highly oriented, and has a melting temperature of 145°C. The comparatively higher melting temperatures for the partially crystalline, partially amorphous, nylons can be attributed to the intermolecular hydrogen bonds and the rigidity of the amide bond. Disregarding for the moment the type of intermolecular forces between polymer chains, a rigid-rod having a large axial ratio is necessary for the formation of the liquid crystalline state. A polyaramide having both rigid-rod segments and the potential to form intermolecular hydrogen bonds would be expected to have a melting temperature occurring just below, or with, polymer degradation. PPTA, for example is an all-aromatic polyaramide known to degrade before melting. Lyotropic polymers such as PPTA and PBA are intractable in the absence of a suitable solvent. Strongly
polar, amide-containing solvents such as N-methylpyrrolidone, have been employed in combination with inorganic salts such as LiCl to process polyaramides such as PPTA from anisotropic solutions.

The preparation of thermotropic LC polyamides may be a contradictory goal because it necessitates the preparation of polymers having depressed melting temperatures such that a liquid crystalline phase can develop below the onset of polymer degradation. To reduce the melting transitions of a polyamide, intermolecular hydrogen bonding must be reduced. However, a reduction in intermolecular hydrogen bonding may lead to polymers having a compromise in mechanical properties.

The methods which can be employed to depress the melting temperatures of amide-containing polymers include: the synthesis of tertiary polyamides\textsuperscript{11-12}, the synthesis of random copolymers\textsuperscript{13}, the preparation of polymers having bulky substituents which inhibit intermolecular hydrogen bonding\textsuperscript{14-15}, and the synthesis of polymers containing highly polar groups located adjacent to the amide linkage\textsuperscript{16}. The axial ratio of the mesogenic unit, however, cannot be reduced without decreasing the tendency of the polymer to form a liquid crystalline state.

Few investigations have described amide-containing thermotropic liquid crystalline polymers. One example, shown in Figure 1.2(a), is a series of poly(ester-amide)s prepared by Aharoni, et. al.\textsuperscript{17-20}. The poly(ester-amide)s contained alternating sequences of a single aromatic unit and a flexible spacer unit. Because the poly(ester-amide)s contained a very low axial ratio, it would be an unusual example of a liquid crystalline polymer. It was suggested that intermolecular hydrogen bonding stabilized the various mesomorphic transitions which are reported to occur. A study by He, et. al. did not confirm the previous results\textsuperscript{21}. It was suggested that the transitions observed by
Figure 1.2. Thermotropic liquid crystalline polyamides and poly(ester-amine).
Aharoni, et. al. were actually crystal-crystal transitions and not transitions involving a liquid crystalline state. The conflicting data presented by Aharoni, et. al. and He, et. al. illustrates the difficulty encountered in distinguishing between transitions involving a liquid crystalline state and crystal-crystal transitions.

The amide-containing polymers which are reported to form thermotropic liquid crystalline domains are illustrated in Figure 1.2(b-h). With the exception of the polymer shown in Figure 1.2(b), each of the polymers contains a flexible coil either within the main-chain or as a pendant group. The flexible spacer unit acts to depress the melting temperatures of the various amide-containing polymers by decoupling the rigid-rod segments in the main-chain. When attached to the mesogenic unit as a pendant group, substituents reduce the thermal transition temperatures of the resulting polymer by decreasing the packing efficiency of both the crystalline and the liquid crystalline states due to steric effects. Polymers shown in Figure 1.2(c-e), contain a flexible spacer unit within the main-chain in addition to a methyl, ethoxy, or chlorine group located adjacent to the amide linkage. The substituents inhibit intermolecular amide type hydrogen bonding.

By preparing tertiary polyamides, intermolecular hydrogen bonding can be eliminated. Cowie and Wu prepared a poly(ester-amide) containing a diaza-18-crown-6-ether within the main chain, as shown in Figure 1.2(f). McIntyre and Milburn prepared copolymers containing 4-(N-methylamino)-phenol, as shown in Figure 1.2(b).

An alternative to flexible spacer units located within the polymer main-chain is the attachment of flexible spacer groups to the polymer main-chain as pendant groups. Ringsdorf and Tschirner prepared highly substituted polymers structurally similar to PPTA, as shown in Figure 1.2(g).
attaching long pendant groups along the polymer main chain, unique liquid crystalline polymers were prepared having melting points as low as 17°C. The liquid crystalline textures, as observed by polarizing optical microscopy, were reported to be unlike any others previously observed.

A series of poly(ester-amide)s prepared by Khan, et. al., as shown in Figure 1.2(h)\textsuperscript{22}, is noteworthy because the polymers contained an amide linkage which was unsubstituted, and thus free to form intermolecular hydrogen bonds. The mesogenic unit consisted of three \( p \)-substituted aromatic units. The amide linkage was suggested to increase the stability of the nematic phase, contrary to what might be expected.

\textbf{N-methylation as a Synthetic Method}

One objective of the present investigation was the synthesis of amide-containing polymers which had sufficiently low melting temperatures such that the liquid crystalline phase could be obtained below the onset of polymer degradation. It was envisioned that polymers having N-methylated amide units would satisfy this requirement. It has been shown for nylon-6,6 and nylon-10,10, that the incorporation of N-methyl amide units leads to polymers having significantly lower melting temperatures than the analogous unsubstituted polyamides\textsuperscript{23}. N-methylated derivatives of poly(ethylene terephthalamide), poly(propylene terephthalamide), and poly(hexamethylene terephthalamide) were shown to have melting transitions approximately 100°C lower than the analogous unsubstituted polymers\textsuperscript{24}. The N-methylated polymers were also shown to have significantly enhanced solubility in common solvents.

Considerable work has been conducted to make the properties of poly(\( p \)-phenylene terephthalamide) more tractable by attaching various pendant groups to the polymer main-chain\textsuperscript{25}. The synthesis of N-propyl
substituted PPTA lead to a polymer having significantly different physical properties, including increased solubility in common organic solvents such as tetrahydrofuran. N-propyl substituted PPTA was also found to be amorphous, having a softening temperature of 450°C. Alkylation of the amide group is a viable method to drastically reduce melting temperatures. However, the reduction in melting temperature occurs with an analogous reduction in the tendency of the polymer to crystallize.

Characterization of Liquid Crystalline Polymers

There are four common methods used in the characterization of thermotropic liquid crystalline polymers, each of which compliments the other. (1) Because the formation and isotropization of a liquid crystalline state are first order phase transitions, the changes in enthalpy and entropy which occur can be conveniently measured by differential thermal analysis, DSC. (2) Since liquid crystalline phases have anisotropic optical properties, liquid crystalline phases can be identified by polarizing optical microscopy. (3) X-ray diffraction provides reliable information on the type of molecular order present in a LC phase. (4) Polymeric liquid crystals can be further characterized by miscibility studies with small molecule liquid crystals. The miscibility of a polymer which forms an unknown liquid crystalline state with a small molecule liquid crystal with a known liquid crystalline phase indicates that the components have similar liquid crystalline order. The deficiency of this method is that exceptions to the rule have been observed. In addition, the small molecule used for the identification of the mesophase should have a similar chemical composition.
Characterization of LCPs by Polarizing Optical Microscopy

The identification of liquid crystalline polymers to date has relied on the observation of textures obtained from cross-polarized light. Characterization of liquid crystalline phases by polarizing optical microscopy can yield definitive information as to the type of liquid crystalline phase present. Unlike liquids which have isotropic optical properties, and crystals where the optical properties reflect the symmetry of the molecules along three mutually perpendicular directions, liquid crystalline polymers have anisotropic optical properties\(^2\). Light passing through a liquid crystalline domain has a different refractive index depending on the direction in which the rays propagate through the medium. For example, a liquid crystalline polymer consisting of para-substituted aromatic units will have its greatest polarizability along the chain direction rather than the transverse direction. Birefringence occurs as a result of two rays propagating in an optically anisotropic medium in two different directions, having different velocities. For an isotropic domain the birefringence is zero and a dark texture is observed. Because liquid crystalline domains do not have zero birefringence a texture is observed indicative of the type of molecular order. Liquid crystalline polymers are not, however, identified by the observation of birefringence. A thin sample of a liquid crystalline material placed between two glass cover slides consists of many domains separated by domain boundaries. The domains have various defects which are referred to as disclinations. When observed by cross polarized light, a liquid crystalline mesophase can be identified by its unique distribution of line defects and domains boundaries which together comprise what is referred to as a liquid crystalline texture. For example, a characteristic texture of the nematic liquid crystalline phase is the presence of dark threads, which is
commonly referred to as a Schlieren texture. Characteristic of the smectic mesophases are the focal-conic or fan-shaped textures.

Polymeric liquid crystals are more difficult to characterize by polarized optical microscopy than analogous low molecular weight compounds\textsuperscript{28}. Because low molecular weight compounds have low melt viscosities, the formation of identifiable textures occurs at a faster rate than for high molecular weight polymers. Polymeric liquid crystals may require long annealing times to obtain a recognizable texture. The characterization of polymeric liquid crystals which are slow to form recognizable textures is complicated by polymer degradation, molecular interchange reactions, and varying sample thickness.

**Characterization of Liquid Crystalline Polymers by DSC**

Changes in enthalpy and entropy associated with the transition from a crystalline state to a liquid crystalline state or the transition from a liquid crystalline state to an isotropic state can be conveniently measured by differential thermal calorimetry. Although DSC cannot directly indicate which type of liquid crystalline state is present, a DSC thermogram can provide information concerning the temperature at which transitions involving the liquid crystalline state occur, thereby verifying observations from the polarizing optical microscope. Occasionally transitions involving the liquid crystalline state take place over a very wide temperature range. For example, broad transitions are typically observed for LC isotropization temperatures. The broad transitions can be attributed to the distribution of molecular weights and the comparatively higher melt viscosity of high molecular weight polymers relative to small molecules. Because a DSC thermogram provides information on the temperature and quantity of energy associated with a thermal transition, caution must be exercised because a DSC thermogram cannot differentiate
between changes in crystal habit or perfection and a transition involving the liquid crystalline state. However, insight provided by POM and DSC allows the careful planning of experiments involving X-ray diffraction.

Characterization of LCPs by X-ray Diffraction

A reliable method for characterizing the molecular organization of polymeric materials, whether the order is one, two, or three dimensional, is X-ray diffraction. Liquids are highly disordered and only scatter X-rays to yield two diffuse X-ray reflections\(^2\). Three dimensional crystals, however, are highly ordered, and diffract X-rays in a way that reflects the three dimensional lattice packing of the crystal. Consequently, the X-ray pattern obtained from the diffraction of a crystalline solid is well defined, with the distances between the X-ray reflections being proportional to the periodic distances found in crystalline solids. X-ray diffraction is a useful method to probe the molecular arrangement of polymers because the wavelength of X-rays is almost equivalent to the interatomic distances found in organic liquids and solids\(^2\).

The liquid crystalline state is associated with a degree of order which is intermediate between the order found in liquids and solids. By analyzing a liquid crystalline polymer by X-ray diffraction, it is possible to determine the positions of the atoms, the conformational arrangement of the polymer chain, and the degree of short and long range order present.

Liquid crystalline polymers exhibit very different X-ray diffraction patterns depending on the degree of orientation, and the type of mesophase present. X-ray diffraction patterns obtained from oriented fibers provide additional information about the nature of the mesophase due to the well-defined X-ray patterns which can be obtained. Because many liquid crystalline polymers are slow to crystallize, or in some cases do not crystallize
without annealing, it is possible to obtain a frozen LC state by heating a polymer to a temperature where the polymer forms liquid crystalline domains followed by rapid quenching. Thus the mesophase of a liquid crystalline polymer can be studied at room temperature without heating the polymer to temperatures which either exceed the limitations of instrumental analysis or cause extensive degradation.

Because X-ray diffraction was used extensively to characterize the type of LC order present in the polymers prepared in this investigation, a brief overview will be presented. Shown in Figure 1.3(a-c) are schematic representations of the order present in a liquid, a nematic mesophase, and a smectic mesophase. The mesogenic units will be considered as cylindrical rods having a high axial ratio. A liquid should be more appropriately regarded as disordered than ordered. In the nematic phase the polymer chains lie parallel to one another, yet the repeat units are randomly displaced along the polymer backbone. In an unaligned nematic mesophase, some of the mesogenic units may be tilted in relation to its neighbor, although the mesogenic units are constrained in the extent which they can tilt due to their neighbors. In a single nematic domain, the polymer chains may be aligned in the direction shown in Figure 1.3(b). However, the nematic phase may consist of many domains whose directors lie in random directions. Consequently, such an unaligned nematic mesophase will exhibit an X-ray diffraction pattern which is shown in Figure 1.3(d). Two diffuse reflections are observed, thus indicating the broad distribution of spacings which are present. The outer reflection corresponds to the distance between the polymer chains, and is circular indicating that there are many domains in which the various director chains lie in random directions. The inner reflection is related to length of the repeat units along the polymer backbone, and in most instances represents the
Figure 1.3. Schematic representation of the isotropic state and the liquid crystalline state. (a) An isotropic melt. (b) A disordered nematic phase. (c) A highly ordered smectic phase. (d) An X-ray diffraction pattern for an unoriented nematic state. (e) An X-ray diffraction pattern for an oriented nematic state. (f) An X-ray diffraction pattern for an aligned smectic A phase. (g) An X-ray diffraction pattern for a fiber obtained from a nematic melt.
layer spacing of the polymer chains. For a nematic mesophase the reflection is diffuse indicating that the mesogenic rods are randomly displaced along the polymer backbone. Figure 1.3(e) shows a schematic X-ray diffraction pattern for a magnetically aligned nematic mesophase. As shown in Figure 1.3(e), there are two equatorial reflections which appear as arcs indicating that the distribution of distances which are present between the polymer chains has decreased, and that the tilting of one domain with respect to another is also substantially reduced. Typical distances which separate the polymer chains in a nematic or smectic phase are from 4.5-5 Å. Two sharp discs can be observed along the meridian as well as two discs of low intensity. The two sharp discs indicate that the repeat units are periodically spaced along the length of the polymer backbone. However, because the periodicity diminishes over various repeat units, less intense meridional reflections occurring at higher angles are observed.

The smectic mesophases are characterized by a long range ordering of the polymer chains. The smectic B, E, and G mesophases have been regarded as having three dimensional order. Figure 1.3(f) shows a typical X-ray diffraction pattern of an aligned smectic A phase. The periodicity of the reflections along the meridian indicate that the rigid rods have a high degree of order normal to the layers. The periodicity of the arcs along the equator indicates that the organization of polymer chains in parallel arrays persists over large distances.

Highly oriented fibers obtained from the nematic melt may be interpreted as a smectic phase due to the many reflections which are observed. Figure 1.3(g) illustrates the X-ray diffraction pattern of an oriented fiber obtained from a nematic melt. The arcs located along the equator illustrate the long range periodicity of parallel spaced polymer chains. The sharp reflections along the
meridian occurring at low angle corresponds to the distance of one of the repeat units. Because the other meridional reflections are weak, the ordered spacing of the repeat units along the polymer backbone persists only over short distances. Fibers prepared from a polyester derived from \(\text{p}-\text{hydroxybenzoic acid, 2,6-dihydroxynaphthalene, and terephthalic acid}, \) also exhibit many well-defined X-ray reflections, yet have been characterized as nematic\(^{32}\).

Polarizing optical microscopy, differential thermal calorimetry, and X-ray diffraction should be used as complimentary techniques because each provides information necessary for the absolute identification of a liquid crystalline phase.

**Nylon/LCP Blends**

Blends containing amide-containing polymers such as nylon-6,6 have been predominantly incompatible with other polymers which do not belong to the polyamide family. Various polyamides have shown compatibility with one another due to cross hydrogen bonding\(^{33-35}\). Due to strong intermolecular hydrogen bonds, polyamides are strongly self-associating\(^{36}\) and, consequently, have only been shown to form miscible blends with polymers which have strong attractive forces\(^{37-40}\). The objective of preparing a partially miscible blend containing a commercial LCP is further complicated because of the tendency of the liquid crystalline polymer to self-associate. The preparation of compatible blends or incompatible blends having good interfacial adhesion from two strongly self-associating components, will depend on the specific interactions of the components, the processing
conditions used, and additives which may act to compatibilize the polymer pairs.\textsuperscript{41}

The focus of the present investigation was the preparation of novel LC polymers which could be used as molecular reinforcing agents for commercial nylons such as nylon-6,6. One area of research which has not been thoroughly investigated to date relates to methods by which blends containing a thermotropic LCP and a commercial isotropic polymer can be prepared having improved interfacial adhesion or improved miscibility. Blends containing commercial LCPs have been shown in the few cases investigated to be incompatible with commercial nylons\textsuperscript{42-43}, although good interfacial adhesion was reported in a blend containing nylon-6,6 and a LC polyester\textsuperscript{44}. Although various studies have shown rigid-rod containing polymers to be incompatible with isotropic polymers\textsuperscript{35,45}, limited research has been directed towards studying blends of an isotropic polymer with an LCP having a flexible spacer unit.

**Liquid Crystalline Polymers as Molecular Reinforcing Agents**

The principal objective of this research was to improve the mechanical properties of nylon-6,6 by melt-blending with a small percentage of a novel LCP. The mechanical properties of nylon-6,6/LCP blends of primary interest were tensile strength, tensile modulus, elongation at break, and shrinkage. Although many studies have shown that a substantial improvement in tensile properties can be achieved by melt-blending all-aromatic LCPs with various isotropic polymers\textsuperscript{35,46-47}, studies describing blends of isotropic polymers with main-chain LCPs containing flexible spacer units are few\textsuperscript{44,48-49}. 

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Although LCPs can be processed using the same methods used for commercial polymers such as PET or nylon-6,6, the development of highly oriented fibers occurs in a different fashion. The disadvantage of processing isotropic polymers such as nylons and polyesters is the comparatively low degree of orientation present in the melt during extrusion of these polymers. Nylons and polyesters such as PET are semicrystalline and consist of two phases, an amorphous phase, and a crystalline phase. The preparation of fibers is complicated by the presence of molecular entanglements in the melt and premature crystallization, yielding a crystalline phase containing imperfections such as chain folds. A schematic representation of the structure development during the fiber forming process for an isotropic polymer is illustrated in Figure 1.4(a)\textsuperscript{50}. Post drawing steps act to further orientate the crystalline and amorphous domains. However, the properties of these types of polymers are limited by their two phase morphology. Consequently, commercial polymers such as PET and the various nylons have tensile moduli between 1.5 and 22 GPa and tensile strengths of 400 to 1400 MPa\textsuperscript{1}.

Liquid crystalline polymers differ from isotropic polymers in that they spontaneously form highly oriented domains in the melt in the direction of flow where there is little interpenetration of the chains. There are few molecular entanglements in the melt to inhibit further orientation which can be obtained by post drawing procedures. Although LCPs spontaneously form ordered domains in the melt, further alignment of the chains occurs as a result of shear flow during extrusion and subsequent stretching from the melt during take-up procedures. A schematic representation of the extrusion of a liquid crystalline polymer from an anisotropic solution or melt is illustrated in Figure 1.4(b)\textsuperscript{50}. Because the high degree of order present in the melt relaxes at a very slow rate, fibers can be obtained where the same high degree of order present in
Figure 1.4. Structure development of a fiber during the processing of an isotropic polymer and a liquid crystalline polymer. (a) An isotropic polymer such as PET. (b) A liquid crystalline polymer.
the melt can be retained in the solid fiber. Annealing of the LC fiber leads to polymers having even greater levels of orientation. In comparison to the isotropic polymers, Vectra® has a tensile strength of 2.5-3.0 GPa and a tensile modulus of 84-104 GPa, and PPTA has a tensile modulus from 65 to 145 GPa and a tensile strength of 2.4-3.0 GPa. Due to their all-aromatic structure, and the high degree of orientation present in the fiber obtained from an anisotropic solution or melt, PPTA and Vectra® have tensile properties many times greater than nylon-6,6 or PET.

An additional objective of blending novel TLCPs in small quantities with isotropic polymers such as nylon-6,6 is the potential for an improvement in the dimensional stability of the matrix material. Due to the semicrystalline nature of isotropic polymers such as nylon-6,6, the orientation of the amorphous phase which is obtained during post drawing procedures, relaxes at elevated temperatures. Commercial LCPs, however, show very little shrinkage at temperatures where a highly oriented nylon-6,6 fiber would relax. Kevlar®, for example, exhibits a permanent shrinkage of less than 1% when heated at 250°C, a temperature just below where nylon-6,6 would melt. By adding a liquid crystalline component to an isotropic polymer, it is envisioned that dimensional stability of nylon-6,6 can be improved, as well as tensile properties.
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CHAPTER II

PREPARATION AND PROPERTIES OF POLYAMIDES FROM BIPHENOL BASED DIAMINES AND VARIOUS ALIPHATIC AND AROMATIC DIACID CHLORIDES

Introduction

Since the discovery and development of poly(\(\omega\)-phenyleneterephthalamide), PPTA, which forms liquid crystalline (LC) order in solution, there has been interest in the development of thermotropic LC polyamides. Because most rod-like polyamides have high melting transitions, these polymers typically decompose with melting. Therefore, examples of thermotropic liquid crystalline polyamides are rare\(^1\text{-}^5\). For example, PPTA is a polymer known to decompose before melting, but substitution of PPTA units with a pendant phenyl or a biphenyl group leads to polymers with melting transitions between \(375\text{-}500^\circ\text{C}\)\(^6\text{-}^7\). Such high melting transitions result from the sequences of aromatic units, the inherent rigidity of the amide linkage, and interchain hydrogen bonding. For the same reason, the observation that some potentially mesogenic polyurethanes have less frequently displayed liquid crystalline properties has also been attributed to specific interactions involving hydrogen bonds\(^8\text{-}^10\). Strong intermolecular interchain interactions can stabilize the crystalline state and increase the melting temperatures to the point where the liquid crystalline state cannot form below the decomposition temperature.

Biphenyl is a mesogenic group which is well known to promote the liquid crystalline phase in small molecules\(^11\). A derivative of the biphenyl mesogen, biphenol, has recently attracted attention as a precursor for mesogenic units for
various types of polymers, and it has been successfully used as a mesogenic unit in many polyesters\textsuperscript{12-13}, polycarbonates\textsuperscript{14}, and polyurethanes\textsuperscript{8-10}. The objective of the present investigation is to obtain a thermotropic, liquid crystalline polyamide by using this mesogenic group which is known to promote the liquid crystalline phase, in combination with flexible spacers to reduce melting points and other transition temperatures. The structure of the biphenol-based diamine monomers, A, is represented below.

\[
\text{NH} (\text{CH}_2)_n \text{O} - \begin{array}{c}
\text{Y} \\
\end{array} 
\text{O} (\text{CH}_2)_m \text{NH} ; Y = \text{H, CH}_3
\]

N-methylation of the biphenol-based diamines was used to eliminate amide-type hydrogen bonding in the polyamides prepared. It was thought that by using N-methylated secondary amines, polymers could be obtained which had properties analogous to those found in polyesters. That is by lowering the melting temperatures significantly, it might be possible to obtain polymers which were capable of forming stable liquid crystalline domains above their melting transitions and below their thermal decomposition temperatures. It is well known that the substitution of amide linkages containing hydrogen atoms with alkyl substituents in polyamides results in polymers having significantly reduced melting points and increased solubility in common solvents\textsuperscript{15}.

The synthesis of polyamides by interfacial polymerization is a well known polymerization method\textsuperscript{16}, and the synthetic route to biphenol-based diamines readily yielded the diamine hydrochloride salts which could be used conveniently and directly in an interfacial polymerization to synthesize the polyamides. Alternatively, the synthesis of N-methylated polyamides from N,N'-dimethylidiamines by solution polymerization differed from the interfacial polymerizations in that the aqueous phase did not serve as a solvent, but as a
basic medium to neutralize both the monomer hydrochloride salt and the HCl generated during the polymerization reaction.

**Experimental**

All chemicals were obtained from the Aldrich Chemical Company and used as received unless otherwise indicated. Tetrahydrofuran was dried by continuous distillation over lithium aluminum hydride. Dichlorobenzene was purified by shaking with H$_2$SO$_4$, washing with water, drying with calcium chloride, and then distilling over calcium hydride. Diethylene glycol diethyl ether was dried over magnesium sulfate and distilled over lithium aluminum hydride. Methylene chloride was purified by washing with H$_2$SO$_4$, 5% sodium carbonate, water, drying over calcium chloride, and then distilling from P$_2$O$_5$. Terephthaloyl chloride, p-phenylenediamine, and hexamethylenediamine were purified by sublimation. Adipoyl chloride, sebacoyl chloride, and 5-bromocapronitrile were distilled before use. 5-Bromocapronitrile was obtained from Lancaster Synthesis. 4,4'-dihydroxybiphenyl was recrystallized from ethanol. A 10 Molar solution of HCl in methanol was obtained from American Tokyo Kasei and was used as received.

**Monomer and Polymer Characterization**

Inherent viscosities for all polymers were determined at 29.5°C in trifluoroacetic acid using a Cannon-Ubbelohde viscometer. Infrared spectra were obtained using a Perkin Elmer 1600 Series FTIR. A Varian XL-200 spectrometer was used to obtain proton spectra. Carbon-13 solids NMR spectra were obtained at 50 MHz with an IBM AC200 spectrometer with an IBM solids accessory and Doty Magic Angle spinning probe. Proton and carbon 90
degree pulses were 5 microseconds. The cross polarization time was 2 milliseconds and samples were spun at near 5 kilohertz. A carbon-13 solid spectra for polymer Via was additionally carried out at 75.4 MHz using a Bruker MSL-300 NMR spectrometer for improved resolution. The samples were spun at approximately 4 kHz. The $^{13}$C and $^1H$ radiofrequency 90° pulse width were 4.0µs. Characterization of the polymers by polarizing optical microscopy, POM, was conducted using a Zeiss optical microscope equipped with a Mettler hot stage. Thermal analysis and thermal stability were measured on a Perkin Elmer 7 series instrument equipped with a differential scanning calorimeter and a thermogravimetric analyzer under a stream of nitrogen at 10°C/minute. The temperature and power ordinates of the DSC-7 were calibrated using an indium standard. Elemental analyses were conducted by the Microanalysis Laboratory of the University of Massachusetts at Amherst. Probe Mass Spectrometry was performed by the Akzo Chemical Company, Dobbs Ferry, New York. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected.

**Monomer Synthesis**

Scheme 1 outlines the synthesis of the monomers and intermediates used in this study.

(1a-c) 6,6'-[[1,1'-biphenyl]-4,4'-diylbis(oxy)]-bis-capronitrile

The following procedure describes the synthesis of lc which follows a previously described literature preparation\(^{17}\) but is a general procedure for the synthesis of intermediates la-c. To a 500 ml. three-neck flask equipped with a 125 ml.
Figure 2.1. Synthesis of biphenol-based diamine monomers.
additional funnel, reflux condenser, and a mechanical stirrer, under a nitrogen atmosphere, was added 18.62 g. (0.10 mol) of 4,4'-dihydroxybiphenyl, 79.0 g. 5-bromocapronitrile (0.6 mol), and a 60 percent aqueous solution of 9.11 g. (0.04 mol) benzyltriethylammonium chloride in 13.7 mls. of water. The reaction contents were heated to 92°C, after which 12.08 g. of potassium hydroxide (0.40 mol) dissolved in distilled water (60.0 ml.) was added over a thirty minute period. The reaction was heated at reflux for 80 minutes and cooled to 0°C for one hour. A crystalline precipitate was collected by filtration and washed with copious amounts of cold ethanol until the color was eliminated. The solid was then recrystallized from a dioxane/ethanol (1:1) solution, and washed with cold ethanol to yield 26.73 g. of Ic as fine plates.

(IIa-c) 6,6'-[[1,1'-biphenyl]-4,4'-dialbis(oxy)]-bis-hexylamine hydrochloride

The following procedure describes the synthesis of IIc, but it is a general preparation for IIa-c. The reaction was conducted under argon using oven-dried glassware. A 1L. three-neck round bottomed flask was equipped with an addition flask, reflux condenser, and a magnetic stirrer. A total of 33 g. of Ic (86.9 mmol) and 700 ml. of dry tetrahydrofuran was added. The mixture was heated until dissolution of the starting material occurred. Borane dimethyl sulfide (26.41 g., 0.348 mol) was added slowly through the addition flask. The solution was heated at reflux for twelve hours. The solution progressively became blue in color and formed a thick gel. The gel was cooled to room temperature and 68.14 ml. of a 10 molar solution of HCl in methanol was cautiously added. Rapid evolution of hydrogen gas occurred. The solution was then heated for three days at reflux, after which the 1L. round-bottom flask was cooled and equipped with a distillation apparatus. One half the volume of tetrahydrofuran was removed. To the remaining solution was added 400 ml. of
distilled water. Refluxing for three additional days yielded 40-50% of product. Three weeks of refluxing yielded 65% of product. The remaining THF and methanol were then distilled from the reaction vessel. The aqueous mixture was diluted with enough water to afford dissolution at reflux, filtered until the aqueous solution was clear, cooled, and the precipitate collected by filtration. The diamine hydrochloride salt was then recrystallized from a water/ethanol solution (60:40; 1g./100 ml.) to yield 25.84 g. of llc as a fine crystalline powder.

\[(\text{IIIa-b})\ 6.6'\text{-}[1,1'\text{-biphenyl}]\text{-4.4'}\text{-diylbis(oxy)]-bis-hexylisocyanate}\]

The following procedure describes the preparation of IIIb, but it is a general procedure for the preparation of IIIa-b. llc (10 g., 0.0219 mol.) was dissolved in 150 ml. distilled water at reflux, after which 2.58 g. potassium hydroxide (0.046 mol.) was added to obtain a basic solution. The solution was heated at reflux for one hour to insure complete conversion of the diamine hydrochloride to the neutralized diamine, cooled, and extracted with chloroform until the aqueous layer was clear. The chloroform extracts were combined, filtered, and concentrated to dryness. The diamine was then vacuum-dried overnight and used without additional purification. Under nitrogen, the diamine (9.0 g, 0.0242 mol) was added to an oven-dried 500 ml. three-neck round bottom flask equipped with a reflux condenser, 125 ml. addition flask, magnetic stirrer, to which was added 300 ml. of dry 1,2-dichlorobenzene. The diamine was heated until complete dissolution. To the addition funnel was added 19.05 g. of triphosgene (0.064 mol) dissolved in 100 ml. of dry 1,2-dichlorobenzene. The triphosgene solution was added dropwise to the diamine solution, producing an immediate precipitate of a white solid. After the addition of the triphosgene solution, the addition flask was removed and the resulting solution was heated for five days at 100°C. The reaction is completed when the evolution of
hydrogen chloride has ceased and the solution has become clear. The reaction flask was cooled to room temperature and then equipped with a distillation apparatus. The solvent volume was reduced by one-half. To the cooled solution was added 600 ml. of dry hexane. The solution was heated to reflux, filtered, and allowed to cool to room temperature. The resulting precipitate was filtered and discarded. The clear solution was cooled to 0°C to give 7.23 g. of IIIb as fine crystals.

(IVa) 6,6’-[[1,1’-biphenyl]-4,4’-diylbis(oxy)]-bis-N,N’-dimethylhexanediamine
To an oven dried 250 ml. three-neck flask equipped with a reflux condenser, and a magnetic stirrer, was added under a nitrogen purge 1.33 g. of lithium aluminum hydride (0.035 mol.), 100 mls. of dry 2-ethoxyethylether, and 8.0 g. of IIIb (.0183 mol.) dissolved in 50 ml. of 2-ethoxyethylether. The reaction was heated to 115°C for one hour and then heated at 180°C for 90 minutes. To this mixture was added 2.0 ml. of distilled water and 20 g. of sodium hydroxide. The reaction was heated at 180°C for an additional three hours. The mixture was cooled, filtered, and the solid was washed with hexane and subsequently discarded. To the filtrate was added 600 additional mls. of hexane. The solution was cooled to 0°C yielding 5.0 g. (64% yield) of crude product which was collected and recrystallized from hexane, vacuum-dried and distilled at 210°C and 0.15 torr using a Kugelrohr distillation apparatus. The distilled solid was then recrystallized from hexane to yield fine crystals.
Polymer Synthesis

Scheme 2 outlines the synthesis of the polyamides prepared in this study and is shown below.

\[
\text{Scheme 2}
\]

\[
X(CH_2)_nO-\begin{array}{c}
\text{O} \\
\text{O} \\
\end{array}(CH_2)_nX
\]

II, \( x = \text{NH}_3^+\text{Cl}^- \)

IV, \( x = \text{NHCH}_3 \)

\[
\begin{array}{c}
\text{CH}_2\text{Cl}_2, \\
\text{CICRCICl} / \text{KOH, H}_2\text{O}
\end{array}
\]

\[
\text{V}, \ R = \text{H} \\
\text{VI}, \ R = \text{CH}_3
\]

Figure 2.2. Synthesis of biphenol-based polyamides.

(Va) Poly[iminooxyetheneoxy-4,4'-biphenylenoxyetheneiminocarbonyl-p-phenylene carbonyl]. Polyamide Va was obtained from terephthaloyl chloride and IIa. The following is a general procedure for the synthesis of Polymers Va-d. To a Waring Blender was added 1.364 g. (24.3 mmol.) of potassium hydroxide dissolved in 20 ml. of water. To this solution was simultaneously added a solution of 2.0 g. of IIa (5.79 mmol.) dissolved in 200 ml. of distilled water and an equimolar amount of terephthaloyl chloride (1.18 g) dissolved in 300 ml. of dry methylene chloride. The two phase solution was stirred at high speed under argon for twenty minutes. The white polymer was collected, washed with water and methanol, extracted in a Soxhlet for one day with methanol, and vacuum-dried at 100°C for 36 hours to yield 2.01 grams of
polymer (86.3%). Characterization of polymers Va-Vd by infrared spectroscopy showed the following vibrations (KBr): 3294 cm\(^{-1}\) (broad single N-H stretch), a very weak absorption at 3071 cm\(^{-1}\) (aromatic C-H stretch), 2935, 2870 cm\(^{-1}\) (aliphatic C-H stretch, asymmetric and symmetric), 1646 cm\(^{-1}\) (amide carbonyl stretch), 1607 cm\(^{-1}\) (aromatic C-C stretch), 1541 cm\(^{-1}\) (N-H bend), 1243 cm\(^{-1}\) (asymmetric C-O-C stretch), 1054-1034 cm\(^{-1}\) (symmetric C-O-C stretch).

(Vla) Poly[N-methyliminohexamethyleneoxy-4,4'-biphenyleneoxyhexamethylene-N-methyliminocarbonyl-p-phenylenecarbonyl]. Polyamide Vla was obtained from terephthaloyl chloride and IVa. The following is a general procedure for the preparation of polymers Vla-d. Terephthaloyl chloride (0.39 g, 1.94 mmol) and IVa (0.80 g, 1.94 mmol) were separately dissolved in 75 ml. of dry methylene chloride. To a Waring Blender was first added an aqueous solution of 0.218 g. potassium hydroxide (3.88 mmol) dissolved in 150 ml. of distilled water. The acid chloride and diamine solutions were added simultaneously to the Waring blender and stirred at high speed for thirty minutes. The white polymer was collected, washed with methanol, extracted in a Soxhlet with methanol for one day, and vacuum-dried to yield 0.73 g. of polymer. Characterization of polymer Vla-b by infrared spectroscopy showed the following vibrations (KBr): 3017 cm\(^{-1}\) (aromatic C-H stretch), 2931, 2856 cm\(^{-1}\) (asymmetric and symmetric C-H stretch), 1617 cm\(^{-1}\) (amide carbonyl stretch), 1241 cm\(^{-1}\) (asymmetric C-O-C stretch), 1073 cm\(^{-1}\) (symmetric C-O-C stretch). Polymers derived from p-phenylene diamine and hexamethylene diamine, Vlc and Vld, had an additional N-H vibration at 3320 cm\(^{-1}\) and a weak N-H bending vibration at 1541 cm\(^{-1}\).
Post Treatment of Polymers Vc and Vd

A general description involves dissolving 1 g. of polymer Vc at 150°C in 20 ml. of dry DMAC which contained 5% LiCl. The solution was cooled to 100°C, after which distilled benzoyl chloride (0.602 g., 4.28 mmol) and dry triethylamine (0.27 g., 2.68 mmol) was added under an argon purge. This solution was stirred with a magnetic stirrer for two hours at 100°C and twelve hours at 50°C and then precipitated in methanol, collected by filtration (0.75 g. crude yield), extracted in a Soxhlet with methanol for one day, and then vacuum-dried at 75°C for two days to give 0.44 g. (44% yield) of polymer Vc-P.

Results and Discussion

Monomer Synthesis

Scheme 1 illustrates the synthesis of the monomers used for the polymerization reactions. Data for the synthesis and characterization of the monomers is given in Tables 2.1 and 2.2. By using phase transfer conditions the dinitriles, Ia-c, were readily obtained from 4,4′-biphenol and the appropriate bromonitrile. After attempting unsuccessfully to reduce the dinitriles using lithium aluminum hydride¹⁹, or lithium aluminum hydride with the crown ether 15-crown-5²⁰, borane-dimethyl sulfide¹⁸ was found to yield the diamines, IIa-c, in satisfactory yields. The diamine salts obtained from the reduction of the dinitriles were purified and used in the syntheses of Polymers Va-d.

The conversion of the diamine salts, IIb-c, to the isocyanates, Illa-b, was accomplished by neutralizing the diamine hydrochloride, isolating the free diamine, and then directly converting the diamine to the isocyanate as shown in Scheme 1, without intermediate purification of the diamine. Isolation of the
Table 2.1. Yields, melting points and elemental analyses of biphenol-based intermediates and monomers.

\[
X = -(CH_2)_nO-\begin{array}{c}
\text{aryl}
\end{array}-O(CH_2)_n-X
\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield(%)</th>
<th>Mp(°C)</th>
<th>Formula</th>
<th>Calculated</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>x</td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>la</td>
<td>1</td>
<td>CN</td>
<td>99</td>
<td>114-115</td>
<td>C_{16}H_{12}O_2N_2</td>
</tr>
<tr>
<td>lb</td>
<td>4</td>
<td>CN</td>
<td>99</td>
<td>158-159</td>
<td>C_{22}H_{24}O_2N_2</td>
</tr>
<tr>
<td>lc</td>
<td>5</td>
<td>CN</td>
<td>78</td>
<td>118-119</td>
<td>C_{24}H_{28}O_2N_2</td>
</tr>
<tr>
<td>Ila</td>
<td>2</td>
<td>NH_2·HCl</td>
<td>53</td>
<td>&gt;300</td>
<td>C_{16}H_{22}O_2N_2Cl_2</td>
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<tr>
<td>Iib</td>
<td>5</td>
<td>NH_2·HCl</td>
<td>62</td>
<td>&gt;300</td>
<td>C_{22}H_{34}O_2N_2Cl_2</td>
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<tr>
<td>Iic</td>
<td>6</td>
<td>NH_2·HCl</td>
<td>65</td>
<td>&gt;300</td>
<td>C_{24}H_{38}O_2N_2Cl_2</td>
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<tr>
<td>IIla</td>
<td>5</td>
<td>NCO</td>
<td>60</td>
<td>78-80</td>
<td>C_{24}H_{28}O_4N_2</td>
</tr>
<tr>
<td>IIlb</td>
<td>6</td>
<td>NCO</td>
<td>69</td>
<td>86-87</td>
<td>C_{26}H_{32}O_4N_2</td>
</tr>
<tr>
<td>IVa</td>
<td>6</td>
<td>NHCH_3</td>
<td>64</td>
<td>112</td>
<td>C_{26}H_{40}O_2N_2</td>
</tr>
</tbody>
</table>
Table 2.2. NMR and IR absorptions of biphenol-based intermediates and monomers.

![Structural formula]

<table>
<thead>
<tr>
<th>Compound*</th>
<th>$^1$H-NMR (S)$^4$</th>
<th>IR (cm$^{-1})^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^1$H</td>
<td>Functional Group Absorption</td>
</tr>
<tr>
<td></td>
<td>$^1$H</td>
<td>Other $^1$H</td>
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<tr>
<td>la</td>
<td>7.48</td>
<td>7.02</td>
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<tr>
<td>lb</td>
<td>7.48</td>
<td>6.95</td>
</tr>
<tr>
<td>kc</td>
<td>7.48</td>
<td>6.91</td>
</tr>
<tr>
<td>llb</td>
<td>7.49</td>
<td>6.98</td>
</tr>
<tr>
<td>llc</td>
<td>7.58</td>
<td>7.05</td>
</tr>
<tr>
<td>llia</td>
<td>7.48</td>
<td>6.95</td>
</tr>
<tr>
<td>llib</td>
<td>7.49</td>
<td>6.96</td>
</tr>
<tr>
<td>lliv$^1$</td>
<td>7.46</td>
<td>6.92</td>
</tr>
</tbody>
</table>

$^*$ See Table I for identity of compounds in this column.

1 The structure of llva was also confirmed by Probe Mass spectrometry and had the following fragments: M+, m/e=412; M-(CH$_3$)$_2$+, m/e=397; M-(CH$_2$NH$\text{CH}_3$)$_2$+, m/e=368; M+(CH$_2$)$_5$NH$\text{CH}_3$, m/e=312; (biphenol)$^+$, m/e=186; +(CH$_2$)$_6$NH$\text{CH}_3$, m/e=114; +CH$_2$CH$_2$NH$\text{CH}_3$, m/e=58; +CH$_2$NH$\text{CH}_3$, m/e=44.

2 (d), 4H; $^3$ (d), 4H; $^4$ (a-c, IIIa-b, and llva (CD$_3$)$_2$, IIa-c (D$_2$O); $^5$ KBr; $^6$ very broad N-H stretch with superimposed C-H stretch at 2932 cm$^{-1}$; $^7$ broad absorption between 3700-2750 with strong N-H stretches at 3519 and 3396 cm$^{-1}$ and a superimposed C-H stretch at 2945 cm$^{-1}$; $^i$ asymmetric C-H stretch (CH$_3$, CH$_2$); $^ii$ symmetric C-H stretch (CH$_3$, CH$_2$); $^iii$ Aromatic ring C=C stretch; $^iv$ asymmetric C-O-C stretch; $^v$ symmetric C-O-C stretch.
primary amine obtained from the neutralization of Ila-c was not necessary to obtain the desired isocyanate in satisfactory yield. Conversion of the diamine to diisocyanate\textsuperscript{21} was best accomplished at reduced temperatures over long time periods. The rate of the reaction could be increased using chloronaphthalene as a solvent and temperatures between 150-200°C for five hours. These conditions yielded the desired product, but in significantly reduced yields. Better yields were obtained by carrying out the reaction at 100°C over a five day period.

The diisocyanate IIIb was reduced to IVa using lithium aluminum hydride in 2-ethoxyethylether\textsuperscript{22}, followed by the addition of solid sodium hydroxide. An attempt to reduce the diisocyanate with lithium aluminum hydride in ether, followed by alkaline hydrolysis, yielded predominantly the primary amine.

Repeated purification of IVa by Kugelrohr distillation and subsequent recrystallization failed to improve the purity as indicated by elemental analysis. However, the structure was consistent with spectra obtained from infrared, NMR, and mass spectroscopy.

**Polymer Syntheses**

The polyamides prepared in this study are summarized in Table 2.3, and the polymerization reactions are shown in Scheme 2. Polymers Va-d were readily obtained by interfacial polymerization. The diamines were obtained as diamine hydrochloride salts and could be conveniently dissolved in distilled water and condensed with the acid chloride by interfacial polymerization reaction. The solubility of the diamine hydrochloride salt in water was greater
Table 2.3. Yields and solution viscosities of polyamides prepared.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Acid Chloride</th>
<th>Diamine</th>
<th>Yield (%)</th>
<th>[η]inh. 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Va</td>
<td>Terephthaloyl</td>
<td>Ila</td>
<td>86</td>
<td>0.18</td>
</tr>
<tr>
<td>Vb</td>
<td>Adipoyl</td>
<td>Ila</td>
<td>89</td>
<td>0.39</td>
</tr>
<tr>
<td>Vc</td>
<td>Adipoyl</td>
<td>Ib</td>
<td>79</td>
<td>0.28</td>
</tr>
<tr>
<td>Vd</td>
<td>Adipoyl,</td>
<td>Iib, Sebacoyl (1:1)</td>
<td>75</td>
<td>0.47</td>
</tr>
<tr>
<td>Vla</td>
<td>Terephthaloyl</td>
<td>IVa</td>
<td>69</td>
<td>0.32</td>
</tr>
<tr>
<td>Vlb</td>
<td>Isophthaloyl</td>
<td>IVa</td>
<td>89</td>
<td>0.50</td>
</tr>
<tr>
<td>Vlc</td>
<td>Terephthaloyl</td>
<td>IVa, p-PDA² (90:10)</td>
<td>47</td>
<td>0.27</td>
</tr>
<tr>
<td>Vld</td>
<td>Terephthaloyl</td>
<td>IVa, HMDA³ (80:10)</td>
<td>43</td>
<td>0.35</td>
</tr>
</tbody>
</table>

1 Inherent viscosities were measured at 29.5°C in trifluoroacetic acid (0.1g/dL).
2 p-Phenylenediamine.
3 Hexamethylenediamine.

with shorter spacer lengths. The aqueous diamine solution, the appropriate acid chloride dissolved in methylene chloride, and a separate basic aqueous phase were added simultaneously to a Waring Blender and stirred at high speed. Polymers Vc and Vd were post-treated (Vc-P and Vd-P) with benzoyl chloride in DMAC at 100°C in order to end-cap amine end groups, with the intent to improve the thermal stability of the polyamides.

Polymers Vla-d were obtained by solution polymerization at room temperature using the free diamine in methylene chloride. The basic aqueous phase was used to neutralize the hydrogen chloride formed during the polymerization reaction.

Polymer Characterization

The reduction of hydrogen bonding in polymers Vla-d by using an N-methyl substituted monomer, IVa, leads to polymers having better solubility in common solvents than the polymers prepared from the primary amines, Ila-b. The unsubstituted polymers, Va and Vb were soluble only in acidic solvents.
such as trifluoroacetic acid and sulfuric acid. Polymers Vc and Vd which contained longer aliphatic spacer groups had somewhat better solubilities, since they dissolved in highly polar solvents such as dimethyl sulfoxide and 1-methyl-2-pyrrolidinone at elevated temperatures. Polymers Vla-d had greater solubilities than the unmethylated polyamides in common solvents. Polymers Vla-b dissolved in NMP, N,N-dimethylformamide, DMSO, and N,N-dimethylacetamide with minimal heating.

The inherent viscosities for Polymers Va-d and Vla-d are given in Table 2.3. The preparation of high molecular weight polymers was limited by the poor solubility of the polymers in dichloromethane. Polymers having longer aliphatic spacer groups, Vd, or unsymmetrical groups such as the isophthaloyl unit, Vlb, had higher inherent viscosities, which can be attributed to their greater solubility in dichloromethane.

Confirmation of the polymer structures was obtained using solid state C$^{13}$ NMR. The solid state $^{13}$C NMR spectrum for polymer Va is given in Figure 2.3 and the solid state C$^{13}$ spectra for Polymer Vla is given in Figure 2.4. Solid state $^{13}$C spectra for the methylated and unmethylated polyamides were consistent with their structures. The N-methyl carbon atom in the substituted polymer Vla was identified at 36.7 ppm. Identification of the methyl carbon atom was accomplished by the preparation of the model compound N,N'-bis(benzoyl)-N,N'-dimethylbutanediame, which is shown below:

![Chemical Structure]

A full discussion of the $^1$H and $^{13}$C NMR spectra for the model compound will be described in chapter 3. Peak assignments for both the model compound
Figure 2.3. Solid state $^{13}$C NMR spectrum of polymer Va.
Figure 2.4. Solid state $^{13}$C NMR spectrum of polymer VIa.
and the N-methylated polymers prepared in this investigation reflect the fact that
the amide linkage occurs in the cis and trans forms. Characterization of the
model compound by \( ^{13} \text{C NMR} \) showed that two signals exist for the methyl
carbons, the methylene carbons located adjacent to the nitrogen atom, and the
two aliphatic carbon atoms located in the \( \beta \) position to the two nitrogen atoms.
The fact that two \( ^{13} \text{C NMR} \) signals are observed for various carbon atoms is
due to the anisotropy of the carbonyl group, where the carbon atoms located
adjacent to the amide linkage having the cis confirmation occur at lower field.
Absolute identification of the methyl and methylene carbon atoms for the model
compound was obtained using the DEPT pulse sequence (Distortionless
Enhancement by Polarization Transfer)\(^{23-27}\). Peak assignments for the model
compound for the cis and trans methyl groups are 37.4 and 32.7 ppm.
respectively. From the characterization of the model compound, identification of
the aliphatic region of the N-methylated polyamides was possible. Because of
the broadness of the peak (Figure 2.4) corresponding to the methyl carbon
atoms (36.7 ppm.) and the methylene carbon atoms (50.8, 47.3 ppm.) adjacent
to the nitrogen atoms of the amide units, it is probable that polymer Vla also
consists of cis and trans rotational isomers.

Characterization of Polymers Va-d and Vla-d by thermogravimetric
analysis (TGA) showed the N-methylated polymers to be more thermally stable
than the unsubstituted polymers. The N-methyl substituted polymers, Vla-d,
showed a 1% weight loss up to 350°C. The unsubstituted polymers, Va-b,
showed significant degradation before melting as indicated by severe browning
of the polymers on a melting point apparatus. Polymers Vc and Vd lost
approximately 2% of their weight by 300°C. Polymers Vc and Vd were
redissolved in DMAC and reacted with benzoyl chloride to improve their thermal
stability. A comparison of the thermal stability of polymer Vc, untreated and
post-treated, is shown in Figure 2.5. The post-treated polymers showed considerably less weight loss up to a temperature of 300°C.

The improved thermal stability of the post-treated polymers may be attributed to either polymer purification or the end-capping of amine end groups to yield a new amide group. The elemental analyses for the post-treated polymers were in better agreement with the theoretical values than the untreated polymers which may indicate that the post-treatment yielded the polymers in higher purity. Elemental analyses for the post-treated and untreated polymers are given in Table 2.4. Infrared spectra for the post-treated polymers showed a slight broadening in the carbonyl region which may be indicative of end-capping. No change in the structure of polymers Vc-d following post-treatment was observed by solid state carbon-13 NMR. The post-treated polymer showed little change in viscosity relative to the corresponding untreated polymers.

The infrared spectra for polymers Vla-d were very similar to the spectra obtained for polymers Va-d. The unsubstituted polymers, Va-d, had strong N-H stretching vibrations in the region of 3300 cm⁻¹. N-H stretching and bending vibrations were not observed for the N-methyl substituted polymers, Vla and

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Calculated</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Vc</td>
<td>72.38</td>
<td>7.81</td>
</tr>
<tr>
<td>Vc-P</td>
<td>72.38</td>
<td>7.81</td>
</tr>
<tr>
<td>Vd</td>
<td>72.65</td>
<td>8.70</td>
</tr>
<tr>
<td>Vd-P</td>
<td>72.65</td>
<td>8.70</td>
</tr>
</tbody>
</table>
Figure 2.5. Thermogravimetric analyses of polymer Vc. (a) Post-treated (Vc-P). (b) As synthesized.
VIb, while there were very weak absorptions in the N-H stretching region which may be indicative of amine end groups. Polymers containing p-phenylene diamine (VIc) and hexamethylene diamine (VIIId) had a medium absorption in the N-H stretching region (3320 cm\(^{-1}\)) and a weak absorption in the N-H bending region (1541 cm\(^{-1}\)).

A summary of the transition temperatures of polymers Vc-d and VIIa-d by DSC is given in Table 2.5. Glass transition temperatures were not observed by DSC for any of the polymers in this study. Characterization of polymers Va-d by DSC was not performed because of the poor thermal stability of these polymers. DSC thermograms of the post-treated polymers Vc-P and Vd-P were obtained, however. The DSC thermogram for polymer Vd-P is given in Figure 2.6. Polymers Vc-P and Vd-P showed only endothermic melting transitions during the heating cycles and exothermic recrystallization transitions during the cooling cycles.

The N-methyl substituted polyamides, VIIa-d, had significantly different DSC thermograms than for the unsubstituted polyamides. The N-methyl substituted polymers, VIIa-d, had significantly lower melting transitions than the unsubstituted polyamides, Va-d, which was expected from the reduction of hydrogen bonding. The N-methyl substituted polymers, VIIa-d, had no recrystallization exotherms during the cooling cycles, whereas the unsubstituted polyamides, Vc-d, readily crystallized during the cooling cycles. The DSC thermogram for Polymer VIIa is given in Figure 2.7. Polymer VIIa did not have a recrystallization exotherm during the cooling cycles even with a cooling rate of 1°C/minute. With the exception of polymer VId, the N-methylated polyamides, polymers VIIa-c, had cold crystallization exotherms during the second heating cycles. Polymer VIIa showed two cold crystallization exotherms before the melting transition.
Figure 2.6. DSC thermogram of polymer Vd-P: (a) Second heating cycle. (b) Second cooling cycle.
Figure 2.7. DSC thermogram of polymer Vla. (a) Second heating cycle. (b) Second cooling cycle.
Table 2.5. Thermal properties of polyamides prepared (°C)\(^1\).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(T_m^{(4)}) 1st heating</th>
<th>(T_k^{(5)}) 1st cooling</th>
<th>(T_c^{(6)}) 2nd heating</th>
<th>(T_m) 2nd heating</th>
<th>(T_k) 2nd Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Va(^2)</td>
<td>dec.~ 270</td>
<td>~270</td>
<td>-</td>
<td>dec.~ 270</td>
<td>~270</td>
</tr>
<tr>
<td>Vb(^2)</td>
<td>dec.~ 270</td>
<td>~270</td>
<td>-</td>
<td>dec.~ 270</td>
<td>~270</td>
</tr>
<tr>
<td>Vc(^3)</td>
<td>200</td>
<td>215, 200, 120</td>
<td>-</td>
<td>225</td>
<td>200,120</td>
</tr>
<tr>
<td>Vd(^3)</td>
<td>215</td>
<td>215</td>
<td>-</td>
<td>215</td>
<td>215</td>
</tr>
<tr>
<td>Vla</td>
<td>165</td>
<td>-</td>
<td>93,134</td>
<td>165</td>
<td>-</td>
</tr>
<tr>
<td>Vlb</td>
<td>135</td>
<td>-</td>
<td>98</td>
<td>117</td>
<td>-</td>
</tr>
<tr>
<td>Vlc</td>
<td>160</td>
<td>-</td>
<td>110,137</td>
<td>160</td>
<td>-</td>
</tr>
<tr>
<td>Vld</td>
<td>160</td>
<td>-</td>
<td>-</td>
<td>160</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^1\) DSC thermograms were obtained at a 10°C/minute heating and cooling rate.

\(^2\) Thermal transitions as observed on a Fisher-Johns melting point apparatus.

\(^3\) Thermal transitions of the post-treated polymers as measured by DSC.

\(^4\) Melting transitions as observed on a Fisher-Johns melting point apparatus, Va-d, or by DSC, Vla-d.

\(^5\) Crystallization exotherm in DSC thermogram during cooling.

\(^6\) Cold crystallization exotherm in DSC thermogram during heating.

Although glass transitions were not observed by DSC, it is probable the \(T_g\) for polymer Vla occurs below the first cold crystallization exotherm. The effect of N-methyl substitution appeared to reduce the tendency for the substituted polymers to crystallize. These results are consistent with previous studies on N-methyl, N-butyl, and N-phenyl substituted polyamides which showed that substitution leads to polymers having greater solubility, reduced melting points, reduced crystallinity, and lower glass transition temperatures\(^{28-30}\).

The observation of polymers Va-d, and Vla-d using a hot stage and cross-polarized light gave no indication of any liquid crystalline phases. Extensive shearing of the polyamides between glass cover slides and surface treatment of the glass cover slides with N-methyl-3-aminopropyltrimethoxysilane, a reagent known to orient liquid crystalline
domains, failed to induce a liquid crystalline state\textsuperscript{31}. In the case of the unsubstituted polyamides, the absence of liquid crystalline domains may be a result of interchain amide type hydrogen bonds. The polymers containing N-methyl substituents, V1a-d, which had appreciably less interchain amide type hydrogen bonds, also gave no indication of a liquid crystalline phase. In that regard, it has been previously stated that methyl-substituted polyamides form less stable liquid crystalline domains because the formation of the trans state is not as highly favored in a N-methylated polyamide and the trans state is required for a linear confirmation\textsuperscript{32}. N-methylated polyamides have been shown to have a smaller fraction of their amide units in the planar trans conformation\textsuperscript{6}. Furthermore, the barrier to rotation in a substituted amide in solution has been estimated to be 9-20 Kcal/mole, depending on the size of the substituents\textsuperscript{33}, and in the molten state, the barriers to rotation of an amide group in a polyamide could be significantly greater. Random sequences of cis and trans amide linkages along the polymer backbone may inhibit the formation of liquid crystalline domains.

**Conclusions**

A number of new polyamides have been prepared containing the biphenol moiety. Biphenol has been successfully used as a mesogenic unit in polyesters, polycarbonates, and polyurethanes\textsuperscript{8-10,12-14}. However, biphenol-based polyamides prepared from primary amines and various acid chlorides gave no indication of liquid crystallinity. The few liquid crystalline polyamides which have been cited in the literature have employed methods to reduce hydrogen bonding. N-methyl substituted polyamides were subsequently prepared which also gave no indication of liquid crystallinity. It is apparent that
the preparation of a thermotropic liquid crystalline polyamide is a challenge which cannot be overcome by the simple elimination of hydrogen bonding. The fact that polyamides are less likely to form stable liquid crystalline domains may be attributed to the fact that polyamides form stable three dimensional crystalline structures and do not readily form a less ordered one or two dimensional packing below their decomposition temperatures which is required for the formation of the liquid crystalline state.

N-methyl substitution of the polyamide backbone was shown to significantly change the properties of the polymers. N-methylated polyamides demonstrated enhanced solubility in common solvents, reduced melting points and crystallinity, and improved thermal stability.

References


(29) Biggs, B.S.; Frosch, C.J.; Erickson, R.H. Industrial and Engineering Chemistry. 1946, 38(10), 1016.


SYNTHESIS AND CHARACTERIZATION OF LIQUID CRYSTALLINE POLY(ESTER-AMIDE)S BASED ON N,N'-DIMETHYLPOLYALKYLENEDIAMINES AND TEREPTHALOXYLBIS(4-OXYBENZOYL CHLORIDE)

Introduction

Because few amide-containing thermotropic liquid crystalline polymers, TLCPs, have been synthesized to date\textsuperscript{1-11}, while many ester-containing TLCPs have been prepared, the objective of this study was to prepare an amide-containing TLCP. In doing so it was thought necessary to synthesize a polymer having properties analogous to a polyester. Since aromatic amide-containing polymers generally have very high melting temperatures in which a liquid-crystalline phase cannot develop before polymer decomposition or isotropization, an aromatic amide-containing polymer would have to be designed having a melting temperature low enough to allow the formation of the liquid-crystalline phase below that of polymer degradation or isotropization. Consequently a series of poly(ester-amide)s were synthesized in which hydrogen bonding was significantly reduced by polymerizing N-methylated secondary diamines with various diacid chlorides to yield tertiary amides. The synthesis of the LC poly(ester-amides) takes advantage of a polymer structure which includes a rigid well-defined mesogenic unit and a flexible spacer unit.

The basic structure of the mesogenic unit selected for this study can be described as a "triad", in which a series of three aromatic units are linked in the \textit{para} position. The basic "triad" units consists of two \textit{para}-substituted
oxyphenylene units linked together by a central terephthaloyl group. The basic triad unit used in this study is shown below and is denoted as (I), the "triad acid chloride" when \( X = \text{COCl} \):

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{C} \\
\text{O} \\
\text{O} \\
\end{array}
\begin{array}{c}
x \\
\text{C} \\
\text{C} \\
\text{O} \\
x
\end{array}
\]

(I)

Another related "triad" type mesogenic units consists of two para-substituted benzoyl groups linked together by an internal hydroquinone unit. Dewar and Goldberg prepared various small molecules containing both internal terephthaloyl and hydroquinone units which were shown to form liquid crystalline nematic phases\(^\text{12}\). These small molecules were shown to form stable nematic phases having a range of terminal alkoxy groups (X) from methoxy to pentoxy. Bilibin, et. al. have also reported numerous low molecular weight model compounds based on the "triad acid chloride", (I), and various aliphatic diols\(^\text{13}\). Consequently, by linking an aliphatic flexible spacer group with a rigid "triad" unit to form a polymer, it would be expected that the resulting polymers would show analogous liquid crystalline behavior to the small molecules.

The first reports of polymers incorporating the triad mesogenic unit were by Jin, et. al., which had the following general structure\(^\text{14}\):

\[\left[ \begin{array}{c}
x' \\
\text{O} \\
\text{C} \\
\text{C} \\
\text{O} \\
\end{array}
\begin{array}{c}
x \\
\text{C} \\
\text{C} \\
\text{O} \\
x
\end{array}\right]_p\]

(II)

The flexible spacer unit (X') contained a carbonyloxypolymethyleneoxycarbonyl group having from 2-12 methylene units. Ober, et. al. reported that these polymers show nematic liquid crystalline behavior when the polymethylene
spacer is less than nine units and smectic behavior when the polymethylene spacer has 9, 10 or 12 units\textsuperscript{15-16}. Similar polymers prepared by Antoun, et. al containing an oxypolymethyleneoxy (X') group were also shown to have behavior consistent with the nematic phase\textsuperscript{17}. The polymers consisted of either an internal hydroquinone moiety or a terephthalate unit and were linked by a polymethylene group having from 5-10 methylene units. A large series of LC polyesters has been prepared by Bilibin, et. al from the "triad acid chloride", (I), and various flexible spacer units\textsuperscript{2,18-21}, including hydroxy terminated oligomers of propylene oxide ranging from 200 to 400 molecular weight units\textsuperscript{2}. These polymers were shown to exhibit behavior consistent with both the nematic and smectic states, depending on the length of the flexible spacer. The fact that the triad mesogen has been shown to form liquid crystalline domains with a wide range of flexible spacers allows the preparation of polymers with controlled transition temperatures. For example, Pino, et. al. prepared LC polyesters based on the "triad acid chloride" and 2,5-hexanediol\textsuperscript{22}. The short methyl branches in the resulting polymer lead to thermal transitions 100\textdegree C lower than the corresponding polymers based on 1,4-butane diol. Another significant consequence of the methyl branches was the loss of three dimensional crystallinity. The polymers formed a liquid crystalline phase upon initial polymer melting and failed to crystallize upon subsequent cooling. A three dimensional crystalline solid could only be obtained from solvent precipitation and annealing.

Because numerous studies have shown that polyesters containing the "triad" group exhibit liquid crystalline behavior over broad temperature ranges, the triad unit was selected as the mesogenic unit for amide-containing polymers in this study. The basic structure of the poly(ester-amide)s prepared is shown below:
Three different synthetic methods were employed to synthesize a series of poly(ester-amide)s based on terephthaloybis(4-oxybenzoyl chloride), (I), and various N,N'-dimethylalkylenediamines. The N,N'-dimethylalkylenediamines were synthesized using the method of Devinsky. The preparation of the poly(ester-amide)s are shown in Figures 3.1 and 3.2. The extensive investigation into the various synthetic routes and the optimal reaction conditions for the preparation of the poly(ester-amide)s was motivated by the desire to prepare high molecular weight liquid crystalline polymers for use as a molecular reinforcement in blends containing nylon-6,6. It was envisioned that by using high molecular weight liquid crystalline polymers, firm conclusions could be drawn as to the extent of molecular reinforcement an LCP could provide for an isotropic polymer such as nylon-6,6.

The first synthetic method involved the high temperature reaction of 2a with either terephthaloyl chloride or isophthaloyl chloride in 1-chloronaphthalene yielding polymers 1A and 2A, respectively, as shown by Scheme 1. The disadvantage of this synthetic route was the fact that the synthesis involved no fewer than four synthetic steps. The hydroxyl units must be blocked by reaction with ethyl chloroformate and deblocked in a later step by hydrolysis. p-Ethoxycarbonyloxybenzoic acid was prepared from p-hydroxybenzoic acid and ethyl chloroformate and converted to p-ethoxycarbonyloxybenzoyl chloride by reaction with thionyl chloride according to the literature preparation.
Figure 3.1. Synthesis of poly(ester-amide)s using N,N'-bis(4-hydroxybenzoyl)-N,N'-dimethyl-1,6-hexamethylenediamine, 2a, and various acid chlorides.
Figure 3.2. Synthesis of poly(ester-amide)s using various N,N'-dimethylpolyalkylenediamine-based monomers and terephthaloylbis(4-oxybenzoyl chloride).

Polymers 1-7B were prepared by the second synthetic method using the direct condensation of (I) with a N,N'-dimethylpolyalkylenediamine using an acid acceptor. The acid chloride used in this study was prepared according to the method of Bilibin, et al. by the condensation of α-hydroxybenzoic acid with terephthaloyl chloride to yield terephthaloylbis(4-oxybenzoic acid), which can be readily converted to the "triad acid chloride", (I), by reaction with thionyl chloride\(^\text{18}\). This preparation involves fewer synthetic steps because the basic "triad" unit is prepared without a series of protection and deprotection steps. Using the method of Bilibin, the "triad acid chloride" can be conveniently used in a polymerization reaction as shown by Scheme 2. In the method of Ober, the triad unit is prepared during the polymerization reaction\(^\text{16}\).

Polymers 1-10C were prepared using the third synthetic method, as shown in Scheme 3, by the direct condensation of the "triad acid chloride" with trimethylsilyl-substituted derivatives of various N,N'-dimethylpolyalkylenediamines without the need for an added base.
Bowser, et. al. demonstrated the utility of this method by showing that silated derivatives of various aliphatic amines could be condensed with various acid chlorides to produce monofunctional amides in reasonable yields (60-90%)\textsuperscript{24}. Polycondensation reactions involving trimethylsilyl derivatives of aromatic diamines have been shown to yield polyaramides in high yields\textsuperscript{25-31}. Oishi, et. al. have shown that the use of silyl derivatives of aromatic diamines such as N,N'-bis(trimethylsilyl)-1,4-phenylenediamine was an effective means of obtaining wholly aromatic polyamides in both high yield and high inherent viscosity\textsuperscript{25}.

The use of trimethylsilyl-substituted diamines has many advantageous features\textsuperscript{32}. In the condensation between an acid chloride and a silyl-substituted amino group, a silylchloride is liberated which does not undergo further reaction. In the reaction between an unsubstituted diamine and an acid chloride, HCl is released which can inhibit a polymerization reaction by protonating an unreacted amino group. Because HCl is not liberated during the polymerization reaction using silyl-substituted derivatives, the need to use an added base to neutralize the acid byproduct is eliminated. Thus side reactions between monomer units or the growing polymer chain with bases can be avoided. Silyl-substituted amine derivatives also have the advantage that they can be readily purified by distillation. One further advantage of silyl-substituted monomers is the ease of removal of the liberated silyl compound following polymerization because of their volatility and their solubility in common solvents. Trimethylchlorosilane, for example, could be used in a continuous process where it is first used to convert a diamine to a disilyl-substituted derivative, after which it is regenerated during the polymerization reaction, and can then be recycled. One disadvantage of silyl-substituted monomers is that they are moisture sensitive and are readily hydrolyzed.
Representative general synthetic methods for the preparation of the various poly(ester-amide)s in this study are given in the following experimental section. Because of the unique rotational phenomenon associated with polymers containing N-methylated amides, a model compound was prepared (4a) in order to evaluate the cis/trans content of the analogous amide units contained in the poly(ester-amide)s prepared and to help in the assignment of the polymer structure using $^1$H and $^{13}$C NMR spectroscopy. The model compound was synthesized from benzoyl chloride and \(N,N'-1,4\)-dimethylbutanediamine.

**Experimental**

All chemicals were obtained from the Aldrich Chemical Company and used as received unless otherwise indicated. \(p\)-Ethoxycarbonyloxybenzoic acid and \(p\)-ethoxycarbonyloxybenzoyl chloride were prepared as described by Ober, et al.\(^{16}\). Methylene chloride was purified by successive washing with concentrated sulfuric acid, aqueous sodium carbonate, water, pre-dried with calcium chloride, and then distilled over \(P_2O_5\). Triethylamine was pre-dried with calcium sulfate and distilled from calcium hydride. Benzoyl chloride and chlorotrimethylsilane were distilled before use. Benzene was washed successively with concentrated sulfuric acid, water, and dilute aqueous sodium hydroxide, pre-dried with calcium chloride, and distilled over lithium aluminum hydride. \(1\)-Chloronaphthalene was washed with aqueous sodium bicarbonate, dried with sodium sulfate and then fractionally distilled at reduced pressure. Terephthaloyl chloride and isophthaloyl chloride were purified by sublimation. Chloroform was washed with water to remove ethanol, pre-dried with calcium chloride, distilled from \(P_2O_5\), and stored over 4Å molecular sieves.

60
Hexamethylphosphoramide, HMPA, was distilled from calcium hydride. 1-Methyl-2-pyrrolidinone, NMP, was purified by vacuum distillation. 1,1,2,2-tetrachloroethane was purified by successive washing with concentrated sulfuric acid, aqueous sodium carbonate, water, pre-dried with calcium chloride, fractionally distilled from phosphorus pentoxide, and stored over 4Å molecular sieves.

**Monomer and Polymer Characterization**

Inherent viscosities for all polymers were determined at 29.5°C in either trifluoroacetic acid or 1,1,2,2-tetrachloroethane using a Cannon-Ubbelohde viscometer. Infrared spectra were obtained using a Perkin Elmer 1600 Series FTIR. Varian XL-200 and XL-300 spectrometers were used to obtain carbon and proton spectra. The DEPT spectra were obtained using a standard Varian package DEPT pulse sequence. Characterization of the poly(ester-amide)s by polarizing optical microscopy, POM, was conducted using a Zeiss optical microscope equipped with a Mettler hot stage. Thermal analysis and the thermal stability of the LCPs prepared were measured on a Perkin Elmer 7 series instrument equipped with a differential scanning calorimeter and a thermogravimetric analyzer under a stream of nitrogen at 10°C/minute. Peak maxima were used for the assignment of melting and cooling transition temperatures. The temperature and power ordinates of the DSC-7 were calibrated using an indium standard. Elemental analyses were conducted by the Microanalysis Laboratory of the University of Massachusetts at Amherst. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected.

The X-ray diffraction patterns were obtained using point collimated Ni-filtered Cuα radiation from a Rigaku Denki X-ray generator on a Statton flat
film camera. Two sample-to-film distances were employed, 49.64 and 168.78 mm. The sample-to-film distances were calibrated using calcium carbonate. The samples were placed in 1.5mm Mark-Rohrchen glass capillaries within a copper heating cell. The dependence of X-ray intensity with 1/d (Å) was measured using an Optronics microdensitometer using a raster size of 50 microns.

Characterization of the molecular weights of polymers 4B, 4C, and 8C by GPC was conducted using a Waters Model 6000A Solvent Deliver System equipped with a R401 Differential Refractometer and two Jordi polydivinylbenzene columns: column 1 having a 1000 Å pore size and column 2 containing a mixed bed (10^3-10^5Å). The GPC data was referenced to narrow molecular weight polystryrene obtained from Polysciences. The GPC traces were obtained in chloroform at a flow rate of 1.0 ml./minute.

Synthesis of Monomers

(1a) N,N'-bis([4-ethoxycarbonyloxybenzoyl])-N,N'-dimethyl-1,6-hexamethylenediamine. To a flame-dried 250 ml. three-neck round bottom flask equipped with an addition flask and a magnetic stirrer was added under nitrogen 5.0 g. (0.035 mol.) of N,N'-dimethyl-1,6-hexamethylenediamine, followed by the slow addition of 16.16 g. (0.071 mol.) of p-ethoxycarbonyloxybenzoyl chloride in 50 ml. of dry methylene chloride through the addition flask, and then 70 additional ml. of methylene chloride. The solution was stirred for one hour at room temperature, after which 14.16 g. (0.14 mol.) of triethylamine was slowly added through the addition flask. The mixture was stirred overnight at room temperature and became light brown in color. Triethylamine hydrochloride was removed by filtration. To the filtrate was added 250 ml. of diethyl ether. The solution was left overnight at 0°C and
subsequently filtered. The solution was evaporated to yield 16.0 g. (88%) of a light brown liquid. Purification of 1a was not necessary to obtain 2a in good yields. The only impurity observed by thin layer chromatography was the starting material p-ethoxycarbonyloxybenzoyl chloride which was used in slight excess. One gram of 1a was purified by flash chromatography using a silica gel column which was 137 cm. in length and 3 cm. in diameter. p-Ethoxycarbonyloxybenzoyl chloride was first eluted from the column using only acetonitrile as the eluant. 1a was eluted from the column using a 5% methanol/95% acetonitrile solution. The fractions containing 1a were combined, evaporated, and vacuum-dried at 60°C for one day to yield 1a as a clear liquid in almost quantitative yield. The purer product may crystallize over a period of weeks at room temperature.

(2a) N,N'-bis(4-hydroxybenzoyl)-N,N'-dimethyl-1,5-hexamethylenediamine. To a solution containing 200 ml. each of water and of ethanol, was added 16.0 g. (0.03 mol.) of 1a and 5.58 g. (0.135 mol) of sodium hydroxide. The solution was refluxed for one hour at 70°C, cooled, and a white precipitate filtered to yield a pale yellow liquid. The ethanol was removed by rotary evaporation after which the aqueous solution was filtered to remove orange-colored impurities. To the aqueous solution was added glacial acetic acid which caused the immediate precipitation of a gummy solid mass. The mixture was refluxed, cooled to 0°C, the precipitate collected by filtration, and washed with copious amounts of water. The crude product was recrystallized from 30% aqueous ethanol (1 g/100 ml.), filtered, and washed with cold ethanol to yield 7.38 g. (64% yield) of 2a.
(3a-c) \( \text{N,N'}-\text{bis(trimethylsilyl)-N,N'}-\text{dimethyl-1,12-dodecamethylene} \text{diamine} \).

A silyl-substitued diamine having 12 methylene units will be described for illustrative purposes: \( \text{N,N'}-\text{dimethyl-1,12-dodecamethylene} \text{diamine} \) (52.37g, 0.229 mol), prepared according to the method of Devinsky\textsuperscript{23}, was placed in an oven-dried reaction vessel consisting of a 1,000 ml. three-neck round-bottom flask equipped with a large magnetic stirrer, a reflux condenser, and an addition funnel. All manipulations were carried out under an argon atmosphere due to the sensitivity of the silyl derivatives to moisture. To the flask was added 600 ml. of dry benzene, followed by the slow addition of chlorotrimethylsilane (66.68 ml., 0.525 mol), after which the reaction vessel was heated at reflux for 90 minutes. A white gel-like precipitate was generated. The reaction vessel was cooled to room temperature. Triethylamine (97.4 ml., 0.70 mol.) was added to the reaction vessel and the reaction was refluxed for one additional day. Triethylamine hydrochloride readily precipitated from the reaction mixture. The mixture was allowed to cool to room temperature, and then filtered under argon pressure through a cannula equipped with a filter into a flame-dried three-neck 2000 ml. round-bottom flask equipped with a distillation apparatus. To the triethylamine hydrochloride residue was added 400 ml of dry benzene. The additional benzene was also cannulated in a similar fashion. The distillation apparatus was heated to 100°C to remove solvent and other volatiles at atmospheric pressure. The liquid residue was cannulated into an oven-dried, 200 ml. single-neck flask equipped with an insulated 20 cm. Vigreux column and a short path distillation head. The desired product was distilled at 145°C at 0.9 mm of mercury and was obtained in 81% yield.
(4a) N,N'-bis(benzoyl)-N,N'-dimethyl-1,4-butanediamine.
To a flame-dried 100 ml. three-neck flask equipped with an addition flask and a
magnetic stirrer was added 2.43 g. (0.021 mol.) of N,N'-dimethyl-1,4-
butanediamine and 20 ml. of dry dichloromethane under argon. To this solution
was added dropwise 6.0 g. (0.043 mol.) of benzoyl chloride in 10 ml. of dry
dichloromethane. A vigorous reaction occurred yielding a light pink solution.
After ten minutes of stirring, 8.5 g. (0.084 mol.) of triethylamine was added
followed by 20 ml. of dichloromethane. The reaction was stirred for one day,
and the resulting triethylamine hydrochloride precipitate was filtered and
discarded. The filtrate was added to 300 ml. of diethyl ether, cooled to 0°C, and
any additional triethylamine hydrochloride precipitate removed by filtration. The
solution was concentrated to dryness to yield the crude product which was
dissolved in 10 ml. of chloroform, washed with 1 normal NaOH, distilled water,
and then filtered. To the solution was added 90 ml. of hexane to crystallize the
product which yielded 4.5 g. (66% yield) of a powder consisting of small
crystallites.

Polymer Synthesis

(1A) Poly[oxy-p-phenylenecarbonyl-N-methyliminohexamethylen-N-
methyliminocarbonyl-p-phenyleneoxycarbonyl-p-phenylenecarbonyl].
This polymer was obtained from (2a) and terephthaloyl chloride. To an oven-
dried flask equipped with a reflux condenser and an argon inlet was added 2.0
g. (5.2 mmol.) of 2a and 1.056 g. (5.2 mmol.) of terephthaloyl chloride, followed
by 40 ml. of dry 1-chloronaphthalene. The reaction vessel was heated at
240°C for two days under argon and then cooled; the polymer was precipitated
in methanol, filtered, extracted in a Soxhlet with methanol for one day, and
vacuum-dried for two days at 50°C to yield 1.89 g. of polymer.

A solution of 0.88 g (3.8 mmol.) of N,N'-dimethyldecamethylene diamine in 100 ml. of dry chloroform and a solution of 1.71 g. (3.8 mmol.) of (I) in 200 ml. of dry chloroform were added simultaneously to a Waring Blender containing 0.426 g. (7.6 mmol.) of potassium hydroxide dissolved in 200 ml. of distilled water. The resulting mixture was mixed at high speed under a nitrogen purge for 40 minutes. The product was precipitated in methanol, filtered, extracted in a Soxhlet for one day with methanol, and vacuum-dried to yield 0.95 g. of polymer.


0.47 g (2.73 mmol.) of N,N'-dimethyloctamethylene diamine was added to 5.45 ml of 1N HCL to yield a clear solution. This solution was further diluted with 70 ml of distilled water. An equimolar amount of (I) (1.22 g., 2.73 mmol.) was dissolved in 200 ml of chloroform. A solution of 0.673 g. of potassium hydroxide in 100 ml. of distilled water was first added to a Waring blender, followed by the simultaneous addition of the diamine and diacid chloride solutions. The reaction mixture was stirred at high speed in the Waring Blender for one hour under an argon purge. The polymer was precipitated in methanol, collected by filtration, extracted in a Soxhlet with methanol for one day, and then vacuum-dried for one day to yield 0.57 g. of polymer.
All manipulations were carried out in thoroughly dried glassware because of the sensitivity of the disilamines to moisture. A 500 ml. three-neck round-bottom flask was equipped with a magnetic stirrer and an addition flask. The disilyl derivative 3a (20.125 g., 69.7 mmol.) was weighed into the addition flask under argon. An equimolar amount (30.90 g., 69.7 mmol.) of (I) was added to the round-bottom flask under nitrogen. Two hundred ml. of dry tetrachloroethane were added to the diacid chloride solid to yield a mixture which was cooled to -30°C. The silyl-substituted monomer, 3a, was slowly added to the round-bottom flask through the addition funnel. The reaction was stirred between -10°C and -30°C for four hours. The acid chloride gradually dissolved in the tetrachloroethane as it reacted to form polymer. After 4 hours the solution was allowed to warm to room temperature. The reaction was stirred further for two days at room temperature to yield a viscous solution. The solution was precipitated in methanol to yield a fibrous polymer, which was filtered, extracted in a Soxhlet with methanol for one day, and vacuum-dried to yield 35.3 g. of polymer.

Sample Preparation for X-ray Diffraction Studies

Polymer fiber consisting of polymer 8C was prepared by compression molding the neat polymer at 275°C for six minutes under vacuum, after which it was ground into a fine powder, vacuum-dried for an additional day, melt-extruded through a Randcastle Microtruder where the maximum temperature was 271°C, and collected as a continuous filament at a pickup speed of 115 m/min. Fiber obtained from polymer 8C was denoted as poly(ester-amide) 8C, or PEA-8C. Samples of the fiber were placed in glass capillaries as previously
described and exposed to X-rays successively for four hours at the following temperatures: RT, 138, 180, 218, and 238°C. A separate investigation was employed using a longer sample-to-film distance (168.78 mm.) in order to characterize the X-ray reflections occurring at lower angles. These fibers were exposed for at least 24 hours at each temperature interval employed (RT, 120, 180, and 213°C).

Polymer 7C was also compression molded, ground up into a fine powder, and melt-extruded through the Randcastle Microextruder where the maximum temperature was 300°C. A continuous filament was stretched from the melt by hand. The fiber obtained from polymer 7C will be designated PEA-7C.

Polymer 4B was investigated by X-ray diffraction as a powder. A sample was exposed successively for 2.5 hours at room temperature, 2.5 hours at 175°C, and 4.0 hours 250°C. Another sample of 4B was sealed in a glass capillary and heated on a Fisher-Johns melting point apparatus for six minutes at 280°C to ensure complete melting of the polymer. The sample was then cooled at a rate of approximately 10°C/minute to room temperature. The cooled sample was then exposed to X-rays at room temperature and was designated PEA-4B.

**Results and Discussion**

**Monomer and Polymer Preparation**

The physical properties, elemental analyses, and $^1$H NMR peak assignments for 1a, 2a, and 4a are given in Tables 3.1 and 3.2. Scheme 1 yielded the intermediate (1a) and monomer (2a) in reasonable yields, in spite of the difficult purification of 1a due to its reluctance to crystallize. However, 2a
could be synthesized in reasonable yield and purity without purification of 1a. Although Scheme 1 yielded monomer 2a in relatively high purity, the method is tedious due to the large number of synthetic steps.

After extensive investigation, polymers having the highest molecular weight, as indicated by their solution viscosities, were those polymers prepared from the trimethylsilyl-substituted N,N'-dimethylpolyalkylenediamines. The polymers prepared according to Scheme 1 had the lowest solution viscosities. The low inherent viscosities can be attributed to the lack of solubility of 2a in non-polar solvents such as 1-chloronaphthalene. Significant degradation occurred at the temperatures necessary to solubilize the diphenol, 2a. It is possible that with further investigation, the preparation of the poly(ester-amide)s using 2a could have been improved to yield polymers having higher molecular weights. However, the four synthetic steps necessary to generate 2a motivated the search for a less complicated and less time consuming route.

Polymers prepared according to Scheme 2 using the unsubstituted N,N'-dimethylalkylenediamines and (I) yielded polymers having inherent viscosities

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield</th>
<th>Mp (°C)</th>
<th>Formula</th>
<th>Elemental Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>6</td>
<td>CH₃CH₂O.CO</td>
<td>88</td>
<td>54-55</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>6</td>
<td>HO</td>
<td>64</td>
<td>209-211</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4a</td>
<td>4</td>
<td>H</td>
<td>66</td>
<td>117-118</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1. Yields, melting points and elemental analyses of derivatives of various N,N'-dimethylpolyalkylenediamines.
between 0.3 and 0.4 dl/g. Because the N,N'-dimethylpolyalkylenediamines had limited solubility in water, the polymers were prepared by dissolving both the "triad acid chloride", (I), and the appropriate N-methylated diamine in separate solutions of chloroform followed by rapid mixing. The polymerization was conducted in a Waring blender using a basic aqueous phase to neutralize the HCl liberated during the polymerization reaction. The deficiency of this synthetic method was the poor solubility of (I) in common solvents. The "triad acid chloride" has a solubility in chloroform of approximately 1 g./100 ml. Consequently, the polymerizations were conducted under very dilute conditions. Polymer 7B was prepared by condensing the hydrochloride salt of

Table 3.2. NMR and IR absorptions of N,N'-dimethylpolyalkylenediamine based derivatives.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp.</th>
<th>1H-NMR (δ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>1/°C</td>
</tr>
<tr>
<td>----------</td>
<td>-------</td>
<td>------------</td>
</tr>
<tr>
<td>1a1</td>
<td>6</td>
<td>RT</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1a4</td>
<td>6</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2a2</td>
<td>6</td>
<td>RT</td>
</tr>
<tr>
<td>4a1</td>
<td>4</td>
<td>RT</td>
</tr>
<tr>
<td>4a4</td>
<td>4</td>
<td>80</td>
</tr>
</tbody>
</table>

1 CDCl₃; 2CD₃OD; 3 Very broad peak which appears as a singlet; 4 d₆-DMSO.
N,N'-dimethyl-1,8 octamethylene diamine with the "triad acid chloride". However, an interfacial type polymerization yielded polymer in low yield and with low inherent viscosity.

The highest molecular weight poly(ester-amide)s, polymers 1-10C, were synthesized using trimethylsilyl derivatives of various N,N'-dimethylpolyalkylenediamines, as shown by Scheme 3. The yields, physical properties, and $^1$H NMR and IR absorption spectra for the disilyl derivatives of the various N,N'-dimethylalkylenediamines are summarized in Tables 3.3 and 3.4. The disilyl-substituted N-methylated diamines (3a-c) could be readily purified by distillation. The main disadvantage of the method is the sensitivity of 3a-c to moisture.

<table>
<thead>
<tr>
<th>Compound</th>
<th>n</th>
<th>Yield (%)</th>
<th>bp °C</th>
<th>bp torr</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Calculated</th>
<th>Obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>6</td>
<td>86</td>
<td>63</td>
<td>0.13</td>
<td>58.26</td>
<td>12.57</td>
<td>9.71</td>
<td>58.07</td>
<td>12.44</td>
</tr>
<tr>
<td>3b</td>
<td>8</td>
<td>66</td>
<td>103</td>
<td>0.9</td>
<td>60.68</td>
<td>12.73</td>
<td>8.85</td>
<td>60.40</td>
<td>12.49</td>
</tr>
<tr>
<td>3c</td>
<td>12</td>
<td>81</td>
<td>145</td>
<td>0.9</td>
<td>64.44</td>
<td>12.98</td>
<td>7.52</td>
<td>64.33</td>
<td>12.84</td>
</tr>
</tbody>
</table>

The synthesis of the polymers by Scheme 3 using 3a-c yielded the highest molecular weight polymers at low temperatures. The reaction proceeded in a fashion which was not typical for a polycondensation reaction. Generally, the monomers have good solubility in the polymerization solvent and the polymer precipitates from the solution as high molecular weight is obtained. Sometimes, both the the monomer and polymer have poor solubility in the
Table 3.4. NMR and IR absorptions of N,N'-trimethylsilyl-N,N'-
dimethylpolyalkylenediamines.

\[
\begin{align*}
\alpha & \quad \gamma \quad \delta, \epsilon \quad \gamma & \quad \delta, \epsilon \quad \alpha \\
(CH_3)_3Si - N - CH_2 - CH_2 - (CH_2)_n - CH_2 - CH_2 - N - Si(CH_3)_3
\end{align*}
\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\alpha (\delta))</th>
<th>(\beta (\delta))</th>
<th>(\gamma (\delta))</th>
<th>(\delta (\epsilon))</th>
<th>(\epsilon (\epsilon))</th>
<th>(\text{IR}(\text{cm}^{-1})^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a²</td>
<td>0.12</td>
<td>2.43</td>
<td>2.72</td>
<td>1.47</td>
<td>1.28</td>
<td>2929 2854 1248 834</td>
</tr>
<tr>
<td>3b²</td>
<td>0.14</td>
<td>2.49</td>
<td>2.68</td>
<td>1.49</td>
<td>1.35</td>
<td>2927 2854 1248 834</td>
</tr>
<tr>
<td>3c³</td>
<td>0.05</td>
<td>2.45</td>
<td>2.74</td>
<td>1.42</td>
<td>1.30</td>
<td>2925 2853 1248 836</td>
</tr>
</tbody>
</table>

\(^1\text{IR spectra were obtained using NaCl plates; }^2\text{Pyridine-d}_6; ^3\text{CDCl}_3\)

i, ii C-H stretching, iii Si-CH₃ (CH₃ symmetric deformation), iv Si-C stretching and methyl rocking.

reaction medium and elevated temperatures are required for polymerization. In this study of the polymerization reaction yielding polymers 1-10C, one of the monomers, (I), had poor solubility in the polymerization solvent (1,1,2,2-
tetrachloroethane). (I) was soluble at a ratio of 1 g./100 ml. in chloroform at reflux. At -30°C, (I) and tetrachloroethane existed as a mixture and no appreciable dissolution occurred. As the polymerization proceeded, (I) very slowly dissolved in the polymerization medium as it is reacted with the appropriate silyl-substituted monomer to form polymer. After four to six hours, (I) was totally consumed to yield a viscous polymer solution. Polymers 1-10C were soluble in 1,1,2,2-tetrachloroethane at a ratio of approximately 1.0 g. per 2 ml. of solvent. Thus halogenated solvents were excellent solvents for these polymeric materials. When the polymerization reactions using the silyl-
substituted derivatives were conducted at elevated temperatures, polymers having lower inherent viscosities and in reduced yields were obtained (1-6C).

A summary of the reaction conditions, polymerization yields, and solution viscosities of all the polymers prepared is shown in Table 3.5.

72
Table 3.5. Reaction conditions, yields and solution viscosities of the poly(ester-amide)s prepared.

![Chemical Structure]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>n</th>
<th>Temperature</th>
<th>Base</th>
<th>Solvent</th>
<th>Yield (%)</th>
<th>ln[η] pH (^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>6</td>
<td>270°C</td>
<td>-</td>
<td>1-Chloronaphthalene</td>
<td>71</td>
<td>0.09</td>
</tr>
<tr>
<td>2A</td>
<td>6</td>
<td>240°C</td>
<td>-</td>
<td>1-Chloronaphthalene</td>
<td>60</td>
<td>0.13</td>
</tr>
<tr>
<td>1B</td>
<td>12</td>
<td>RT</td>
<td>KOH</td>
<td>Chloroform</td>
<td>42</td>
<td>0.36</td>
</tr>
<tr>
<td>2B</td>
<td>10</td>
<td>RT</td>
<td>KOH</td>
<td>Chloroform</td>
<td>64</td>
<td>0.38</td>
</tr>
<tr>
<td>3B</td>
<td>75% 12, 25% 6(^3)</td>
<td>RT</td>
<td>KOH</td>
<td>Chloroform</td>
<td>64</td>
<td>0.39</td>
</tr>
<tr>
<td>4B</td>
<td>50% 12, 50% 6(^3)</td>
<td>RT</td>
<td>KOH</td>
<td>Chloroform</td>
<td>56</td>
<td>0.38</td>
</tr>
<tr>
<td>5B</td>
<td>25% 12, 75% 6(^3)</td>
<td>RT</td>
<td>KOH</td>
<td>Chloroform</td>
<td>46</td>
<td>0.34</td>
</tr>
<tr>
<td>6B</td>
<td>6</td>
<td>RT</td>
<td>KOH</td>
<td>Chloroform</td>
<td>39</td>
<td>0.31</td>
</tr>
<tr>
<td>7B</td>
<td>8</td>
<td>RT</td>
<td>KOH</td>
<td>Chloroform/H(_2)O</td>
<td>40</td>
<td>0.24</td>
</tr>
<tr>
<td>1C</td>
<td>8</td>
<td>100°C</td>
<td>-</td>
<td>HMPA/NMP</td>
<td>28</td>
<td>0.25</td>
</tr>
<tr>
<td>2C</td>
<td>8</td>
<td>RT to 70°C</td>
<td>-</td>
<td>Chloroform</td>
<td>76</td>
<td>0.35</td>
</tr>
<tr>
<td>3C</td>
<td>8</td>
<td>RT to 100°C</td>
<td>-</td>
<td>NMP</td>
<td>65</td>
<td>0.49</td>
</tr>
<tr>
<td>4C</td>
<td>8</td>
<td>RT to 150°C</td>
<td>-</td>
<td>Tetrachloroethane</td>
<td>81</td>
<td>0.54</td>
</tr>
<tr>
<td>5C</td>
<td>6</td>
<td>RT to 150°C</td>
<td>-</td>
<td>Tetrachloroethane</td>
<td>78</td>
<td>0.45</td>
</tr>
<tr>
<td>6C</td>
<td>6</td>
<td>RT to 150°C</td>
<td>-</td>
<td>Tetrachloroethane</td>
<td>79</td>
<td>0.53</td>
</tr>
<tr>
<td>7C</td>
<td>6</td>
<td>-10 to -30°C</td>
<td>-</td>
<td>Tetrachloroethane</td>
<td>99</td>
<td>0.84 (0.38)</td>
</tr>
<tr>
<td>8C</td>
<td>46% 12, 54% 6(^3)</td>
<td>-10 to -30°C</td>
<td>-</td>
<td>Tetrachloroethane</td>
<td>98</td>
<td>1.23</td>
</tr>
<tr>
<td>9C</td>
<td>46% 12, 54% 6(^3)</td>
<td>-10 to -30°C</td>
<td>-</td>
<td>Tetrachloroethane</td>
<td>96</td>
<td>1.61 (1.00)</td>
</tr>
<tr>
<td>10C</td>
<td>6</td>
<td>-10 to -70°C</td>
<td>-</td>
<td>Tetrachloroethane</td>
<td>95</td>
<td>- (0.88)</td>
</tr>
</tbody>
</table>

Superscript notes:
\(^1\) Inherent viscosity measurements were obtained in trifluoroacetic acid at a concentration of 0.5g./dL. The values given in parentheses are inherent viscosities measured in 1,1,2,2-tetrachloroethane at the same concentration. Polymer 10C did not dissolve in trifluoroacetic acid, where the polymer seemed to form an oily emulsion.

\(^2\) The internal aromatic group is an isophthaloyi unit.

\(^3\) Mole (%).
Characterization of Monomers and Polymers Using Infrared Spectroscopy

Characterization of 1a by IR spectroscopy showed the following absorptions (KBr): aromatic C-H stretch at 3075 cm\(^{-1}\), aliphatic C-H stretches at 2962 and 2936 cm\(^{-1}\), carbonate carbonyl stretch at 1767 cm\(^{-1}\), and an amide carbonyl stretch at 1635 cm\(^{-1}\). After the hydrolysis of 1a, 2a had the following IR absorptions (KBr): broad O-H stretch at 3189 cm\(^{-1}\), aliphatic C-H stretches at 2932 and 2855 cm\(^{-1}\), amide carbonyl stretch at 1607 cm\(^{-1}\), and a ring carbon-carbon stretch at 1602 cm\(^{-1}\). Model compound 4a had the following IR absorptions (KBr): aromatic C-H stretch at 3060, 3009 cm\(^{-1}\); aliphatic C-H stretches at 2928, 2866 cm\(^{-1}\); an amide carbonyl stretch at 1625 cm\(^{-1}\); and a ring carbon-carbon stretch at 1600 cm\(^{-1}\). Characterization of the silyl-substituted derivatives of the various N,N'-dimethylpolyalkylenediamines by FTIR spectroscopy are summarized in Table 3.4. Characterization of the various "triad" polymers by FTIR showed fairly consistent absorption spectra. The IR spectrum for 4B is described here as an example (KBr): aromatic C-H stretch 3060 cm\(^{-1}\), aliphatic C-H stretches at 2927 and 2853 cm\(^{-1}\), a carbonyl stretch at 1739 cm\(^{-1}\) (ester), the Amide I stretch at 1632 cm\(^{-1}\), and a ring carbon-carbon stretch at 1603 cm\(^{-1}\). IR spectra of these compounds were consistent with their structures.

Characterization of Monomers and Polymers Using NMR Spectroscopy

\(^1\)H NMR peak assignments for the intermediates and monomers 1a, 2a, and 4a are shown in Table 3.2. \(^1\)H NMR peak assignments for the disilyl-substituted monomers, 3a-c, are given in Table 3.4. The \(^1\)H NMR spectrum for the model compound N,N'-bis(benzoyl)-N,N'-dimethylbutanediamine is shown in Figure 3.3. The \(^1\)H NMR spectrum of the model compound illustrates the possible conformations which may be present in solution for the "triad" type
polymers due to the anisotropy of the amide carbonyl group and suggests possible conformational isomers which may exist for the polymers in the solid state.

Since the discovery of the hindered rotation of the amide linkage in DMF, numerous studies have been conducted investigating the cis/trans isomerization of the amide group both for small molecules and for polymers. As shown in Figure 3.3, multiple peaks were present for the methyl group and the methylene groups. Depending on the barrier to rotation around the amide group, interconversion between the cis and trans state of the amide group could occur very slowly. The fact that multiple peaks were observed for the methyl and methylene protons reflect the magnetic nonequivalence of their hydrogens which can be cis or trans to the carbonyl oxygen atom.

Three singlets were observed for the N-methyl groups in an approximate ratio of 1:2:1 for the model compound. Three broad singlets which correspond to the methylene groups located in the α-position to the nitrogen atom were also observed. These observations can be explained by the fact that the amide linkage can exist in one of two rotational isomeric forms, the cis (c) or the trans (t) state. Because the model compound contains two amide linkages separated by four methylene units, the following isomers are possible: c:c', c:t'; t:c', and t:t'. However, upon rotation of the molecule it can be shown that the c:t' state and the t:c' state are identical. If the cis and trans isomers are assumed to be thermodynamically equivalent, the peak intensities would be expected to occur in the following ratios 1:2:1 (c:c, c:t = t:c, t:t), which was approximately observed.

Three possible rotational states (c:c, c:t = t:c, t:t) were also shown to occur for N,N'-diacetyl-N,N'-dimethylethlenediamine and N,N'-dibenzoyl-N,N'-dimethylethlenediamine. When the amide linkages were separated by six methylene units, as is the case with intermediate 1a, only a pair of peaks was
Figure 3.3. $^1$H NMR spectrum of model compound N,N'-bis(benzoyl)-N,N'-dimethylbutanediamine. (a) CDCl$_3$, RT. (b) DMSO, 80°C.
observed for the methyl groups and the methylene groups. With longer flexible spacer units, such as in intermediate 1a, the magnetic anisotropy of one carbonyl group did not influence the magnetic environment of protons located in proximity to the other carbonyl group, thus the molecule existed in only a cis or a trans state. Consequently, for the intermediate 1a, one peak was observed for the cis form and one peak was observed for the trans form. As shown in Figure 3.3(b), the anisotropy of the carbonyl group which was present at room temperature disappeared upon heating for the model compound and intermediate 1a, indicating that the amide bond freely rotated between the cis and trans conformations at a rate which was faster than the chemical shift difference of the respective methyl or methylene protons. Increased temperatures effectively lead to a magnetic environment which was averaged between the cis and trans forms. Miron, et. al. studied various model compounds at both ambient temperature and elevated temperature (117°C) and showed the same phenomena for amide-containing compounds such as N,N'-diacetylpyperazine. No cis and trans forms were observed for the monomer 2a.

Further support for the existence of cis and trans isomers can be found in the $^{13}$C NMR spectrum of the model compound 4a. As shown in Figure 3.4, the aliphatic region of the spectrum was complex and the carbon peaks could not be readily assigned without a multipulse NMR experiment. Spectrum b of Figure 3.4 was obtained using the DEPT pulse sequence (Distortionless Enhancement by Polarization Transfer)$^{36-40}$. The DEPT experiment consists of the following series of carbon and hydrogen pulses$^{40}$:
The DEPT experiment involves polarization transfer of the proton magnetization onto the carbon nuclei for enhanced sensitivity followed by a pulse which is represented by \( \theta \). The final \( \theta \) pulse serves to flip the magnetization of the protons such that with the appropriate choice of flip angles, 45, 90 and 135°, methyl, methylene and methine groups can be distinguished from each other. When the flip angle is 45°, all of the carbon atoms are positive. At 90° the methine units are positive and the methyl and methylene groups have zero intensity. For the monomers and polymers used in this study, the 135° pulse provided the most valuable information. In the 135° pulse, the methylene carbon atoms are negative and the methyl carbon atoms are positive. From this pulse, as shown in Figure 3.4(b), the methyl groups could be readily distinguished from the methylene groups.

Using the raw spectra obtained at various \( \theta \) values, subspectra could be obtained in which one spectrum was subtracted from another spectrum to yield a spectrum containing only carbon atoms of a single type. For example, the \( \text{CH}_3 \) subspectrum could be generated by adding the \( \theta = 45° \) pulse spectrum to the \( \theta = 135° \) spectrum to yield a subspectrum containing only methine and methyl groups. Subtraction of the \( \theta = 90° \) pulse spectrum yielded a subspectrum containing only methyl carbon atoms which appeared as positive peaks in the NMR spectrum. Spectrum editing to yield subspectra containing only certain types of carbon atoms is however, susceptible to certain limitations and cannot always be accomplished due to errors in addition and subtraction of
Figure 3.4. $^{13}$C NMR spectrum of the model compound N,N'-bis(benzoyl)-N,N'-dimethylbutanediameine (CDCl₃, RT). (a) Standard $^{13}$C NMR spectrum. (b) $^{13}$C NMR spectrum of the model compound using the DEPT pulse sequence with no spectrum editing, where $\theta = 135^\circ$. 
the spectra. Inhomogeneities in the magnetic field, correct calibration of the flip angle, and a compromise value of the coupling constant \( J \), contribute to errors in spectrum editing\(^{40}\).

Using the DEPT pulse experiment, the methyl carbon atoms for the model compound could be assigned to the peaks at 37.4 and 32.7 ppm., respectively, with the \textit{cis} form (37.4) occurring slightly downfield from the \textit{trans} form (32.7). Unlike the \( ^1\text{H} \) spectrum for the model compound, only a \textit{cis} or \textit{trans} state was observed for the carbon spectrum, indicating that the two amide groups were far enough removed, such that the anisotropy of one amide linkage did not significantly influence the magnetization of carbon atoms which were well removed.

The NMR spectra obtained for the model compound provided insight into the carbon and proton spectra obtained for the "triad" polymers. The proton spectrum for polymer 8C is shown in Figure 3.5. Because the flexible spacer length was six methylene units, the amide groups were separated to such an extent that only two peaks were observed for the methyl protons and the protons located on the methylene units in the \( \alpha \) position to the amide group. Consequently, only the \textit{cis} and \textit{trans} states were observed in which the magnetic nonequivalence of one amide group did not affect the magnetic environment of the methyl or methylene protons located near the other amide group. The molecular anisotropy of the carbonyl group could be directly observed in the \( ^{13}\text{C} \) NMR spectrum for polymer 9C, as shown in Figure 3.6. The amide carbonyl carbon appeared as a doublet at 170.9 and 170.3 ppm., indicating the presence of the \textit{cis} and \textit{trans} groups which appeared with equal intensity.
Figure 3.5. $^1$H NMR spectrum of polymer 8C (CDCl$_3$, RT).
Figure 3.6. $^{13}$C NMR spectra of polymer 9C (CDCl$_3$, RT). (a) Standard $^{13}$C NMR spectrum. (b) $^{13}$C NMR spectrum obtained using the DEPT pulse sequence with spectrum editing to reveal the methyl carbon atoms, where $\theta = 135^\circ$C.
Assignment of the aromatic carbon atoms was consistent with the assignments made by Pino, et. al. for the triad polymer poly[tetramethyleneterephthaloylbis(4-oxybenzoate)]\textsuperscript{41}. Figure 3.6(b) shows the $^{13}$C DEPT spectrum after spectrum editing for the aliphatic region of polymer 9C where $\theta = 135^\circ$. The DEPT subspectrum clearly shows the two methyl groups corresponding to the cis and trans amide groups, with the methyl carbon resonances occurring at almost the same downfield positions as the cis and trans amide linkages in the model compound.

These studies involving $^1$H and $^{13}$C NMR spectroscopy indicated that the poly(ester-amide)s which were prepared in this study actually contained random sequences of cis and trans amide groups at ambient temperatures. The activation energy for the interconversion between the cis and trans states would be expected to be higher for polymers than for small molecules because cis/trans isomerization for the polymer would be expected to require motion along the polymer backbone. However, Miron, et. al. showed that the activation energy for the interconversion between the cis and trans states was equivalent in solution for various polymers and analogous model compounds\textsuperscript{33}. It was suggested that the rotation of the amide group in the polymers occurred without the rotation of the polymer backbone but by the cumulative small distortion of many other valence bond angles. This mechanism suggests that at elevated temperatures, interconversion between the cis and trans states could occur without rotation of the entire chain.

**Characterization of the Poly(ester-amide)s by GPC and Elemental Analysis**

The molecular weights of the poly(ester-amide)s determined by GPC showed the dramatic increase in molecular weight obtained from the low temperature solution condensation method using the disilyl-substituted
derivatives, 3a-c. Characterization of the polymers by GPC was referenced to samples of narrow molecular weight polystyrene. As shown in Table 3.6, polymer 4B which was prepared directly from the N-methylated diamines had a number average molecular weight of 5,600 which corresponds to approximately 10 repeat units. Polymer 4C was prepared from the trimethylsilyl-substituted monomer 3b at room temperature followed by subsequent heating. The molecular weight was significantly higher than 4B but was still appreciably lower than 8C. Polymer 8C was prepared at -10 to -30°C. A very high degree of polymerization was observed indicating the lack of side reactions at low temperatures and demonstrating the utility of the method.

A direct relationship was observed between the degree of polymerization and the agreement between the calculated and observed elemental analyses. The highest molecular weight polymers, 8-10C, showed good agreement with the calculated values, while the lowest molecular weight polymer, 4B, showed greater deviation.

Table 3.6. Summary of polymers characterized by GPC and elemental analysis (%).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Mn</th>
<th>Mw</th>
<th>PDI</th>
<th>DP</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>4B</td>
<td>5,598</td>
<td>7,892</td>
<td>1.32</td>
<td>10</td>
<td>71.07</td>
<td>6.48</td>
<td>5.07</td>
<td>70.23</td>
<td>6.25</td>
<td>4.58</td>
</tr>
<tr>
<td>4C</td>
<td>29,027</td>
<td>46,056</td>
<td>1.59</td>
<td>54</td>
<td>70.83</td>
<td>6.32</td>
<td>5.16</td>
<td>70.25</td>
<td>6.30</td>
<td>5.10</td>
</tr>
<tr>
<td>8C</td>
<td>48,900</td>
<td>68,011</td>
<td>1.39</td>
<td>88</td>
<td>71.03</td>
<td>6.43</td>
<td>5.10</td>
<td>70.67</td>
<td>6.48</td>
<td>5.05</td>
</tr>
<tr>
<td>9C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>71.03</td>
<td>6.43</td>
<td>5.09</td>
<td>70.79</td>
<td>6.48</td>
<td>5.05</td>
</tr>
<tr>
<td>10C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>70.02</td>
<td>5.88</td>
<td>5.45</td>
<td>69.77</td>
<td>5.80</td>
<td>5.40</td>
</tr>
</tbody>
</table>

Polymers Thermal Analysis

The poly(ester-amide)s prepared in this investigation were shown to be fairly stable by thermogravimetric analysis, TGA, under nitrogen, with approximately a 1% weight loss when heated to 350°C. In air, however, the
poly(ester-amide)s exhibited less thermal stability. Polymer 7C, for example, showed a 1% weight loss when heated to 263°C and 2.5% weight loss at 329°C. Because TGA evaluates the loss in weight which occurs during heating, molecular rearrangement could occur without a weight loss.

Analyses of the various polymers by DSC showed that the thermal transitions varied greatly with increasing molecular weight and flexible spacer chain length. Data from the characterization of the LC poly(ester-amide)s by DSC are summarized in Table 3.7. Both the homopolymer and the copolymers containing the 12 methylene spacer unit showed an endotherm during the first melting cycle which occurred between 150°C and 179°C, an example of which is shown in Figure 3.7 for polymer 1B. This transition may be attributed to conformational changes between the trans and gauche methylene units in the flexible spacer. No analogous endotherm was observed prior to polymer melting for any of the LC polymers containing only the shorter six methylene spacer group (6B, 7C, and 10C).

The observation that the polymers having the shorter, six spacer methylene group did not show this endotherm during heating suggests that the endotherm might be attributed to motion of the methylene flexible spacer units, in which conformational changes within the longer flexible spacer units occur. Motion of the flexible spacer units may occur with concerted changes in the cis and trans amide units. The polymer containing the twelve methylene spacer unit, 1B, as shown in Figure 3.7 and Table 3.7, showed the largest change in enthalpy and entropy for this endotherm.

An investigation by Pino, et. al. has shown that solvent-induced crystallization of poly[tetramethyleneterephthaloylbis(4-oxybenzoate)], a polyester having only a short four-methylene spacer unit, lead to a crystalline state containing gauche-trans-gauche conformations. However, after melting
and subsequent cooling, the crystalline state obtained from solvent-induced precipitation appeared to be converted to a different crystalline form in which he flexible spacer units adopted a more planar trans conformation. A change

Table 3.7. Thermal properties of LC poly(ester-amide)s prepared\(^1\).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>n</th>
<th>1st Melting Endotherms (°C) ((\Delta H, \Delta S))</th>
<th>1st Cooling Exotherms (°C) ((\Delta H, \Delta S))</th>
<th>2nd Melting Endotherms (°C) ((\Delta H, \Delta S)) [3rd Heating(^4)]</th>
<th>2nd Cooling Exotherms (°C) ((\Delta H, \Delta S)) [3rd Cooling(^4)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1B</td>
<td>12</td>
<td>179 (10.5, 23.2) 234 (25.5, 50.3)</td>
<td>178 (-12.9, -28.6) 200 (13.4, 28.3)</td>
<td>147 (2.7, 6.4) 218 (5.2, 10.6)</td>
<td>174 (-6.0, -13.4)</td>
</tr>
<tr>
<td>2B</td>
<td>10</td>
<td>246 (22.8, 43.9)</td>
<td>217 (-4.4, -9.9)</td>
<td>212 (8.0, 16.5)</td>
<td>-</td>
</tr>
<tr>
<td>3B</td>
<td>12,6 (3:1)</td>
<td>163 (2.9, 6.7) 230 (21.3, 42.3)</td>
<td>177 (-3.4, -7.6)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4B</td>
<td>12,6 (1:1)</td>
<td>154 (2.3, 5.4) 223 (12.5, 25.2)</td>
<td>171 (-4.4, -9.9)</td>
<td>217 (8.3, 16.9)</td>
<td>177 (-1.8, -4.0)</td>
</tr>
<tr>
<td>5B</td>
<td>12,6 (1:3)</td>
<td>274 (22.0, 40.2)</td>
<td>200 (-1.6, -3.4)</td>
<td>255 (10.6, 20.1)</td>
<td>-</td>
</tr>
<tr>
<td>6B</td>
<td>6</td>
<td>293 (20.5, 36.2)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7C</td>
<td>6</td>
<td>302 (21.3, 37.0)</td>
<td>249 (-14.3, -27.4)</td>
<td>286 (11.6, 20.8)</td>
<td>233 (-3.8, -7.51)</td>
</tr>
<tr>
<td>8C</td>
<td>12,6 (1:1)</td>
<td>150 (4.6, 10.9) 260 (12.1, 22.7)</td>
<td>213 (-8.8, -18.1)</td>
<td>244 (11.2, 21.7)</td>
<td>208 (-9.1, -18.9)</td>
</tr>
<tr>
<td>9C</td>
<td>12,6 (1:1)</td>
<td>144 (2.93, 7.0) 258 (19.6, 36.9)</td>
<td>214 (-8.9, 18.3)</td>
<td>250 (13.7, 26.3)</td>
<td>207 (1.7, 16.5)</td>
</tr>
<tr>
<td>10C</td>
<td>6</td>
<td>308 (28.3, 48.7)</td>
<td>271 (-12.9, -23.7)</td>
<td>294 (-1.9, -3.35)</td>
<td>298 (20.8, 36.4)</td>
</tr>
</tbody>
</table>

\(^1\) 10°C/minute heating and cooling rate.
\(^2\) (KJ/mol).
\(^3\) (J/mol K).
\(^4\) Third heating and cooling.
\(^5\) A weak exotherm which appears as a shoulder.

The polymers prepared in our study are structurally very similar to the polymer studied by Pino. However the N-methylated poly(ester-amide)s are further complicated by the double bond character of the C-N group, in which the orientation of the phenyl groups was also proposed.
Figure 3.7. DSC thermogram of polymer 1B. (a) First heating cycle. (b) First cooling cycle. (c) Second heating cycle. (d) Second cooling cycle.
populations of cis and trans amide linkages will vary with temperature as shown by the previous NMR studies. Furthermore, the flexible spacer groups used in this investigation contained from 6 to 12 methylene units, which would be expected to have a significantly greater number of gauche conformations. It is interesting to note that it is only the twelve methylene spacer polymer, 1B, which showed this endotherm both on the first and second heating cycle of the DSC.

The fact that the polymers containing the twelve-methylene spacer showed this first order transition between 150°C and 180°C and that the polymers containing the shorter six spacer methylene unit did not, suggests that the endotherm may be more appropriately attributed to changes in the conformation of the flexible spacer units rather than changes in the orientation of the phenyl group or the isomeric state of the amide bond, although some concerted change in the orientation of the phenyl groups, the isomeric state of the amide linkage, and the conformations of the flexible spacer, might also be expected to occur.

As shown in Figure 3.7, an endotherm was also observed as a shoulder at approximately 220°C during the first heating cycle, prior to the principal melting transition which occurred at 234°C. Similar endotherms were also observed for other poly(ester-amides) such as polymer 6B. The endotherm was not specifically investigated, but may involve the melting of a less stable crystalline form, a crystal-crystal transition, or perhaps a crystal to LC transition.

The first melting transitions of the polymers varied greatly with the flexible chain length, composition, and molecular weight of the polymers. The change in polymer melting point with flexible spacer length is shown below in Figure 3.8(a-b) for the polymers 1B, 3-6B.
Figure 3.8. Change in the principal DSC thermal transition during heating for copoly(ester-amide)s (1B,3-6B) containing varying quantities of 6 and 12 methylene spacer units. (a) First DSC heating cycle. (b) Second DSC heating cycle.
The principal endotherm in the DSC thermograms during the first melting cycle might be attributed to the melting of the crystalline state resulting from solvent-induced crystallization. The melting point increased significantly with increasing content of the six methylene spacer. As shown in Table 3.7, the first melting transition increased from 293°C for the lowest viscosity polymer containing the six methylene spacer (6B) to 308°C for the highest viscosity polymer. The effect of molecular weight on polymer melting was more dramatic for the copolymers containing mixtures of six and twelve methylene spacer units. The principal melting transition for the lowest viscosity copolymer containing a 1:1 ratio of six and twelve methylene spacer units occurred at 223°C while the highest molecular weight copolymer (9C) melted at 258°C.

Unlike the first DSC heating cycles, the principal endotherm of the various copolymers showed a different dependence on copolymer composition during the second DSC heating cycle, as shown in Figure 3.8(b). The melting temperature of the copolymers increased in a linear fashion with increasing content of the six methylene spacer group.

The first DSC cooling cycle and subsequent heating and cooling cycles are not well understood. The DSC thermograms for polymer 6B, 7C, and 10C, are shown in Figures 3.9, 3.10, and 3.11 respectively. Polymer 6B, the polymer with the lowest inherent viscosity (0.31 dl/g), contained only the six methylene spacer group. After the first DSC heating cycle, polymer 6B did not show a distinct exotherm during the cooling cycle. Polymer 7C, which had the same composition but a significantly higher inherent viscosity (0.84), showed an exotherm during the first cooling cycle at 249°C. Polymer 10C showed a weak exotherm at 294°C followed by a much larger exotherm at 271°C. The fact that no exotherm was observed during the first cooling cycle for the lowest viscosity six spacer containing poly(ester-amide), 6B, may indicate that the exotherms...
Figure 3.9. DSC thermogram of polymer 6B. (a) First heating cycle. (b) First cooling cycle. (c) Second heating cycle. (d) Second cooling cycle.
Figure 3.10. DSC thermogram of polymer 7C. (a) First heating cycle. 
(b) First cooling cycle. (c) Second heating cycle. (d) Second cooling cycle. 
(e) Third heating cycle. (f) Third cooling cycle.
Figure 3.11. DSC thermogram of polymer 10C. (a) First heating cycle. (b) First cooling cycle. (c) Second heating cycle. (d) Second cooling cycle.
which were observed in the higher molecular weight polymers having the same chemical composition were molecular weight dependent. The effect may be kinetic in nature and may be related to the significant differences in melt viscosity which would influence the mobility of the chains in the melt.

Copolymers containing an equal molar ratio of six and twelve methylene spacer units, 4B, and 8-9C, showed similar changes with increasing molecular weight. The DSC thermograms for polymers 4B, 8C, and 9C are illustrated in Figures 3.12-3.14. The polymer having the lowest inherent viscosity, polymer 4B (0.38 dL/g.), showed a weak exotherm upon cooling which corresponds to a change in enthalpy of -4.4 Kj./mol. Copolymers 8 and 9C having inherent viscosities of 1.23 and 1.61 dL/g., respectively, showed changes in enthalpy of approximately -8.9 Kj/mol for the principal exotherms. The higher molecular weight polymers would be expected to have smaller changes in enthalpy upon cooling if the transitions are presumed to be crystallization transitions because higher molecular weight polymers have reduced chain mobility and generally crystallize at a slower rate with more defects.

The cooling cycles of polymers 8 and 9C were further complicated by the appearance of a shoulder, which occurred at 250°C for both polymers. The DSC thermogram of Polymer 10C showed a sharp exothermic peak at 301°C during the first cooling cycle prior to the principal exotherm which occurred at 260°C. The principal exotherms which occurred during the cooling cycles of all the poly(ester-amide)s, and the weak exotherms which appeared at higher temperature, were very complicated in nature and could not be entirely explained. Because the thermal transitions occurred at increasingly lower temperature and with increasingly smaller changes in enthalpy and entropy with each successive DSC heating cycle, molecular rearrangement may have occurred yielding polymers having different chemical structures.
Figure 3.12. DSC thermogram of polymer 4B. (a) First heating cycle. (b) First cooling cycle. (c) Second heating cycle. (d) Second cooling cycle.
Figure 3.13. DSC thermogram of polymer 8C. (a) First heating cycle. (b) First cooling cycle. (c) Second heating cycle. (d) Second heating cycle.
Figure 3.14. DSC thermogram of polymer 9C. (a) First heating cycle. (b) First cooling cycle. (c) Second heating cycle. (d) Second heating cycle. (e) Third heating cycle. (f) Third cooling cycle.
Characterization of the polymers by X-ray diffraction, which will be presented below, show that the polymers did not appear to crystallize upon cooling and that the polymers formed a disordered solid, which is tentatively described below as a frozen nematic state.

Polymer Characterization by X-ray Diffraction

Because many of the polymers were prepared in relatively high molecular weight, it was possible to melt-extrude the poly(ester-amide)s while in the liquid crystalline state to obtain highly oriented fibers having well-defined X-ray diffraction patterns. Figures 3.15(a-d) and 3.16(a-d) show the X-ray diffraction patterns of PEA-8C with increasing temperature. The reflections for all samples characterized by X-ray diffraction are summarized in Table 3.8. The X-ray diffraction patterns can be described as nematic with local preferred azimuthal orientation. The fiber direction for the X-ray diffraction patterns shown in Figure 3.15 and 3.16 is vertical.

The X-ray diffraction pattern in Figure 3.15(a) is characterized by two arcs located on the equator which correspond to an interchain distance of 4.45 Å. The reflections are sharp indicating that the spacings between the parallel chains were regular. Figure 3.15(b-c) show the X-ray diffraction patterns in which the reflections at the lower angles appear more clearly. Two diffuse streaks can be observed along the equator. These types of reflections have been previously observed in highly ordered nematic liquid crystals, although the source of the reflections is unknown. The diffuse streaks may be attributed to voids. Also observed in Figure 3.15(b-c) are reflections along the meridian, which can be attributed to the short range order present between the repeat units along the polymer backbone, while the diffuse halo located at the center of the film was probably related to scatter caused by the beam stop.
Figure 3.15. Wide angle X-ray diffraction patterns of PEA-8C as an oriented melt-extruded fiber (sample-to-film distances were 49.64 mm, w, and 168.78 mm, s). (a) RT, w. (b) RT, s. (c) 120°C, s. (d) 138°C, w.
Figure 3.16. Wide angle X-ray diffraction patterns of PEA-8C as an oriented melt-extruded fiber (sample-to-film distance was 49.64 mm). (a) 180°C. (b) 218°C. (c) 238°C. (d) Fiber heated directly from room temperature to 240°C without exposures at intermediate temperatures.
Figure 3.16(a-c) show that the liquid crystalline order present at room temperature changed significantly at higher temperatures. At 180°C the reflections which occurred at lower temperature along the meridian, became diffuse in nature suggesting that there was a loss in short range periodicity along the polymer backbone. Reflections along the meridian corresponding to the periodic distance along the polymer backbone were barely detectable when a longer sample-to-film distance of 168.78 mm was used. At higher temperature no reflections were discerned from the diffuse halo which appeared at temperatures exceeding 180°C, even when a longer sample-to-

Table 3.8. X-ray diffraction reflections for various poly(ester-amide)s at various temperatures.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Crystalline State¹</th>
<th>Liquid Crystalline State¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Form² Temp. (°C)</td>
<td>Crystalline Reflections</td>
</tr>
<tr>
<td>PEA-4B</td>
<td>(P) RT</td>
<td>3.18 (w,s); 3.96, 4.34 (s); 4.69 (s); 7.58 (w,d); 16.2 (s,d)</td>
</tr>
<tr>
<td>PEA-4B</td>
<td>(P) 180</td>
<td>3.18 (w,s); 4.05, 4.42 (s); 4.69 (s); 8.38 (w,d); 16.2 (s,d)</td>
</tr>
<tr>
<td>PEA-4B</td>
<td>(M) 250</td>
<td>-</td>
</tr>
<tr>
<td>PEA-4B</td>
<td>(S) RT</td>
<td>-</td>
</tr>
<tr>
<td>PEA-7C</td>
<td>(F) RT</td>
<td>-</td>
</tr>
<tr>
<td>PEA-8C</td>
<td>(F) RT</td>
<td>-</td>
</tr>
</tbody>
</table>

¹ W=low intensity; s=sharp; d=diffuse; m=moderate intensity.
² P=powder sample; F=fiber sample; M=molten sample; S=solid obtained after slow cooling from the melt.
³ Equatorial layer spacing between adjacent mesogenic units.
⁴ Meridional layer spacing associated with the length of the polymer repeat unit.
⁵ Calculated layer spacing assuming an all trans conformation for the six methylene flexible spacer unit.
⁶ Calculated layer spacing assuming an all trans conformation having from six to twelve methylene flexible spacer units.
film distance was used. However, the reflections along the equator, which corresponds to the distance between the chains, became progressively more ordered.

At 238°C, the arcs became very sharp indicating that the distance and the degree of packing between the chains was very uniform. On the other hand, the periodicity along the polymer backbone successively diminished, indicating that the highly ordered nematic texture obtained from melt-spinning relaxed at high temperature forming a less ordered nematic state.

These results suggest that with increasing temperature the separation between the chains became much more regular, while the loss of order along the polymer backbone indicated that the polymer chains appeared to have sufficient mobility to slide past each other in the fiber direction. Because the arcs which appeared along the equator progressively became sharp points with increasing temperature, it is probable that there was a very low degree of tilt between both adjacent polymer chains and adjacent domains. The high degree of order observed in the equatorial reflections of Figure 3.16(c) may even suggest that the liquid crystalline phase existed as large parallel monodomains.

Figure 3.16(d) shows another PEA-8C fiber sample which was heated directly from room temperature to 240°C without exposure at intermediate temperatures. This diffraction pattern also shows nematic order, with no periodicity along the polymer backbone but significant order between the chains, although the degree of organization between the chains was less than the order present in the previously described fiber samples. The fact that the otherwise sharp arcs along the equator became an outer ring indicates the loss of orientation in the fiber, in which many domains developed which were tilted with respect to each other.
The present study indicates that it may not be enough to simply classify a polymer as capable of forming a nematic liquid crystalline state. The degree of short and long range order in the nematic state will be less than that in a smectic state, however, it will vary depending on thermal history and experimental conditions. The X-ray diffraction patterns seem to be consistent with periodically spaced parallel chains having random sequences along the polymer backbone.

The changes which occurred in the X-ray diffraction pattern of the powder sample PEA-4B illustrate the complexity of the thermal transitions which these types of polymers can undergo. Figures 3.17(a-d) show the dependence of X-ray intensity with \(1/d\) (Å) for various temperatures. Figure 3.17(a) shows the X-ray diffraction pattern of the sample obtained from solvent precipitation with no thermal heat treatment. The X-ray diffraction patterns showed multiple reflections indicative of the crystalline state. During the first DSC heating cycle, polymer 4B was shown (Figure 3.12) to have an endotherm at 154°C corresponding to an enthalpy change of 12.5 Kj./mol. This sample was heated to 175°C and exposed for 2.5 hours. The X-ray intensity dependence as a function of \(1/d\) (Å) is shown in Figure 3.17(b). The observation that the crystalline state did not significantly change indicates that the endotherm may be related to either changes in the organization of the crystalline lamellae or conformational changes between the gauche and trans states of the flexible spacer unit. Because the greatest change in enthalpy in the first and second heating cycles between 150°C and 180°C occurred in the polymer containing the twelve methylene spacer unit, the endotherm likely involves motion of the methylene flexible spacer units between the trans and gauche conformations, which may occur with concerted conformational changes between the cis and trans amide units.\(^{41}\)
Figure 3.17. Dependence of X-ray intensity with $1/d$ (Å) for polymer 4B at various temperatures. (a) RT. (b) 180°C. (c) 250°C. (d) Sample heated to 280°C and cooled to RT at approximately 10°C/minute.
When polymer 4B was heated to and held at 250°C, which is a temperature that is slightly higher than the crystalline melting transition, a diffuse outer halo was observed, indicating a lower degree of order between the chains, as well as a diffuse inner halo at the lower angles which suggested the random displacement of the repeat units along the polymer backbone. The dependence of X-ray intensity with 1/d (Å) is shown in Figure 3.17(c). However, because polymer 4B was heated at 250°C for a prolonged time period, the diffuse reflections may be attributed to an irregular polymer structure resulting from molecular interchange reactions, thus the conclusions should be considered tentative.

Sample PEA-4B was melted at 280°C in a sealed glass capillary on a Fisher-Johns melting point apparatus and slowly cooled to room temperature at a rate of approximately 10°C/minute. The dependence of X-ray intensity with 1/d (Å) is shown in Figure 3.17(d). The polymer did not appear to crystallize upon cooling from the melt. As shown in Table 3.8, the reflection having the highest intensity in the crystalline state for polymer 4B corresponds to 4.69 (Å). The only reflection which was observed for PEA-4B after the previously described heat treatment was a very sharp reflection occuring at 4.51 (Å). Although solidification occurred, the polymer did not appear by X-ray diffraction to have crystallized. A disordered solid was obtained which had a degree of order resembling that of the liquid crystalline nematic state.

This result indicates that the crystalline state could only be obtained through solvent-induced precipitation or, perhaps, by annealing, although no attempts were made to obtain the crystalline state through annealing. The observation that the cooled sample exhibited such a sharp reflection along the equator indicated the presence of a high degree of order between the chains. The absence of either a reflection or a diffuse halo at the lower angles, as
shown in Figure 3.17(d), seems to suggest that the displacement of the repeat units along the polymer backbone was random. In this case, a disordered solid may have been formed in which the rigid aromatic blocks had a strong tendency to crystallize, but crystallization was inhibited by the random order of the flexible spacers that separated the hard segments.

Fiber sample PEA-7C was observed by X-ray diffraction 13 months after the initial melt-extrusion and showed no reflections indicative of polymer crystallization. The X-ray diffraction pattern of Fiber PEA-7C had a pair of arcs along the equator, which correspond to a d-spacing of 4.51 Å, and low angle reflections along the meridian, which were difficult to distinguish from a diffuse halo at even lower angle. The meridional reflections correspond to a d-spacing of 28.04 Å. At higher angle there were two additional reflections along the meridian which were relatively weak and correspond to a d-spacing of 5.97 Å.

The observed layer spacings for fibers obtained from polymers 7C and 8C (PEA-7C and PEA-8C) showed good agreement with the calculated layer spacings, as shown in Table 3.8. The calculated layer spacing assumes an all trans conformation for the polymethylene flexible spacer units, and an amide linkage where the attached phenyl group is located cis to the methyl group and trans to the methylene unit. A C-N bond having appreciable double bond character would have a longer theoretical repeat unit.

Characterization of the Poly(ester-amide)s by Polarized Optical Microscopy

Observation of the poly(ester-amide)s by polarized optical microscopy revealed the complex nature of these transitions. After polymer 10C was melted on a hot-stage between two cover slides and observed under cross-polarizers at 315°C only a dark isotropic texture was seen. As shown in Figure 3.11(b,d), the polymer had a weak exotherm at 301°C during the cooling cycle.
As the sample was cooled to below 301°C a dense nematic Schlieren texture developed, as shown in Figure 3.18. It is probable that the LC phase most readily formed below the melting temperature of the crystalline state.

If the melt was sheared at 280°C, a brilliantly birefringent texture developed which apparently contained one or two types of liquid crystalline textures. Indeed, Figure 3.19 shows that two different liquid crystalline textures were present at 280°C. The two different textures may be a result of varying sample thickness. Figure 3.20 shows a sheared sample containing only one type of LC texture. After annealing the sample for one hour at 280°C, a well-defined threaded nematic Schlieren texture remained indicating that the threaded nematic texture appeared to be the equilibrium state at this temperature. Subsequent cooling to 250°C, which was a temperature below the exotherms which occurred at 271°C for the first cooling and 260°C for the second cooling cycle of polymer 10C, and after annealing for one hour, caused no change in the homogeneous threaded nematic texture which was observed by polarized optical microscopy. If the sample was heated again to above 301°C, the temperature at which an endotherm is observed during the second DSC heating cycle, the texture became highly birefringent and flowed, although the texture still appeared to be a nematic Schlieren texture. The LC phase was stable up to 350°C, the limiting temperature of the microscope’s hot state employed, although dark isotropic regions could be observed. Only tentative conclusions can be drawn from annealing studies at these temperatures. As shown in Table 3.7, melting endotherms and cooling exotherms became progressively weaker with the length of heating, which probably reflects a randomization of the polymer structure with prolonged heatings.

Because the lower molecular weight polymers had thermal transitions which occurred at lower temperatures, annealing studies could be conducted at
Figure 3.18. Observation of polymer 10C at 280°C by polarizing optical microscopy (magnification equals 400X).
Figure 3.19. Observation of polymer 10C at 280°C by polarizing optical microscopy after shearing (magnification equals 400X).
Figure 3.20. Observation of polymer 10C at 280 °C by polarizing optical microscopy after extensive shearing (magnification equals 400X).
various temperatures without significant thermal degradation. When polymer 4B was heated to 240°C, melted between glass slides, and annealed for one hour, a threaded nematic texture was observed, as shown in Figure 3.21. Upon cooling to approximately 210°C, the sample solidified and could no longer be sheared. After subsequent heating and annealing at 225°C for one hour, the well-defined threaded nematic texture appeared to flow. Upon cooling to 160°C at 10°C/minute, which is a temperature below that of the cooling exotherms, which occurred at 171 and 177°C, respectively, in the first and second DSC cooling cycle of 4B, the density of the nematic threads slightly diminished but could clearly be observed. After one hour of annealing at this temperature the sample still appeared as a threaded nematic liquid crystal, as shown in Figure 3.22. The sample appeared to have solidified and could not be readily sheared. Upon heating to 240°C, the sample readily flowed and appeared as a dense threaded nematic texture. After cooling at 10°C/minute to 110°C and annealing for 15 hours the sample still appeared as a threaded nematic texture, although the sample appeared to be in a solid state.

Because various first order transitions, which were observed in the DSC thermograms, may be associated with conformational changes within the long flexible spacer groups, observation by POM of polymer 1B which contained the 12 methylene spacer will be discussed. Polymer 1B melted at 234°C to yield a dark isotropic melt which flowed but showed no birefringence. Shearing failed to induce a liquid crystalline texture. Upon cooling to 160°C at 10°C/minute, a threaded nematic texture developed, although the texture did not appear to flow. When the sample was subsequently heated to 225°C, the intensity of the threaded nematic texture decreased until isotropization occurred at 225°C, a temperature at which the sample flowed. The polymer containing the
Figure 3.21. Observation of polymer 4B by polarizing optical microscopy after one hour of annealing at 240°C (magnification equals 400X).
Figure 3.22. Observation of polymer 4B by polarizing optical microscopy after one hour of annealing at 160°C (magnification equals 400X).
twelve methylene spacer seemed to have the lowest isotropization temperature. This result can probably be attributed to the many conformations which are possible within such a long flexible spacer unit in the liquid state. Polymer 1B showed the greatest change in entropy upon melting during the first DSC heating cycle.

From the results of polymer characterization by POM, DSC, and X-ray diffraction, the following tentative conclusions are suggested concerning the nature of the phase transitions involved. It is believed that prior to any thermal treatment, the polymer existed in a crystalline state, as indicated from the various reflections in the X-ray diffraction pattern of samples obtained by solvent-induced precipitation. With the exception of polymer 1B, the polymers melted during the first heating cycle and a transition was observed from the crystalline state to the nematic state. Initial melting of the poly(ester-amide)s yielded, in some cases, a dark isotropic texture, as observed by POM, depending on the length of the flexible spacer unit. Polymers containing the 6 methylene spacer unit formed highly birefringent textures upon melting, with the exception of the high molecular weight polymer 10C, which formed highly birefringent textures upon slight cooling.

For all of the polymers containing the 6 methylene spacer unit, shearing induced the formation of the liquid crystalline state directly upon melting. When cooled below the initial melting point, the samples readily formed threaded nematic textures. The transition to a liquid crystalline state was verified by DSC. The higher molecular weight polymers passed through either a weak shoulder, or a distinct, weak exothermic transition upon cooling, a temperature at which the formation of the liquid crystalline state was observed by POM. As the sample was cooled below the lower principal exotherm, solidification occurred, as indicated by both visual inspection, and the resistance to shearing, to yield a
disordered solid in which the threaded nematic texture appeared to be frozen. Subsequent annealing at temperatures as low as 100°C for 15 hours lead to a texture that appeared as a threaded nematic LC phase. This conclusion was substantiated by X-ray scattering which showed only a single reflection for PEA-4B upon cooling from the melt.

These results seem to indicate that once the liquid crystalline state was formed, a three dimensional crystalline ordering did not occur on cooling. Apparently, as the LCPs were cooled, the mobility of the chains was reduced until solidification occurred. The solid may have consisted of a frozen nematic state with the possible coexistence of crystalline domains, although there was no evidence by X-ray diffraction which suggested that crystallization occurred. As the samples were heated in the second and third DSC heating cycles, endotherms occurred at temperatures where the polymer again readily flowed, as indicated by the brilliant LC textures which were observed by POM. The endotherms which occurred in the second and third heating cycles might involve a transition from a frozen nematic state, to a flowing nematic state consisting of highly ordered parallel chains which slide past each other or rotate, as indicated by the X-ray diffraction studies of PEA-8C.

**Dependence of Polymer Melting Temperature on Copolymer Composition**

The dependence of the first DSC melting transition temperature on copolymer composition for the low molecular weight polymers 1B, 3-6B, showed a typical relationship for copolymers in which no isomorphic replacement of one component with the other occurs. As shown in Figure 3.8(a), the copolymer containing an equimolar amount of the six and twelve methylene spacer groups exhibited the lowest first melting transition, a melting temperature lower than that of the polymers containing only twelve or six
methylene spacer groups, which can be attributed to the irregularity of the chain packing.

However, the dependence of the principal endotherm observed during the second DSC heating cycles, as shown in Figure 3.8(b), on copolymer composition, showed a different relationship. The temperature at which the principal endotherm occurred for the second heating cycle increased with increasing content of the six methylene spacer in an almost linear fashion. As observed by POM, the endotherms in the second DSC heating cycles occurred at the temperatures at which the polymers began to readily flow. The endotherm observed during the second heating cycles may be associated with the temperature at which the polymer chains attain significant mobility, in contrast to a transition involving the melting of a crystalline solid. A transition from a disordered solid, a frozen nematic state, to the molten state, or a transition from one nematic state to another, are suggested as explanations for the thermal transitions observed in the second and third DSC heating cycles.

**Dependence of Mesophase Stability on Molecular Weight**

It has been shown by Bilibin, et. al.\textsuperscript{18} and Majnusz,\textsuperscript{43} et. al. that polymer melting and isotropization temperatures increase linearly with increasing molecular weight. The melting and isotropization of poly[oxydecamethylenecarbonyl-p-phenyleneoxycarbonyl-p-phenyleneoxy-p-phenylenecarbonyloxy-p-phenylenecarbonyl] was shown to increase linearly with increasing polymer inherent viscosity up to a viscosity of approximately 0.75 dl/g., at which point a plateau was reached and subsequent increases in viscosity did not show an appreciable increase in melting and isotropization temperatures\textsuperscript{18}.
In this present study, because the high molecular weight polymers had such high melting transitions, the formation of the liquid crystalline phase did not readily occur upon initial melting, but upon subsequent cooling. After the initial melting of the high molecular weight polymer 10C, sharp exothermic transitions between 301°C and 294°C were observed in the first and second DSC cooling cycles which corresponded to the formation of the LC state, while no analogous exotherms were observed for the low molecular weight polymer having the same chemical composition (6B). The small change in enthalpy and entropy which occurred upon the formation of the LC phase were indicative of a transition from the isotropic to the nematic state. A transition to a more highly ordered smectic phase would be expected to be associated with a greater change in enthalpy or entropy, although this is not always the case. After initial polymer melting, the highest molecular weight copolymers, 8 and 9C, also showed an exothermic shoulder upon cooling, whereas the low molecular weight polymer 4B did not, indicating that the formation of the LC state for the high molecular weight polymers occurred most readily below the polymer melting temperature. The fact that the high molecular weight polymers showed well-defined exotherms by DSC upon formation of the LC state, and the low molecular weight polymers did not, is not well understood. However, upon formation of the LC, stable mesophases were observed for both the high and low molecular weight polymers at 350°C, the limit of the microscope's hot stage.

Conclusions

A series of liquid crystalline poly(ester-amide)s were prepared based on terephthaloylbis(4-oxybenzoyl chloride) and various N,N'-dimethylpolyalkylenediamines. The poly(ester-amide)s were prepared by three
different synthetic methods yielding polymers having a broad distribution of molecular weights. Polymers having the highest molecular weights were prepared from terephthaloylbis(4-oxybenzoyl chloride) and various N,N'-trimethylsilyl-N,N'-dimethylpolyalkylenediamines. The formation of the LC phase for the low molecular weight polymers occurred upon initial polymer melting. However, in the absence of shearing, the high molecular weight polymers only showed a dark isotropic texture upon initial melting. After initial melting, the formation of the LC phase for the high molecular weight polymers occurred most readily upon cooling. The poly(ester-amide)s were shown by polarizing optical microscopy and X-ray diffraction to form nematic liquid crystalline phases. The poly(ester-amide) which showed the lowest isotropization temperature had a long twelve methylene flexible spacer unit, which may be attributed to an entropic effect associated with the great number of possible conformations of the flexible spacer unit. LCPs containing shorter six methylene flexible spacer units exhibited the most birefringent LC textures and showed no isotropization temperature below 350°C. Upon cooling from the LC phase, a disordered solid was obtained which appeared to be a frozen nematic state. After initial melting, there was no indication of subsequent crystallization for these N-methyl substituted poly(ester-amide)s.
References


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CHAPTER IV

BLENDs OF VARIOUS NOVEL LIQUID CRYSTALLINE
POLy(ESTER-AMIDE)s WITH NYLON-6,6

Introduction

The search for new polymers having novel properties has led to a large number of studies on polymer blends. By combining two different polymers, blends can be produced having a combination of properties which reflect the properties of the pure components. For example, when nylon-6 is blended with polyethylene, poor physical properties of nylon-6 such as moisture absorption and impact strength can be improved. One of the earliest studies of polymer blending was conducted by MacKnight, et. al., where nylon-6 was blended with poly(ethylene-co-methacrylic acid, PEMA)\(^1\). Whereas nylon-6 and polyethylene are incompatible, it was shown that the size of the PEMA domains diminished with increasing methacrylic acid content and the degree of interfacial adhesion was increased. By employing various methods to impart some degree of compatibility to polymer pairs, which are otherwise incompatible, new materials can be generated having a combination of advantageous properties.

In order to prepare polymers which are truly miscible on a molecular level, a polymer’s tendency to self-associate must be either less than or equal to the affinity of that polymer to the other polymer component of the blend. Few miscible blends exist between high molecular weight polymers because of the small amount of combinational entropy gained upon polymer mixing, which is not sufficient to offset the generally positive enthalpy of mixing. However, various methods can be employed to compatibilize immiscible polymer pairs,
especially the use of specific interactions between two polymers to improve the enthalpy of mixing. An alternative method is to use polymers that have only a weak tendency to self-associate, polymers such as poly(2-vinyl pyridine) or polystyrene, each of which has only weak intermolecular dispersive forces.

The focus of the present investigation was to develop liquid crystalline polymers which could be blended with nylon-6,6. It was hoped that an enhancement in the mechanical properties of nylon-6,6 could be obtained by the addition of an LCP. The number of polymers which form miscible blends with commercial nylons is quite limited. Polyamides are a group of polymers which have strong intermolecular interactions as a result of hydrogen bonding. Consequently the polymer chains are strongly self-associating. To prepare a miscible blend containing a polyamide and another high molecular weight polymer, the strong intermolecular hydrogen bonds must be eliminated and replaced by equally large, new interactions between the blend components. Enhanced reinforcement of a flexible polymer matrix is expected to occur if the mixing of a rigid-rod polymer, with an isotropic polymer, such as nylon-6,6, occurs at a molecular level. However, single phase behavior is not expected because of the inherent tendency of rigid-rod polymers to self-associate.

Nylon-6, 66, 11, and 12 have been shown to be partially miscible with p-phenylene terephthalamide (PPTA). The \( \chi \) parameter became increasingly positive with the increasing length of the aliphatic nylon chain. Partial miscibility between the various nylons and PPTA has been attributed to cross hydrogen bonding. In a blend containing an equivalent amount by weight of PPTA and nylon-6, the thermal transitions associated with the melting and crystallization of nylon-6 were absent, which indicated the high degree of interaction which occurred between the two components.
An additional method of obtaining miscible blends from otherwise immiscible amide-containing polymers involves heating the two components to elevated temperatures, causing exchange reactions to occur. Polyamides and polyesters are known to undergo interchange reactions at elevated temperatures. Improved compatibility between immiscible bisphenol-A-polycarbonate/nylon-6 blends has been accomplished by holding the components at a elevated temperatures where acidolysis and aminolysis reactions are known to occur. The high temperature reaction of two amide-containing homopolymers is a viable method to obtain a copolymer having properties intermediate between the two homopolymers.

The fact that polyamides are insoluble in other polymers such as polystyrene or polyethylene can be attributed to the formation of separate domains where the polar polyamide phase separates from the all-hydrocarbon nonpolar phase. Polyamides, as a family of polymers, have only been shown to be compatible with other polymers when the second component can develop highly specific interactions. Because the imino group of Poly(2-vinyl pyridine) has a free electron pair which can hydrogen bond to an electronegative proton, blends containing Poly(2-vinyl pyridine) have been shown to be miscible in the amorphous phase with an amorphous polyamide prepared from hexamethylenediamine and mixtures of terephthaloyl chloride and isophthaloyl chloride. Blends containing various polyamides have also shown miscibility with the substituted polystyrene, poly(styrene-co-vinyl-phenylhexafluorodimethyl carbinol), PHFA. PHFA has been shown to be miscible in certain blend compositions with the following polyamides: an amorphous polyamide (Trogamide T); a copolymer consisting of nylon -6,12 and N,N'-dimethyl substituted-nylon-6,12; as well as many other commercial polymers such as PMMA which have proton accepting groups.
Recent investigations have characterized blends containing nylon-6 and various salts of sulfonated polystyrene, SPS\textsuperscript{19-21}. When the lithium, zinc, or manganese salts of 10\% SPS were blended with nylon-6, the blends were found to be miscible in all blend compositions\textsuperscript{20}. The level of interaction between the manganese salt of SPS and nylon-6 was described as an inter-polymer complex between the amide group of nylon-6 and MnSO\textsubscript{4}\textsuperscript{19}.

Blends containing both amorphous or semicrystalline polyamides have been shown to be immiscible with thermotropic liquid crystalline polymers, TLCPs, such as Hoechst-Celanese's Vectra\textsuperscript{22-25}. Because TLCPs are strongly self-associating, their blends with an isotropic polymer such as nylon-6 which is also strongly self-associating, would not be expected to show appreciable interaction between the components. Strong interaction was, however, suggested to occur for a blend containing nylon-6 and an LC polyester, poly(4,4-biphenylene sebacate)\textsuperscript{22}.

With the objective of obtaining a blend having some level of phase mixing, it was thought necessary to employ a liquid crystalline polymer containing the amide moiety. Liquid crystalline poly(ester-amide)s were prepared from the trimethylsilyl-substituted derivatives of various N,N'-dimethylpolyalkylenediamines and terephthaloylbis(4-oxybenzoyl chloride), in a low temperature solution condensation polymerization yielding high molecular weight polymers. Nylon-6,6/LCP blends were prepared both as solution cast films and as melt-extruded fibers. An investigation of the degree of phase mixing between the components was conducted using differential thermal analysis, (DSC), dynamic mechanical thermal analysis, (DMTA), and electron microscopy.
Experimental

The preparation of the various poly(ester-amide)s used in this study was described previously. The chemical compositions and solution viscosities of the poly(ester-amide)s prepared are summarized in Table 4.1. Polymers 5-9C were shown previously to form liquid crystalline domains consistent with the nematic phase.

Table 4.1. Chemical compositions and solution viscosities of TLCPs prepared.

<table>
<thead>
<tr>
<th>LCP</th>
<th>Flexible spacer length (x)</th>
<th>n_inh. (dL/g.)¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>5C</td>
<td>6</td>
<td>0.45</td>
</tr>
<tr>
<td>7C</td>
<td>6</td>
<td>0.84</td>
</tr>
<tr>
<td>8C</td>
<td>6 (54%), 12 (46%)²</td>
<td>1.23</td>
</tr>
<tr>
<td>9C</td>
<td>6 (54%), 12 (46%)</td>
<td>1.61</td>
</tr>
</tbody>
</table>

¹ Inherent viscosities were measured in trifluoroacetic acid, TFA, at a concentration of 0.5 g./dL (29.5°C).
² Mole percent.

Nylon-6,6 was obtained from the AKZO Chemical Company and was vacuum-dried at temperatures between 125°C and 150°C. A general description will be given for the preparation of various solution cast films containing the pure LCPs and their blends with nylon-6,6. Using a magnetic stirrer, 1.5 g of nylon-6,6 was first dissolved in 15 ml. of trifluoroacetic acid, TFA, which had been dried over 4Å molecular sieves, followed by the addition of 0.5 g of polymer 8C. After the dissolution of both blend components, the solution was poured onto a petri-dish, after which the trifluoroacetic acid was allowed to evaporate. The resulting film was gently removed and bathed for one hour in
an aqueous solution containing sodium carbonate. The film was then extracted in a Soxhlet with water, and then vacuum-dried at 100°C for one day.

Films containing Polymer 5C were prepared both from a trifluoroacetic acid solution using the method previously described and also by compression-molding. Polymer 5C was compression-molded into a sheet at 290°C under vacuum for six minutes using a Carver press. The compression-molded film was very brittle, yet showed better mechanical integrity than the solution cast film.

Melt-extruded fibers containing Polymer 7C and nylon-6,6, were prepared having various blend compositions. Nylon-6,6 was first completely dissolved in trifluoroacetic acid using a magnetic stirrer followed by the addition of Polymer 7C to obtain an overall solution concentration of 1.5 g/10 ml. After complete dissolution, the blend was precipitated in methanol. The polymer precipitate was washed with a copious amount of aqueous sodium carbonate and extracted in a Soxhlet with water using an aqueous sodium carbonate reservoir to neutralize any residual trifluoroacetic acid. After vacuum-drying, the blends were analyzed for fluorine by the Microanalysis Laboratory of the University of Massachusetts. Microanalysis indicated that the blends contained 0.15 % fluorine which approached the detection limit of the method employed. The blend was vacuum-dried for one day at 130°C, ground into a fine powder using a grinding mill equipped with a 1x1 mm mesh filter, vacuum-dried at 150°C for an additional day, then melt-extruded through a Randcastle microtruder using a melting zone temperature of 300°C, equipped with a 1575 micron circular die. The approximate residence time at 300°C was 30 seconds, while the total residence time of the blend in the extruder was approximately 2 minutes. All of the fibers prepared in this study were stretched from the melt by a take-up machine located 76 cm. below the die. The nylon-6,6/Polymer 7C
fiber was obtained at a pickup speed of 75 meters/minute, (m/min), and subsequently cold drawn at 100°C.

Melt-blended nylon-6,6/LCP fibers containing polymers 8 or 9C were prepared by first compression-molding each LCP at 275°C for six minutes under vacuum into a sheet using a Carver press. The respective LCP was then ground into a fine powder, vacuum-dried, tumble-mixed for one day with a finely ground nylon-6,6 powder, and melt-extruded using a melting zone temperature of 275°C, and collected at a pick-up speed of 75 m/min. The melt-blended fibers were then cold drawn at 100°C and hot drawn at temperatures between 225-245°C.

Polymer 8C was also prepared from the Randcastle microtruder as a pure melt-extruded LCP fiber. Polymer 8C was compression-molded at 275°C for six minutes under vacuum, ground into a fine powder, vacuum-dried for an additional day, melt-extruded using a melting zone temperature of 271°C, and collected at a pick-up speed of 115 m/min.

The cold and hot drawing procedures were conducted separately and involved stretching a continuous monofilament over a hot plate equipped with a thermocouple to maintain constant temperatures.

Polymer Characterization

Characterization of the various LCPs and blends by differential scanning calorimetry, (DSC), was conducted using a Perkin-Elmer DSC-7 under a stream of nitrogen using a heating and cooling rate of 10°C/minute. Dynamic mechanical thermal analysis, (DMTA), of the various fibers and films was conducted using a Polymer Laboratories Dynamic Mechanical Thermal Analyzer at a heating rate of 3°C/minute. The films were analyzed using a bending deformation at a frequency of 1 Hz. The films were analyzed by DMTA
using a free length of 1 mm. The fibers were analyzed at 1 Hz in the tensile mode using a 4.7-10 mm free length.

Characterization of the various fibers by DMTA was carried out in the following manner. From 20-30 mono-filaments were stretched between two thin, heavy manila strips by embedding their ends in epoxy. The mono-filaments were carefully spaced apart to eliminate any contact. The fibers were analyzed under tension using an initial static force ranging from 0.1 to 0.4 N. The static force was adjusted during a heating cycle in proportion to $E'$ to prevent excessive elongation of the fibers.

Characterization of the "as spun" and post drawn fibers by scanning electron microscopy, (SEM), was conducted using a JOEL 35CF Scanning Electron Microscope. Analysis of the blends by transmission electron microscopy, (TEM), was conducted using a JEM 1000CX Transmission Electron Microscope in the bright field mode at 100 KV on unstained samples. Bundles of mono-filaments were embedded in an epoxy resin, cured at 60°C for one day, and microtomed across the diameter of the fibers at room temperature to obtain a smooth block surface for SEM and a thin section for TEM. Prior to characterization by SEM, the embedded mono-filaments were sputter-coated with gold using a Polaron E5100 Series II Cool Sputtering System.

Melt-extruded fiber containing Polymer 7C and nylon-6,6 was further characterized by carbon-13 Nuclear Magnetic Resonance spectroscopy, (NMR), using a Varian XL-200 spectrometer. Concentrated sulfuric acid was used as the NMR solvent. The spectrum was referenced to the carbonyl peak of nylon-6,6.
Results and Discussion

Characterization of the Various Blends by DSC

Blends of Polymer 7C and nylon-6,6 were prepared by coprecipitating the blends in methanol from a trifluoroacetic acid solution. Analysis for fluorine indicated a small trace of fluorine which approached the detection limit of the method employed. Characterization of a blend containing an equal weight percent of nylon-6,6 and polymer 7C by DSC, as shown in Figure 4.1, showed that the thermal transitions of nylon-6,6 were appreciably influenced by the presence of the LCP phase. The melting transitions of nylon-6,6 and Polymer 7C occurred at 266 and 305°C respectively during the first heating cycle. An exotherm which presumably corresponds to the crystallization of nylon-6,6 segments occurred at 158°C during the first cooling cycle. A sample of pure nylon-6,6 was characterized by DSC under the same heating and cooling conditions and showed a crystallization exotherm at 216°C, a temperature 78°C higher than the crystallization of nylon-6,6 which was observed in the blend containing Polymer 7C. Subsequent heating and cooling cycles of the blend indicated, as shown in Figure 4.1(d,f), no thermal transition which could be attributed to the pure LCP. A broad endotherm which occurred at 209°C during the second heating cycle, a temperature which is 56°C below the typical melting temperature of nylon-6,6 suggests either appreciable miscibility between the blend's components leading to a melting point depression of nylon-6,6 or that interchange reactions have occurred. Further heating and cooling cycles by DSC showed even further decreases in the thermal transition temperatures of nylon-6,6. The same sample was analyzed in a fourth heating and cooling cycle three months later and was found to have thermal transitions which occurred at even lower temperatures than the third heating and cooling cycles.
The depression in the melting transition of nylon-6,6 suggests partial miscibility of the components, although miscibility might have occurred as a result of interchange reactions.

The perturbation of the thermal transitions of nylon-6,6 was reduced when a blend containing 75 wt% nylon-6,6 and 25 wt% Polymer 7C was investigated. As shown in Figure 4.2, the thermal transitions of what was initially the pure nylon-6,6 component occurred at increasingly lower temperature with the length of heating. However, the reduction in the thermal transition temperatures of the principal endotherm was appreciably lower than the blend containing 50 wt% Polymer 7C. Blends containing 5 wt% Polymer 7C showed no perturbation of the thermal transitions of nylon-6,6. Polymer 7C may act as a diluent which inhibits the crystallization of the nylon-6,6 domains. The reduction in the thermal transitions of the nylon-6,6 rich phase may be kinetic in nature, where the nylon-6,6 rich phase was constrained to form small imperfect crystalline domains. However, because the principal melting endotherm occurred at successively lower temperatures with each heating cycle in the absence of mechanical mixing, amide-amide or amide-ester interchange resulting in either a new copolymer or a blend having improved compatibility is suggested.

Blends of nylon-6,6 and Polymer 7C were melt-extruded through a Randcastle Microtruder where the melting zone temperature was 300°C. The total residence time in the extruder was approximately two minutes. During extrusion, the residence time in the melting zone of the extruder was approximately 30 seconds at 300°C. Fiber extrusion was accompanied by gas evolution which can be attributed to either molecular interchange reactions, or polymer degradation. A sample of the resulting fiber was characterized by
Figure 4.1. DSC thermogram of a 50 wt\% nylon-6,6/Polymer 7C solution cast blend. (a) First heating cycle. (b) First cooling cycle. (c) Second heating cycle. (d) Second cooling cycle. (e) Third heating cycle. (f) Third cooling cycle.
Figure 4.2. DSC thermogram of a 75 wt% nylon-6,6/Polymer 7C solution cast blend. (a) First heating cycle. (b) First cooling cycle. (c) Second heating cycle. (d) Second cooling cycle. (e) Third heating cycle. (f) Third cooling cycle.
DSC and is shown in Figure 4.3. The absence of a transition involving the neat LCP and the depression of the melting temperature of nylon-6,6, which occurred 10°C lower than the melting temperature of pure nylon-6,6, indicated that a high level of compatibility existed between the blend components. Alternatively, a melting transition of the LCP phase may not have been observed due to the extent of phase mixing which occurred during melt-extrusion. During melt-extrusion, the LCP phase might be expected to form small, well dispersed domains in the nylon-6,6 matrix, and thus appear to be miscible by DSC.

Investigation of Polymer 7C/Nylon-6,6 Melt-extruded Fibers by NMR

A large quantity of melt-extruded fiber containing polymer 7C and nylon-6,6 which was melt-processed at 300°C, was collected and dissolved in concentrated sulfuric acid. Approximately 15 weight percent of the blend did not dissolve in concentrated sulfuric acid, whereas both of the homopolymers were otherwise soluble in sulfuric acid. This supports the assertion that molecular interchange reactions occurred at 300°C to yield a random copolymer. The 13C NMR spectrum of the portion of the blend which dissolved in sulfuric acid showed various peaks which could not be attributed to the pure homopolymers. A carbonyl peak was present at 189.9 ppm, which was not present in either of the homopolymers. Various new peaks were also observed in the aromatic carbon region between 120 and 130 ppm, which also suggest considerable molecular interchange.

Analysis of the Various LCPs and Their Blends with Nylon-6,6 Using DMTA

A summary of the characterization of various LCPs and their blends with nylon-6,6 by DMTA is shown in Table 4.2. One objective of the present investigation was to characterize the mechanical relaxations of the pure
Figure 4.3. The first DSC heating cycle of a fiber obtained from the melt-extrusion of a 75 wt% nylon-6,6/Polymer 7C blend which was melt-processed at 300°C.
Table 4.2. Characterization by DMTA of various LC poly(ester-amide)s, and their blends with nylon-6,6.

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>LCP/Nylon-6,6 Blends</th>
<th>Drawing</th>
<th>Tg (range)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LCP</strong></td>
<td><strong>LCP (%)</strong></td>
<td><strong>Form</strong></td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>film</td>
</tr>
<tr>
<td>7C</td>
<td>25</td>
<td>film</td>
</tr>
<tr>
<td>8C</td>
<td>25</td>
<td>film</td>
</tr>
<tr>
<td>5C</td>
<td>100</td>
<td>film</td>
</tr>
<tr>
<td>8C</td>
<td>100</td>
<td>fiber</td>
</tr>
<tr>
<td>7C</td>
<td>25</td>
<td>fiber</td>
</tr>
<tr>
<td>7C</td>
<td>25</td>
<td>fiber</td>
</tr>
<tr>
<td>8C</td>
<td>25</td>
<td>fiber</td>
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<tr>
<td>8C</td>
<td>25</td>
<td>fiber</td>
</tr>
<tr>
<td>9C</td>
<td>25</td>
<td>fiber</td>
</tr>
<tr>
<td>9C</td>
<td>25</td>
<td>fiber</td>
</tr>
</tbody>
</table>

\(^1\) B = bending mode; T = tensile mode.
TLCPs by DMTA, so that appropriate comparisons could be made with the TLCP blends containing nylon-6,6. Polymer 5C, an LCP having a six-methylene flexible spacer unit was prepared as a film from trifluoroacetic acid, and also as a pressed sheet by compression-molding. The compression-molded sample showed better mechanical integrity than the solution cast film. The compression-molded film was analyzed by DMTA in the bending mode and showed a mechanical relaxation at 96°C. A higher molecular weight LCP having the same chemical composition, Polymer 7C, was prepared as a blend with nylon-6,6 from a trifluoroacetic acid solution. The LCP component exhibited a maximum in the loss tangent at 116°C, which is presumed to be the glass transition temperature. Due to the brittle nature of Polymer 5C, the solution cast film prepared from nylon-6,6 and Polymer 7C perhaps more accurately represents the true glass transition of the poly(ester-amide) containing the six methylene spacer group.

Polymer 8C, an LCP having a random mixture of 6 and 12 methylene groups as the flexible spacer unit, was prepared as a melt-extruded fiber and was analyzed by DMTA in the tensile deformation mode. A maximum in the loss tangent of Polymer 8C, as shown in Figure 4.4, occurred at 67°C which is probably the glass transition temperature. Melt-extruded fiber prepared from pure Polymer 8C was shown previously by X-ray diffraction to be highly oriented. Characterization of the fiber by X-ray diffraction indicated a parallel arrangement of periodically-spaced chains having no long range order along the length of the repeat units. It is interesting to note that the fiber prepared from the pure Polymer 8C showed a relatively intense relaxation for what is presumed to be an ordered nematic phase. The relaxation associated with the pure LCP fiber may be attributed to either the relaxation of the oriented...
Figure 4.4. Temperature dependence of tanδ for a melt-extruded fiber consisting of pure polymer 8C which was melt-processed at 271°C.
flexible spacer unit obtained from melt-extrusion, or the motion of large chain segments in the fiber direction past one another.

To evaluate the degree of mixing which occurred between the various LCPs and nylon-6,6, nylon-6,6 was first evaluated as a film using a bending deformation mode. The $\alpha$-relaxation for nylon-6,6 was very broad and had a maximum intensity at 100$^\circ$C. The $\alpha$-relaxation for nylon-6,6 has been shown by numerous studies to be associated with the rupture of intermolecular hydrogen bonds caused by the molecular motion of long segments of the polyamide chain in the amorphous regions$^{26-28}$.

The $\beta$-relaxation of nylon-6,6 is strongly influenced by water which is bound both loosely and strongly to the polymer. It was shown that the $\beta$-relaxation increases in intensity when water is added and is almost, but not completely, eliminated after thorough drying. It was suggested that the $\beta$-relaxation of nylon-6,6 involves the motion of a water-polymer complex$^{28-29}$. The $\beta$-relaxation of pure nylon-6,6 was determined to be -45$^\circ$C in this investigation, although the temperature at which this relaxation occurred varied with blend composition and post drawing.

The degree of miscibility of the nylon-6,6/LCP blends was also investigated by DMTA. It is important to note that all solution cast films were subjected to no thermal heat treatment other than vacuum-drying at 100$^\circ$C for one day. Characterization of a film containing of 25 wt% Polymer 8C and nylon-6,6 by DMTA is shown in figure 4.5. The $\alpha$- and $\beta$- relaxations of nylon-6,6 occurred at 95$^\circ$C and -53$^\circ$C respectively. However, the principal relaxation associated with Polymer 8C occurred as a broad shoulder with a peak maximum at 45$^\circ$C. The glass transition of pure Polymer 8C was evaluated as a fiber and showed a sharp peak beginning at approximately 50$^\circ$C and having a
Figure 4.5. Temperature dependence of tanδ for solution cast films containing Polymer 8C and nylon-6,6. (a) Solution cast film containing 25 wt% Polymer 8C and nylon-6,6. (b) Solution cast film containing pure nylon-6,6.
Figure 4.6. Temperature dependence of $\tan\delta$ for solution cast films containing Polymer 7C and nylon-6,6. (a) Solution cast film containing 25 wt% Polymer 7C and nylon-6,6 (1:3). (b) Solution cast film containing pure nylon-6,6.
maximum at 67°C. The perturbation of the glass transition of Polymer 8C in the blend suggests that some level of miscibility existed between the polymers. The level of compatibility, however, appeared quite limited, as indicated by the separate relaxation attributable to the pure LCP which can be distinguished from the broad, fused transition.

Similar conclusions could be drawn from the DMTA analysis of a film containing 25 wt% Polymer 7C and nylon-6,6. As shown in Figure 4.6, a maximum in the loss tangent occurred at 116°C, a relaxation associated with the pure LCP. A shoulder which occurred at 88°C is attributed to the the α-transition of nylon-6,6. Because of the broadness of what appeared to be a fused transition, partial miscibility is suggested, although the level of miscibility appeared limited due to the relaxation associated with Polymer 7C which could clearly be discerned. Thus, characterization of various solution cast films containing nylon-6,6 and novel LC poly(ester-amide)s by DMTA suggests that the blends were relatively incompatible in the absence of any thermal treatment. However, partial miscibility is suggested due to the fused nature of the transitions.

The melt-blended LCP/nylon-6,6 fibers showed significantly different levels of miscibility depending on the temperature of melt-extrusion and post treatment. The melt-blended fibers were extruded at temperatures as high as 300°C, whereas the films were exposed to only modest heating during vacuum-drying. Blends containing 25 wt% Polymer 7C and nylon-6,6 were melt-extruded using a melting zone temperature of 300°C, after which the extrudate was stretched from the melt and collected on a take-up machine. As shown in Figure 4.7 for the "as spun" fiber containing 25 wt% Polymer 7C and nylon-6,6, no relaxation was observed which can be attributed to the pure LCP. Only a single relaxation was observed suggesting that either the level of miscibility was
very high, or that molecular interchange occurred such that a copolymer was obtained. In contrast, the solution cast films containing an equivalent blend composition showed two separate relaxations attributable to the separate blend components. Thus, melt-extrusion caused miscibility to occur between nylon-6,6 and the LCP. The apparent miscibility may have occurred through molecular interchange reactions due to high temperature exposure or as a consequence of extensive mixing during melt-extrusion. The melt-extrusion of the nylon-6,6/Polymer 7C blends may have caused the formation of small, highly dispersed LCP domains in the nylon-6,6 matrix which appeared by DMTA as a single phase. After cold drawing of the Polymer 7C/nylon-6,6 fiber at 100°C, a single maximum in the loss tangent was observed at 103°C. The lack of a mechanical relaxation attributable to the pure LCP phase could indicate that after melt-extrusion of the blends and subsequent drawing procedures, the orientation of the LCP component, which was processed in the nematic state, was such that the intensity of the relaxation was very weak and consequently not observed. However, a clear relaxation was observed for the pure LCP fiber prepared from Polymer 8C, as shown in Figure 4.4, which suggests that even the highly oriented LCP domains obtained from melt-extrusion show some type of mechanical relaxation in the temperature range investigated. In this case, a pure LCP phase may not be present.

Because the high temperature melt-extrusion of Polymer 7C and nylon-6,6 lead to blends having a high degree of compatibility, as indicated by a single glass transition temperature by DMTA, which may be attributed to molecular interchange reactions, blends containing Polymers 8C or 9C and nylon-6,6 were prepared by melt-extrusion at temperatures 25°C lower than the previously described blends. Polymers 8 and 9C which had a random mixture
Figure 4.7. Temperature dependence of tan\(\delta\) for a melt-extruded fiber containing a 25 wt\% Polymer 7C/nylon-6,6 blend which was melt-processed at 300°C. (a) "As spun" fiber without subsequent drawing. (b) The melt-extruded fiber after cold drawing.
The characterization of blends containing Polymer 8C or 9C and nylon-6,6 which were melt-extruded at 275°C support the previously described conclusions. As shown in Figure 4.8, only a very broad maximum in the loss tangent was observed for an "as spun" fiber containing 25 wt% Polymer 9C and nylon-6,6. The maximum in the loss tangent occurred at 77°C, which was appreciably lower than the α-relaxation of 100°C for the pure nylon-6,6 film. The relaxation of the "as spun" fiber was very diffuse, suggesting a broad distribution of domain sizes. A weak shoulder was, however, observed at 31°C for the "as spun" fibers containing 25 wt% Polymer 8C and nylon-6,6. This suggests that due to the lower processing temperatures, a lower extent of phase mixing was observed, which might be attributed to a slower rate of molecular interchange which occurred at these temperatures. As shown in Figure 4.8, the cold and hot drawn fiber clearly exhibited a relaxation which could be attributed to separate LCP domains as indicated by the shoulder which occurred at 41°C. The glass transition of the postdrawn fiber showed a principal maximum at 99°C, 22°C higher than the undrawn fiber which could be directly attributed to the α-relaxation of nylon-6,6. Analysis of the cold and hot drawn fibers containing Polymer 8C and nylon-6,6 yielded analogous results in which a reproducible shoulder occurred at 34°C. The fact that a relaxation associated with the pure LCP domains was more clearly observed after hot and cold drawing of the fiber may indicate that drawing either enhances the degree of phase separation between the LCP/nylon-6,6 domains, or it may orientate the amorphous phase of the nylon-6,6 domains such that the α-relaxation of nylon-
Figure 4.8. Temperature dependence of tanδ for a 25 wt% polymer 9C/nylon-6,6 blend after melt-extrusion at 275°C. (a) "As spun" fiber without subsequent drawing. (b) The melt-extruded fiber after cold and hot drawing.
6,6 occurred over a narrower temperature range, thus exposing the mechanical relaxation associated with the pure LCP phase. The phase separation observed for these blends during the drawing procedures may be more attributable to the heating of the fibers which occurred during cold or hot drawing. The melt-extrusion of these blends may lead to small, well-dispersed LCP domains in the nylon-6,6 matrix which is not an equilibrium condition. Subsequent heating of the blends during drawing may cause phase separation to occur.

The temperature dependence of the storage modulus $E'$ for a solution cast film containing nylon-6,6, a melt-extruded fiber containing polymer 8C, and a nylon-6,6/Polymer 9C cold and hot drawn melt-extruded fiber are shown in Figure 4.9. Because nylon-6,6 was evaluated as a solution cast film using a bending deformation, while the melt-extruded fibers were characterized under tension, values for the storage moduli $E'$ have been normalized. $E'$ is plotted as a percentage of the initial storage modulus for each DMTA scan. Inclusion of the LCP component in the blend provides no reinforcement of the nylon-6,6 component. In fact, the reduction in storage modulus with increasing temperature for the nylon-6,6/Polymer 8C blend seems to occur at a faster rate relative to pure nylon-6,6.

**Characterization of the Blends by Electron Microscopy**

Cold drawn fibers obtained from the melt-extrusion of Polymer 7C and nylon-6,6 at 300°C were microtomed and observed using the scanning electron microscope. As shown in Figure 4.10, at a magnification of 3600X, a grainy texture was observed showing no distinct domains which could be attributed to either of the blend components. Because SEM is a technique which evaluates surface morphology, it was possible that the level of phase mixing or
Figure 4.9. Normalized DMTA scans plotted as a percentage of the initial storage modulus $E'$. (a) Solution cast film containing nylon-6,6 (bending). (b) Nylon-6,6/Polymer 9C cold and hot drawn melt-extruded fiber (tension). (c) Melt-extruded polymer containing pure LC Polymer 8C (tension).
Figure 4.10. Characterization by scanning electron microscopy of a melt- extruded fiber containing 25 wt% Polymer 7C and nylon-6,6 (mono-filaments were embedded in an epoxy resin and microtomed across the diameter of the fiber; magnification equals 3600X).
molecular interchange was such that differences in surface morphology could not be detected.

Cold and hot drawn fibers obtained from the melt-extrusion of Polymer 9C and nylon-6,6 at 275°C were also investigated by SEM. These blends were melt-processed at a significantly lower temperature than blends containing Polymer 7C. No evidence of phase separation by SEM was observed for 25 wt% Polymer 9C/nylon-6,6 melt-extruded fibers at a magnification of 8000X.

Characterization of the "as spun" fibers containing 25 wt% Polymer 7C and nylon-6,6 by TEM suggested, however, that some level of phase separation did occur. Melt-extruded fibers containing Polymers 7C and nylon-6,6 were melt-extruded using a melting zone temperature of 300°C, a temperature at which molecular interchange reactions would be expected to occur at the fastest rate. Blends prepared at these temperatures would, therefore, be expected to have the greatest degree of phase mixing. As shown in Figures 4.11 and 4.12, phase separation could be observed, although the nature of phase separation was not well-defined. The fiber embedded in epoxy is shown in Figure 4.11. The fiber appears heterogeneous, although the degree of phase separation is not well-defined. The micrograph shown in Figure 4.12 is a cross section of the fiber shown in Figure 4.11, but at higher magnification. The undrawn fibers had an average diameter of approximately 90 microns. The inclusion shown in Figure 4.12 had a diameter of 14.8 microns, although no definitive conclusions could be made about the chemical composition of this inclusion. Since a well-defined phase showing the size and shape of the LCP component in the nylon-6,6 matrix could not be discerned, an appreciable level of phase mixing is suggested.
Figure 4.11. Characterization by TEM of an "as spun" melt-blended fiber containing 25 wt% Polymer 7C and nylon-6,6 (mono-filaments were embedded in an epoxy resin and microtomed across the diameter of the fiber; magnification equals approximately 2450X).
Figure 4.12. Characterization by TEM of an "as spun" melt-blended fiber containing 25 wt% Polymer 7C and nylon-6,6 (the micrograph shown here represents the fiber shown in Figure 4.11, but at greater magnification; magnification equals approximately 3350X).
Conclusions

Blends containing novel LC poly(ester-amide)s and nylon-6,6 were prepared from both solution cast films and by melt-extrusion. Blends prepared from solution having no thermal history showed distinctive relaxations associated with separate LCP and nylon-6,6 domains. The fact that the relaxations were fused may suggest partial mixing, although this might be attributed to the broadness of the $\alpha$-relaxation of nylon-6,6. Characterization of the blends by DSC showed the blend components to be initially immiscible. However, prolonged heating of blends containing high percentages of LCP lead to the increasingly depressed melting and crystallization transitions of what was initially pure nylon-6,6, and after prolonged heating at elevated temperatures may be the thermal transitions of a copolymer resulting from molecular interchange reactions. Thus, the high temperature exposure of these polymers lead to improved compatibility between the blend components.

Melt-blended fibers containing the various LCPs and nylon-6,6 showed levels of compatibility which varied with the preparation of the blends and the temperature of melt-extrusion. Blends prepared at 275°C, as shown by DMTA, showed a lower degree of compatibility than similar blends melt-extruded at 300°C. The high degree of compatibility of the melt-extruded fibers prepared at 300°C is attributed to the intimate level of mixing obtained from solution blending, interchange reactions which act to compatibilize otherwise immiscible polymer pairs, and the dispersion of the phases during melt-extrusion. The melt-extrusion of these blends which occurred with extensive mechanical mixing may have caused the formation of small, well-dispersed LCP domains in the nylon-6,6 matrix which may not be the equilibrium state, yet may appear by DMTA, in the case of the "as spun" fibers, to be a single phase.
In the case of the nylon-6,6/LCP blends which were melt-extruded at 275°C, post drawing appeared to enhance phase separation. Because the melt-extrusion of these types of blends may cause the formation of intimately dispersed domains, which are quenched by rapid cooling, the phase morphology of the solid fiber may not be at equilibrium. Subsequent heating of the fibers during the drawing procedures may have caused phase separation to occur. Alternatively, the glass transition temperature of nylon-6,6 occurred at a higher temperature and over a narrower temperature range following post drawing, perhaps revealing the mechanical relaxations associated with the pure LCPs. In conclusion, the degree of compatibility of an LCP phase in a nylon-6,6 matrix was shown to be highly dependent on blend preparation, processing conditions, and extent of molecular interchange.

References

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(2) Skrovanek, D. J.; Coleman, M. M. Polymer Engineering and Science. 1987, 27, 857.


NOVEL THERMOTROPIC LIQUID CRYSTALLINE POLY(ESTER-AMIDE)S AS REINFORCING AGENTS. A STUDY OF LCP/NYLON-6,6 BLENDS

Introduction

Considerable interest exists in the preparation of blends containing isotropic polymers such as PET, PBT, nylon-6,6, nylon-6, or PMMA and a liquid crystalline polymer as a molecular reinforcing agent\(^1\)-\(^{20}\). It has been shown that the inclusion of a liquid crystalline polymer, LCP, such as Hoechst-Celanese’s Vectra®, could substantially improve the mechanical properties of a blend due to the inherent stiffness and high strength of the LCP\(^{10}\). Thermotropic LCPs have been shown to significantly reduce the melt viscosity of a random-coil polymer during processing, and thus have received considerable attention as potential processing aids\(^{21}\). LCPs are sometimes referred to as self-reinforcing materials because they spontaneously form ordered domains in the melt. The relaxation time of extruded thermotropic LCPs has been shown to be much longer than random-coil polymers, such that the high degree of orientation present in the liquid crystalline state during melt-extrusion is retained in the solid state\(^{22-23}\).

The mechanical processing of these types of blends is, however, complicated by other considerations. The mechanical properties will be dependent on the size, shape, and degree of molecular dispersion of the LCP in the matrix material, as well as the degree of chemical reaction which occurs between the blend components\(^2\). Most liquid crystalline polymers are prepared by condensation reactions and typically contain ester or amide groups.
Subsequent melt-blending with isotropic polymers such as PET or nylon-6 can lead to molecular interchange between the blend components, depending on the temperature and residence time of extrusion. Ester-ester interchange, for example, has been shown to increase the miscibility of liquid crystalline copolyesters with isotropic polyesters\textsuperscript{15,24-25}.

The focus of the present investigation was to melt blend liquid crystalline poly(ester-amide)s with nylon-6,6 in various compositions. The liquid crystalline poly(ester-amide)s were prepared from various N,N'-dimethypolyalkylenediamines and terephthaloylbis(4-oxybenzoyl chloride) and have been previously described. N-methylated tertiary amide units were incorporated to reduce amide type intermolecular hydrogen bonding. One objective of this investigation was to prepare polymers having reduced melting transitions which could be melt-extruded in the nematic phase without extensive polymer degradation. The formation of the LC phase becomes less favorable as the polymer melting temperature approaches polymer degradation. The introduction of amide type hydrogen bonding in Vectra®, for example, by the inclusion of amide linkages, has been shown to lead to a reduction in the range of tractability. Vectra® B950 is a LC poly(ester-amide) which is intractable when the polymer contains greater than 25 mole percent of the amide functionality\textsuperscript{23}.

A further objective of the present investigation was to prepare an amide-containing LCP having either good interfacial adhesion or partial miscibility with commercialnylons such as nylon-6,6. Polyamides have been shown to form partially miscible blends with only other amide-containing polymers or polymers having specific interactions\textsuperscript{26-34}. Past studies of nylon/LCP blends have shown the blends to be largely incompatible, although an enhancement in tensile properties was observed\textsuperscript{3,35-38}. A study by Shin and Chung suggested
that the incorporation of a long flexible spacer between the mesogenic segments lead to a LC polyester/nylon-6,6 blend having excellent interfacial adhesion.

In the recent literature there has been considerable interest in the mesogenic unit terephthaloylбis(4-oxybenzoyl chloride)\textsuperscript{39-44}. Many LC polymers containing this mesogenic group have been shown to form both smectic and nematic mesophases depending on the length of the flexible spacer unit employed. However, the tensile properties of such polymers have not been reported. The tensile properties of all-aromatic LCPs such as \( \text{p-phenylene terephthalamide (PPTA)} \) and Vectra\textsuperscript{®} are well known to possess ultra-high moduli and tensile strength as well as low elongations at break\textsuperscript{45}. PPTA, for example, exhibits tensile moduli of 64-145 GPa and a tensile strength near 3 GPa. Although many novel LCPs containing relatively long flexible spacer units have been reported in the literature, few publications have described their mechanical properties\textsuperscript{3,46}.

An additional objective of the present investigation was to reduce the shrinkage of nylon-6,6 through blending with an LCP. PPTA, for example, exhibits less than 1\% shrinkage when heated to 250\degree \text{C}\textsuperscript{45}. It was hoped that by blending nylon-6,6 with an LCP containing both a rigid-rod component and a flexible spacer unit, the rigid-rod component could act to inhibit the relaxation of the polyamide chains at elevated temperatures.

Blends were prepared from liquid crystalline poly(ester-amide)s having a broad range of molecular weights in order to determine the relationship between LCP molecular weight and the tensile properties of the blends. Because the LCPs were prepared on small scales, the experimental conditions should not be considered optimized. The chemical compositions and solution viscosities of the various LCPs are shown in Table 5.1. Polymers 7C and 10C
were homopolymers having identical chemical composition, while Polymers 8 and 9C were random copolymers having equivalent chemical composition. Polymers 7C-10C were fairly stable by thermogravimetric analysis, (TGA), under a nitrogen purge, showing approximately a 1% weight loss when heated to 350°C. However, the polymers showed a 1% weight loss at 263°C and a 2.5% weight loss at 329°C in air.

Table 5.1. Chemical compositions, solution viscosities¹ and first melting transitions of the poly(ester-amide)s.

```
\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{LCP} & \text{n} & [\eta]_{\text{inh.}} \ (\text{dL/g.; TFA}^2) & [\eta]_{\text{inh.}} \ (\text{dL/g.; CHCl}_3) & T_m \\
\hline
7C & 6 & 0.84 & 0.38 & 302 \\
8C & 12 (46%), 6 (54%) & 1.23 & - & 260 \\
9C & 12 (46%), 6 (54%) & 1.61 & 1.00 & 258 \\
10C & 6 & - & 0.88 & 308 \\
\hline
\end{array}
\]
```

¹ 0.5 g/dL, 29.5°C.
² Trifluoroacetic acid.

**Experimental**

Each of the four poly(ester-amide)s shown in Table 5.1 were melt-extruded with various percentages of nylon-6,6. Nylon-6,6 was obtained from the AKZO Chemical Company and was vacuum-drying at temperatures between 125°C and 150°C. Blends containing nylon-6,6 and Polymer 7C were prepared using the following method. Nylon-6,6 was first completely dissolved using a magnetic stirrer in trifluoroacetic acid which had been dried over 4Å molecular sieves. Polymer 7C was added to obtain a solution concentration of approximately 1.5 g/10 ml. After complete dissolution, the blend was
precipitated in methanol. The polymer precipitate was washed with a copious amount of aqueous sodium carbonate. The blend was extracted in a Soxhlet with water using an aqueous sodium carbonate reservoir to neutralize any residual trifluoroacetic acid. After vacuum-drying, the blends were analyzed for fluorine by the Microanalysis Laboratory of the University of Massachusetts. Microanalysis indicated that the blends contained 0.15 % fluorine which approached the detection limit of the method employed. The blend was vacuum-dried for one day at 130°C, ground into a fine powder using a grinding mill equipped with a 1x1mm mesh filter, vacuum-dried at 150°C for an additional day, and melt-extruded through a Randcastle Microtruder equipped with a 1575 micron circular die, having a length to diameter ratio of 10. All fibers prepared in this investigation were obtained as mono-filaments. The Randcastle Microtruder has four heating zones: a feeding zone, a compression zone, a melting zone, and a die zone. The heating zone temperatures for all the melt-extruded fibers prepared in this study are summarized in Table 5.2. The approximate residence time for all blends in the melting zone was 30

Table 5.2. Processing temperatures of the Randcastle Microtruder for the various LCPs, nylon-6,6, and nylon-6,6/LCP blends.

<table>
<thead>
<tr>
<th>LCP</th>
<th>Nylon-6,6 (%)</th>
<th>Feeding Zone (°C)</th>
<th>Compression Zone (°C)</th>
<th>Melting Zone (°C)</th>
<th>Die Zone (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>100</td>
<td>220</td>
<td>260</td>
<td>280</td>
<td>260</td>
</tr>
<tr>
<td>7C</td>
<td>-</td>
<td>230</td>
<td>274</td>
<td>300</td>
<td>262</td>
</tr>
<tr>
<td>8C</td>
<td>-</td>
<td>190</td>
<td>241</td>
<td>271</td>
<td>250-260</td>
</tr>
<tr>
<td>7C</td>
<td>75-100</td>
<td>220</td>
<td>276</td>
<td>300</td>
<td>262</td>
</tr>
<tr>
<td>8C</td>
<td>75-100</td>
<td>220</td>
<td>275</td>
<td>300</td>
<td>257-275</td>
</tr>
<tr>
<td>9C</td>
<td>75-100</td>
<td>220</td>
<td>275</td>
<td>275</td>
<td>260-274</td>
</tr>
<tr>
<td>10C</td>
<td>75-100</td>
<td>220</td>
<td>275</td>
<td>275</td>
<td>262</td>
</tr>
</tbody>
</table>
seconds, while the total residence time was approximately 2 minutes in the extruder. The fibers were air-cooled as they were stretched from the melt during pick-up and collected on a take-up machine located approximately 76 cm. below the capillary die. The blends were subsequently post drawn at various temperatures over a hot-plate equipped with a thermocouple to maintain constant temperatures. Stretch ratios and draw ratios were obtained using six measurements of the diameter of each fiber using an Olympus BH-2 polarizing optical microscope. The stretch ratios are defined as the ratio of the diameter of the initial extrudate from the die to the stretched fiber collected after pick-up, squared. The cold and hot draw ratios were obtained from separate post-drawing procedures.

Tensile measurements were obtained using an Instron Testing Machine and were an average of 8-12 fiber samples. All tensile tests were evaluated using a gauge length of 50 mm. Melt-extruded fibers obtained from nylon-6,6 and Polymer 7C were evaluated using a strain rate of 1.0/min. for both the drawn and undrawn fibers. Moduli were obtained at approximately 1% elongation.

Blends containing Polymers 8 or 9C and nylon-6,6 were prepared by first compression-molding each LCP at 275°C for six minutes. The respective LCP was then ground into a fine powder, vacuum-dried at 125°C, tumble-mixed for one day with nylon-6,6, and melt-extruded in the Randcastle Mictrotruder using the processing temperatures summarized in Table 5.2. The tensile properties of the fibers were evaluated using a strain rate of 2.0/min. for the undrawn fibers and 0.1/min. for the drawn fibers.

Polymer 10C was compression-molded at 305°C for six minutes under vacuum, ground into a fine powder, tumble-mixed with nylon-6,6 for one day, and compression-molded at 280°C for three minutes to ensure an intimate
mixing of the two components. The compression-molded sheet was subsequently ground into a fine powder and melt-extruded using the extrusion temperatures summarized in Table 5.2. Tensile properties for the post drawn blends were evaluated using a strain rate of 0.1/min.

Fibers obtained from the pure LCPs were prepared from the previously described compression-molded sheets, ground into a fine powder, and melt-extruded using the processing temperatures summarized in Table 5.2. Tensile properties for the fibers obtained from the pure LCPs 7 and 8C were evaluated using strain rates of 1.0/min. and 0.1/min. respectively.

Shrinkage measurements were obtained by conditioning fibers having lengths of 25 cm. at a relative humidity of 65% for one day using a water-saturated cobalt chloride mixture. The fiber lengths were measured following conditioning. The fibers were then heated at 190°C for fifteen minutes, cooled, and their final lengths remeasured. Each shrinkage measurement was averaged over six tests. Shrinkages were calculated according to the following equation:

\[ S = \frac{\text{initial length} - \text{final length}}{\text{initial length}} \times 100\% \]

**Results and Discussion**

Melt-spun fibers containing the pure LCPs 7C and 8C were prepared in the Randcastle microtruder using the processing temperatures shown in Table 5.2. Melt-extrusion of Polymer 7C was complicated by the high processing temperatures used. Although Polymer 7C showed a TGA weight loss of approximately 1% when heated to 320°C, the melt-extrusion of these fibers was complicated by significant gas evolution and die swell. Consequently the
extrudate could only be stretched and collected from the melt by hand. The
tensile properties of the pure LCPs are summarized in Table 5.3. Polymer 8C
which contained a longer flexible spacer unit, and thus had a lower melting
temperature, was melt-extruded at a significantly lower temperature. The melt-
extrusion of Polymer 8C still showed significant die swell but occurred in the
absence of gas evolution. The fiber could, therefore, be collected using a
continuous pick-up speed of 115 m/min. Fibers obtained from Polymers 7C and
8C were very brittle and could not be post drawn. As shown by the stretch
ratios in Table 5.3, the extrudates were extensively stretched during take-up,
and were shown previously by X-ray diffraction to be highly oriented. The
tensile properties of the LCPs prepared in this investigation were, however,

Table 5.3. Tensile properties of the melt-extruded LC poly(ester-amide)s and
various commercial polymers45,48.

<table>
<thead>
<tr>
<th>LCP</th>
<th>Pickup Speed</th>
<th>Stretch Ratio</th>
<th>E (GPa)</th>
<th>σb(MPa)</th>
<th>eb (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kevlar® 29</td>
<td>-</td>
<td>-</td>
<td>67</td>
<td>2900</td>
<td>1.5</td>
</tr>
<tr>
<td>Vectran® HS</td>
<td>-</td>
<td>-</td>
<td>84-104</td>
<td>2500-3100</td>
<td>2.2-2.5</td>
</tr>
<tr>
<td>7C</td>
<td>hand drawn</td>
<td>1160</td>
<td>8.8</td>
<td>98</td>
<td>1.3</td>
</tr>
<tr>
<td>8C</td>
<td>115 m/min.</td>
<td>1170</td>
<td>6.7</td>
<td>83</td>
<td>3.1</td>
</tr>
<tr>
<td>Nylon-6,6</td>
<td>-</td>
<td>-</td>
<td>6.0</td>
<td>1000</td>
<td>-</td>
</tr>
</tbody>
</table>

appreciably less than the reported tensile properties of the all-aromatic LCPs
previously mentioned. The tensile moduli and strength of the pure poly(ester-
amide)s were also significantly lower than a similar liquid crystalline polyester
prepared from terephthalic acid and 4,4'-dihydroxy-1,10-diphenoxycane2.
The low tensile properties of these LCPs perhaps could be attributed to the
following: the reduction of intermolecular hydrogen bonds by N-methylation,
the effect of the short methyl branches on chain packing, the nature of the
flexible spacer groups which serves to decouple the hard segments. If the rigid-rod segments are essentially decoupled, a low inherent modulus for the entire polymer chain would be expected. Because small samples of the LCPs were extruded, the spinning conditions and tensile properties of the LCPs should not be considered optimized.

Each of the poly(ester-amide)s listed in Table 5.1 was melt-blended with nylon-6,6. Polymer 7C had a melting transition of approximately 300°C. Consequently, blends of Polymer 7C and nylon-6,6 were melt-processed using a melting zone temperature of 300°C. Extrusion of these blends was accompanied by significant die swell and gas evolution. The undrawn fibers were brown in color and had large variations in diameter (±20 μm.). The "as spun" tensile properties for pure nylon-6,6 and blends containing Polymer 7C are shown in Table 5.4. The tensile properties of nylon-6,6 did not change appreciably with varying pick-up speed. Because of the inhomogeneity of the fiber diameters, the "as spun" properties of the blends were inconsistent. However, an enhancement in the tensile modulus and a decrease in the elongation at break relative to nylon-6,6 was observed.

Table 5.4. Tensile properties for "as spun" nylon-6,6 and blends containing Polymer 7C.

<table>
<thead>
<tr>
<th>LCP (%)</th>
<th>Pickup Speed</th>
<th>Stretch Ratio</th>
<th>E (GPa)</th>
<th>σy (MPa)</th>
<th>σb (MPa)</th>
<th>εb (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>75</td>
<td>390</td>
<td>1.4</td>
<td>43</td>
<td>77</td>
<td>254</td>
</tr>
<tr>
<td>0</td>
<td>225</td>
<td>1360</td>
<td>1.5</td>
<td>45</td>
<td>112</td>
<td>254</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>280</td>
<td>3.0</td>
<td>50</td>
<td>84</td>
<td>51</td>
</tr>
<tr>
<td>10</td>
<td>180</td>
<td>2150</td>
<td>5.2</td>
<td>69</td>
<td>160</td>
<td>56</td>
</tr>
<tr>
<td>15</td>
<td>180</td>
<td>410</td>
<td>3.4</td>
<td>49</td>
<td>66</td>
<td>90</td>
</tr>
<tr>
<td>20</td>
<td>150</td>
<td>290</td>
<td>8.4</td>
<td>91</td>
<td>100</td>
<td>36</td>
</tr>
<tr>
<td>25</td>
<td>215</td>
<td>390</td>
<td>4.6</td>
<td>-</td>
<td>50</td>
<td>1.5</td>
</tr>
</tbody>
</table>

1 m/min.
Blends containing either Polymers 8C or 9C and nylon-6,6 were melt-extruded using a melting zone temperature which was approximately 30°C lower than blends containing nylon-6,6 and Polymer 7C. Polymers 8C and 9C contained a mixture of 6 and 12-methylene spacer groups, and thus had melting temperatures of approximately 260°C. The melt-processing of these blends was accompanied by a significant reduction in die swell and gas evolution. Typical deviations in the diameter were ±1-5μm. The tensile properties of the "as spun" fibers containing polymers 8C or 9C and nylon-6,6 are shown in Tables 5.5 and 5.6 respectively. Representative stress/strain curves for the various melt-extruded fibers are shown in Figure 5.1. Blends containing polymer 8C showed a considerable reduction in the elongation at break as would be expected. Blends containing polymer 8C also showed a modest enhancement in tensile modulus compared to blends containing polymer 9C, which may be attributed to the relative humidity present at the time.

Table 5.5. Tensile properties of "as spun" fibers containing nylon-6,6 and Polymer 8C.

<table>
<thead>
<tr>
<th>LCP (%)</th>
<th>Pickup Speed</th>
<th>Stretch Ratio</th>
<th>E (GPa)</th>
<th>(\sigma_y) (MPa)</th>
<th>(\sigma_b) (MPa)</th>
<th>(\varepsilon_b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>75</td>
<td>390</td>
<td>1.4</td>
<td>43</td>
<td>77</td>
<td>254</td>
</tr>
<tr>
<td>0</td>
<td>225</td>
<td>1360</td>
<td>1.5</td>
<td>45</td>
<td>112</td>
<td>254</td>
</tr>
<tr>
<td>5</td>
<td>75</td>
<td>420</td>
<td>1.6</td>
<td>71</td>
<td>156</td>
<td>171</td>
</tr>
<tr>
<td>5</td>
<td>225</td>
<td>2960</td>
<td>2.5</td>
<td>70</td>
<td>204</td>
<td>191</td>
</tr>
<tr>
<td>10</td>
<td>75</td>
<td>400</td>
<td>2.2</td>
<td>63</td>
<td>142</td>
<td>167</td>
</tr>
<tr>
<td>10</td>
<td>225</td>
<td>7380</td>
<td>3.3</td>
<td>131</td>
<td>177</td>
<td>78</td>
</tr>
<tr>
<td>15</td>
<td>75</td>
<td>320</td>
<td>2.8</td>
<td>72</td>
<td>131</td>
<td>123</td>
</tr>
<tr>
<td>15</td>
<td>225</td>
<td>1610</td>
<td>2.8</td>
<td>66</td>
<td>116</td>
<td>129</td>
</tr>
<tr>
<td>20</td>
<td>75</td>
<td>360</td>
<td>2.6</td>
<td>66</td>
<td>89</td>
<td>108</td>
</tr>
<tr>
<td>20</td>
<td>225</td>
<td>1040</td>
<td>2.7</td>
<td>67</td>
<td>99</td>
<td>122</td>
</tr>
<tr>
<td>25</td>
<td>75</td>
<td>670</td>
<td>2.3</td>
<td>56</td>
<td>65</td>
<td>92</td>
</tr>
<tr>
<td>25</td>
<td>225</td>
<td>1160</td>
<td>2.6</td>
<td>71</td>
<td>117</td>
<td>115</td>
</tr>
</tbody>
</table>

\(1\text{m/min.}\)
Figure 5.1. Representative stress/strain curves for various melt-extruded fibers. (a) "As spun" polymer 8C. (b) "As spun" 15 wt% Polymer 9C/nylon-6,6 melt-extruded fiber (75 m/min. pick-up speed). (c) Cold and hot drawn 25 wt% polymer 10/nylon-6,6 melt-extruded fiber (220 m/min. pick-up speed). (d) Cold and hot drawn nylon-6,6 (75 m/min. pick-up speed)
of testing of the nylon-6,6/polymer 9C blends. Blends containing polymer 9C were melt-extruded, stored, and evaluated during a period of very high humidity. However, the tensile properties for the undrawn fibers containing Polymer 9C appeared to be consistent with pure nylon-6,6. Blends containing Polymer 8C, as shown in Table 5.5, showed in most cases a small increase in tensile modulus and strength for the "as spun" fibers, and these properties increased with increasing take-up speed.

Table 5.6. Tensile properties of "as spun" fibers containing nylon-6,6 and Polymer 9C.

<table>
<thead>
<tr>
<th>LCP (%)</th>
<th>Pickup Speed</th>
<th>Stretch Ratio</th>
<th>E (GPa)</th>
<th>$\sigma_y$ (MPa)</th>
<th>$\sigma_b$ (MPa)</th>
<th>$\varepsilon_b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>75</td>
<td>390</td>
<td>1.4</td>
<td>43</td>
<td>77</td>
<td>254</td>
</tr>
<tr>
<td>0</td>
<td>225</td>
<td>1360</td>
<td>1.5</td>
<td>45</td>
<td>112</td>
<td>254</td>
</tr>
<tr>
<td>5</td>
<td>75</td>
<td>380</td>
<td>1.4</td>
<td>53</td>
<td>112</td>
<td>319</td>
</tr>
<tr>
<td>5</td>
<td>225</td>
<td>1660</td>
<td>1.0</td>
<td>34</td>
<td>196</td>
<td>196</td>
</tr>
<tr>
<td>10</td>
<td>75</td>
<td>280</td>
<td>1.0</td>
<td>39</td>
<td>112</td>
<td>427</td>
</tr>
<tr>
<td>10</td>
<td>225</td>
<td>980</td>
<td>1.2</td>
<td>35</td>
<td>148</td>
<td>292</td>
</tr>
<tr>
<td>15</td>
<td>75</td>
<td>250</td>
<td>1.6</td>
<td>59</td>
<td>95</td>
<td>257</td>
</tr>
<tr>
<td>15</td>
<td>225</td>
<td>850</td>
<td>1.4</td>
<td>44</td>
<td>129</td>
<td>215</td>
</tr>
<tr>
<td>20</td>
<td>75</td>
<td>370</td>
<td>1.4</td>
<td>48</td>
<td>86</td>
<td>263</td>
</tr>
<tr>
<td>20</td>
<td>225</td>
<td>1330</td>
<td>2.1</td>
<td>57</td>
<td>90</td>
<td>95</td>
</tr>
<tr>
<td>25</td>
<td>75</td>
<td>360</td>
<td>1.6</td>
<td>55</td>
<td>85</td>
<td>198</td>
</tr>
<tr>
<td>25</td>
<td>225</td>
<td>1060</td>
<td>1.6</td>
<td>43</td>
<td>83</td>
<td>207</td>
</tr>
</tbody>
</table>

1 m/min.

The effect of the LCPs in the LCP/nylon-6,6 blends was more apparent for the post drawn fibers. Each of the melt-extruded fibers prepared in this investigation were cold drawn at 100°C and hot drawn at a temperature just above which the fiber would collapse on a hot-plate used for post drawing. Fibers prepared from nylon-6,6 and Polymer 7C showed the most anomalous results. These fibers collapsed on the hot plate at temperatures exceeding 170°C, a temperature well below the melting transition of pure nylon-6,6. The
tensile properties for the post drawn fibers containing Polymer 7C are summarized in Table 5.7. As shown in Table 5.7, the modulus of the fibers increased dramatically with increasing LCP content. The elongation at break also decreased steadily with increasing LCP content. The increases in tensile modulus were not consistent with the linear rule of mixing of composites for a fiber in a polymer matrix. According to the Halpin-Tsai equation, blends containing nylon-6,6 and Polymer 7C would be expected to have appreciably lower tensile moduli if the blend components are assumed to have equivalent densities. Contrary to the enhancement in tensile moduli, low tensile strengths relative to nylon-6,6 were observed. The results suggest, in addition to the apparent low melting temperature of the fiber, some compatibility between the matrix and the LCP due to molecular interchange reactions. The high temperature heating of amide or ester-containing polymers is well known to lead to molecular interchange.

Table 5.7. Tensile properties of post drawn nylon-6,6/Polymer 7C melt-blended fibers.

<table>
<thead>
<tr>
<th>LCP (%)</th>
<th>Pickup speed</th>
<th>Cold Draw ratio (100°C)</th>
<th>Hot Draw ratio (170°C)</th>
<th>Total Draw</th>
<th>σ_b (MPa)</th>
<th>E (GPa)</th>
<th>η_b (%)</th>
<th>Shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>75</td>
<td>4.0</td>
<td>1.0</td>
<td>4.0</td>
<td>672 ± 60</td>
<td>4 ± 0.6</td>
<td>17.6 ± 2.6</td>
<td>8.4</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>1.1</td>
<td>2.0</td>
<td>2.2</td>
<td>307 ± 89</td>
<td>9 ± 3.3</td>
<td>8.6 ± 2.8</td>
<td>7.4</td>
</tr>
<tr>
<td>15</td>
<td>180</td>
<td>1.4</td>
<td>1.9</td>
<td>2.6</td>
<td>348 ± 40</td>
<td>14 ± 1.4</td>
<td>5.8 ± 1.5</td>
<td>7.4</td>
</tr>
<tr>
<td>20</td>
<td>150</td>
<td>2.1</td>
<td>1.4</td>
<td>3.1</td>
<td>362 ± 91</td>
<td>16 ± 3.0</td>
<td>3.7 ± 0.5</td>
<td>8.7</td>
</tr>
<tr>
<td>25</td>
<td>215</td>
<td>2.3</td>
<td>2.0</td>
<td>5.0</td>
<td>352 ± 39</td>
<td>21 ± 2.8</td>
<td>3.0 ± 0.8</td>
<td>8.5</td>
</tr>
</tbody>
</table>

1 m/min.
defined by a single glass transition. Characterization of the solution cast films showed maxima in the loss tangents at -51°C and 88°C corresponding, respectively, to the α- and β-relaxations of nylon-6,6. An additional relaxation observed at 116°C was attributed to pure LCP domains. Analysis of the melt-processed nylon-6,6/Polymer 7C fibers by DMTA showed only a single glass transition occurring at 83°C for the "as spun" fibers and 103°C for the cold drawn fibers indicating extensive phase mixing of the blend components.

The reduction in tensile strength of the blends containing Polymer 7C may be attributed to a reduction in the crystallinity of the nylon-6,6 rich phase, which has been confirmed previously by DSC. The observed low tensile strengths relative to nylon-6,6 may also be attributed to the inherent low tensile strength of the pure LCP. The fact that even the blend containing 5 wt% LCP showed a significant reduction in tensile strength with respect to nylon-6,6 suggests that the high temperature reaction of these polymers caused a significant disruption in the ability of the nylon-6,6 phase to crystallize. Characterization of the "as spun" fibers by DSC showed a 10°C depression in the melting temperature of the nylon-6,6 phase which might be attributable to partial miscibility of the components due to interchange reactions. Because there was a substantial increase in tensile modulus, molecular interchange is suggested to occur in which rigid aromatic segments of the mesogenic group were incorporated into the nylon domains. The observation that the elevated heating of ester or amide-containing polymers leads to molecular interchange is well known. However, the rate at which molecular interchange has occurred in this case appears appreciably faster than has been previously observed\(^\text{50-59}\).

Fibers containing Polymer 7C showed no reduction in polymer shrinkage with respect to pure nylon-6,6. The inability of the LCP to inhibit the shrinkage of the nylon-6,6 matrix may be related to the glass transition temperatures of the
pure LCPs. Analysis of the pure LCPs by DMTA has shown a maximum in the loss tangent at 116°C for Polymer 7C and 67°C for Polymer 8C. Because the shrinkage measurements were conducted at 190°C, a temperature well above the glass transition of the pure LCP components, relaxation of the orientation present in the flexible spacer groups, or the motion of large chain segments, would be expected to occur. Consequently, the stiffness of the LCP which is present at room temperature may not serve to reduce the shrinkage of the nylon-6,6 matrix at elevated temperatures.

Cold and hot drawn fibers containing either Polymer 8C or 9C and nylon-6,6 which were processed at lower melting zone temperatures had tensile properties which showed significant deviation from the tensile properties of the blends containing Polymer 7C. The tensile properties of the nylon-6,6/Polymer 8C and nylon-6,6/Polymer 9C blends after cold and hot drawing are shown in Tables 5.8 and 5.9. Because Polymers 8C and 9C were identical in chemical composition and differed only in their solution viscosities, the effect of LCP

Table 5.8. Tensile properties of various melt-blended fibers containing nylon-6,6 and Polymer 8C after cold and hot drawing.

<table>
<thead>
<tr>
<th>LCP (%)</th>
<th>Pickup speed(^1)</th>
<th>Cold Draw ratio (100°C)</th>
<th>Hot Draw ratio (225°C)</th>
<th>Total Draw</th>
<th>(\sigma_b) (MPa)</th>
<th>E (GPa)</th>
<th>(\varepsilon_b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>75</td>
<td>4.0</td>
<td>1.0</td>
<td>4.1</td>
<td>672 ± 60</td>
<td>4.1 ± 0.7</td>
<td>17.6 ± 2.6</td>
</tr>
<tr>
<td>0</td>
<td>225</td>
<td>2.2</td>
<td>1.7</td>
<td>3.6</td>
<td>616 ± 44</td>
<td>4.9 ± 0.1</td>
<td>12.5 ± 2.7</td>
</tr>
<tr>
<td>5</td>
<td>75</td>
<td>-</td>
<td>2.3</td>
<td>2.3</td>
<td>595 ± 47</td>
<td>3.2 ± 0.3</td>
<td>18.0 ± 3.3</td>
</tr>
<tr>
<td>5</td>
<td>225</td>
<td>2.0</td>
<td>1.1</td>
<td>2.1</td>
<td>535 ± 24</td>
<td>5.0 ± 0.4</td>
<td>14.0 ± 2.6</td>
</tr>
<tr>
<td>10</td>
<td>75</td>
<td>2.3</td>
<td>1.5</td>
<td>3.4</td>
<td>566 ± 42</td>
<td>3.9 ± 0.4</td>
<td>11.7 ± 0.8</td>
</tr>
<tr>
<td>10</td>
<td>225</td>
<td>1.0</td>
<td>1.4</td>
<td>1.5</td>
<td>414 ± 21</td>
<td>5.8 ± 0.8</td>
<td>8.0 ± 0.7</td>
</tr>
<tr>
<td>15</td>
<td>75</td>
<td>1.7</td>
<td>1.6</td>
<td>2.8</td>
<td>359 ± 21</td>
<td>3.8 ± 0.4</td>
<td>14.1 ± 3.1</td>
</tr>
<tr>
<td>15</td>
<td>225</td>
<td>1.9</td>
<td>1.4</td>
<td>2.7</td>
<td>329 ± 18</td>
<td>3.9 ± 0.6</td>
<td>14.0 ± 2.5</td>
</tr>
<tr>
<td>20</td>
<td>75</td>
<td>2.3</td>
<td>1.4</td>
<td>3.1</td>
<td>269 ± 20</td>
<td>3.4 ± 0.3</td>
<td>9.25 ± 1.6</td>
</tr>
<tr>
<td>20</td>
<td>225</td>
<td>2.3</td>
<td>1.2</td>
<td>2.8</td>
<td>332 ± 16</td>
<td>4.5 ± 0.6</td>
<td>11.8 ± 2.2</td>
</tr>
<tr>
<td>25</td>
<td>75</td>
<td>1.8</td>
<td>2.5</td>
<td>4.4</td>
<td>441 ± 39</td>
<td>5.8 ± 1.5</td>
<td>18.8 ± 1.8</td>
</tr>
<tr>
<td>25</td>
<td>225</td>
<td>1.8</td>
<td>1.8</td>
<td>3.2</td>
<td>290 ± 15</td>
<td>4.4 ± 0.3</td>
<td>8.6 ± 1.8</td>
</tr>
</tbody>
</table>

\(^1\) m/min.
molecular weight on the tensile properties of the blends could be evaluated. The effect of LCP molecular weight was most pronounced for the tensile strength of the blends. For the blends containing Polymer 8C, a decrease in tensile strength was observed immediately at a 5 wt% LCP content. However, for the blends containing Polymer 9C, no appreciable decrease in tensile strength was observed for the blends containing 5-10% LCP. This might be attributed to the higher molecular weight of Polymer 9C relative to Polymer 8C.

Table 5.9. Tensile properties of various melt-blended fibers containing nylon-6,6 and Polymer 9C after cold and hot drawing.

<table>
<thead>
<tr>
<th>LCP (%)</th>
<th>Pickup speed</th>
<th>Cold Draw ratio (100°C)</th>
<th>Hot Draw ratio (245°C)</th>
<th>Total Draw</th>
<th>σb (MPa)</th>
<th>E (GPa)</th>
<th>εb (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>75</td>
<td>4.0</td>
<td>1.0</td>
<td>4.1</td>
<td>672 ± 60</td>
<td>4.1 ± 0.7</td>
<td>17.6 ± 2.6</td>
</tr>
<tr>
<td>0</td>
<td>225</td>
<td>2.2</td>
<td>1.7</td>
<td>3.6</td>
<td>616 ± 44</td>
<td>4.9 ± 1.0</td>
<td>12.5 ± 2.7</td>
</tr>
<tr>
<td>5</td>
<td>75</td>
<td>3.5</td>
<td>1.2</td>
<td>4.2</td>
<td>644 ± 32</td>
<td>4.0 ± 0.1</td>
<td>12.6 ± 1.5</td>
</tr>
<tr>
<td>5</td>
<td>225</td>
<td>2.4</td>
<td>1.3</td>
<td>3.0</td>
<td>644 ± 29</td>
<td>4.6 ± 0.5</td>
<td>12.4 ± 1.3</td>
</tr>
<tr>
<td>10</td>
<td>75</td>
<td>4.4</td>
<td>1.5</td>
<td>6.6</td>
<td>737 ± 35</td>
<td>4.6 ± 0.4</td>
<td>12.1 ± 1.1</td>
</tr>
<tr>
<td>10</td>
<td>225</td>
<td>2.5</td>
<td>1.4</td>
<td>3.5</td>
<td>698 ± 31</td>
<td>4.9 ± 0.4</td>
<td>11.2 ± 0.8</td>
</tr>
<tr>
<td>15</td>
<td>75</td>
<td>4.1</td>
<td>1.3</td>
<td>5.4</td>
<td>608 ± 44</td>
<td>4.4 ± 0.7</td>
<td>11.9 ± 1.7</td>
</tr>
<tr>
<td>15</td>
<td>225</td>
<td>2.0</td>
<td>1.8</td>
<td>3.5</td>
<td>510 ± 37</td>
<td>4.4 ± 0.3</td>
<td>10.3 ± 0.9</td>
</tr>
<tr>
<td>20</td>
<td>75</td>
<td>3.5</td>
<td>1.2</td>
<td>4.1</td>
<td>581 ± 26</td>
<td>4.5 ± 0.5</td>
<td>11.8 ± 1.4</td>
</tr>
<tr>
<td>20</td>
<td>225</td>
<td>3.1</td>
<td>1.5</td>
<td>4.7</td>
<td>355 ± 24</td>
<td>4.0 ± 0.4</td>
<td>9.4 ± 1.2</td>
</tr>
<tr>
<td>25</td>
<td>75</td>
<td>2.9</td>
<td>1.7</td>
<td>4.8</td>
<td>389 ± 27</td>
<td>3.6 ± 0.4</td>
<td>11.3 ± 1.7</td>
</tr>
<tr>
<td>25</td>
<td>225</td>
<td>3.1</td>
<td>1.2</td>
<td>3.8</td>
<td>380 ± 28</td>
<td>4.1 ± 0.4</td>
<td>12.5 ± 2.3</td>
</tr>
</tbody>
</table>

1 m/min.

as indicated by their solution viscosities. There appeared to be a gradual reduction in tensile strength for the blends containing Polymers 8C and 9C with increasing LCP content, whereas a considerable reduction in tensile strength was observed immediately for blends containing Polymer 7C at a 5 wt% LCP content. This suggests that the gradual loss in tensile strength in the blends containing Polymers 8C or 9C, which were melt-extruded using a melting zone temperature 30°C lower than blends containing Polymer 7C, can be attributed
to the poor tensile strength of the LCP component rather than to molecular interchange. The fact that no enhancement in tensile modulus occurred for these blends containing Polymers 8C or 9C, which had mixtures of 6 and 12 methylene flexible spacer units, suggests that the coupling of such long flexible spacer units to an otherwise all-aromatic rod may prove detrimental to the overall mechanical properties of the resulting LCP.

Because the only enhancement in tensile modulus with respect to nylon-6,6 was accomplished using Polymer 7C, a higher molecular weight polymer having identical chemical composition, Polymer 10C, was synthesized. Blends containing Polymer 7C were prepared from solution and had no prior thermal treatment other than vacuum-drying. A DSC thermogram of the blends containing nylon-6,6 and Polymer 7C showed no appreciable change in the melting temperature of the LCP component relative to the pure LCP, and thus the blends were melt-extruded at 300°C. It was envisioned that the tensile moduli observed in blends containing Polymer 7C, which had an appreciably lower solution viscosity, could be reproduced or even improved using a higher molecular weight LCP, which might be more favorable to the formation of high tenacity fibers.

Polymer 10C was first compression-molded at 305°C, ground into a fine powder, tumble-mixed with nylon-6,6, compression-molded at 280°C for three minutes, and then ground into a fine powder before use. A DSC thermogram of the resulting blend showed only a melting transition at 264°C. The blend was subsequently melt-extruded at 275°C, 25°C lower than blends containing Polymer 7C.

The melt-extrusion of blends containing Polymer 10C and nylon-6,6 was also accompanied by gas evolution and die swell. It appears that an intimate level of mixing prior to extrusion seemed to enhance the rate of interchange
reactions between the blend components. Tensile properties for the cold and hot drawn fibers are summarized in Table 5.10. Due to the large deviation in diameter of these fibers (±1-10 μm.), the tensile strengths were inconsistent. Because a blend containing 25 wt% Polymer 10C showed a tensile strength comparable to pure nylon-6,6, the LCP did not appear to be detrimental to the formation of high strength fibers. A modest increase in tensile modulus was observed for the blends containing 20-25 wt% Polymer 10C.

Table 5.10. Tensile properties of various melt-blended fibers containing nylon-6,6 and Polymer 10C.

<table>
<thead>
<tr>
<th>LCP (%)</th>
<th>Pickup speed1</th>
<th>Cold Draw ratio (100°C)</th>
<th>Hot Draw ratio (215°C)</th>
<th>Total Draw</th>
<th>σb (MPa)</th>
<th>E (GPa)</th>
<th>eb (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>75</td>
<td>4.0</td>
<td>1.0</td>
<td>4.1</td>
<td>672 ± 60</td>
<td>4.1 ± 0.7</td>
<td>17.6 ± 2.6</td>
</tr>
<tr>
<td>0</td>
<td>225</td>
<td>2.2</td>
<td>1.7</td>
<td>3.6</td>
<td>616 ± 44</td>
<td>4.9 ± 1.0</td>
<td>12.5 ± 2.7</td>
</tr>
<tr>
<td>5</td>
<td>145</td>
<td>2.3</td>
<td>1.5</td>
<td>3.4</td>
<td>539 ± 93</td>
<td>4.7 ± 0.5</td>
<td>14.5 ± 2.3</td>
</tr>
<tr>
<td>10</td>
<td>70</td>
<td>2.6</td>
<td>1.5</td>
<td>3.7</td>
<td>444 ± 26</td>
<td>4.5 ± 0.3</td>
<td>10.3 ± 1.8</td>
</tr>
<tr>
<td>10</td>
<td>170</td>
<td>1.7</td>
<td>2.2</td>
<td>3.7</td>
<td>255 ± 34</td>
<td>3.5 ± 0.2</td>
<td>10.8 ± 1.2</td>
</tr>
<tr>
<td>15</td>
<td>70</td>
<td>2.5</td>
<td>1.3</td>
<td>3.3</td>
<td>359 ± 45</td>
<td>4.0 ± 0.4</td>
<td>11.9 ± 1.7</td>
</tr>
<tr>
<td>15</td>
<td>215</td>
<td>2.1</td>
<td>2.1</td>
<td>4.4</td>
<td>301 ± 37</td>
<td>4.9 ± 0.3</td>
<td>11.1 ± 1.8</td>
</tr>
<tr>
<td>20</td>
<td>70</td>
<td>1.9</td>
<td>2.0</td>
<td>3.5</td>
<td>521 ± 55</td>
<td>6.1 ± 0.8</td>
<td>13.2 ± 2.0</td>
</tr>
<tr>
<td>20</td>
<td>190</td>
<td>11.5</td>
<td>-</td>
<td>11.5</td>
<td>367 ± 73</td>
<td>5.1 ± 1.0</td>
<td>14.6 ± 5.3</td>
</tr>
<tr>
<td>25</td>
<td>70</td>
<td>6.0</td>
<td>-</td>
<td>6.0</td>
<td>291 ± 37</td>
<td>5.0 ± 0.5</td>
<td>12.1 ± 2.1</td>
</tr>
<tr>
<td>25</td>
<td>215</td>
<td>2.0</td>
<td>1.3</td>
<td>2.6</td>
<td>660 ± 45</td>
<td>6.3 ± 0.4</td>
<td>11.9 ± 1.4</td>
</tr>
</tbody>
</table>

1 m/min.

increase is what would be expected from the LC poly(ester-amide)s prepared in this study which have been shown previously to have tensile moduli from 7-9 GPa (polymers 7 and 8C). Because nylon-6,6/Polymer 10C blends were extruded at a significantly lower temperature than the blends containing Polymer 7C which had the same chemical composition, this is further evidence that the enhancement in modulus observed in the Polymer 7C/nylon-6,6 blends may be attributed to molecular interchange reactions.
Conclusions

Blends containing novel LC poly(ester-amide)s and nylon-6,6 were prepared using various melt-processing conditions. The effect of the TLCPs on the tensile properties of the blends was most evident for the cold and hot drawn fibers. Although all of the blends prepared exhibited a tensile strength lower than or equivalent to pure nylon-6,6, the tensile strength of the blends appeared to increase with increasing molecular weight of the LCP component. The tensile properties of the pure LCPs were appreciably lower than a related liquid crystal polyester prepared from terephthalic acid and 4,4'-dihydroxy-1,10-diphenyloxydecane\textsuperscript{2,3}. The low tensile properties of the pure LCPs may be attributed to the N-methylated amide units. Polyamides having alkyl-substituted amide linkages have shown a reduced tendency to crystallize due to frustrated chain packing and the loss of strong intermolecular hydrogen bonds\textsuperscript{55-58}. Blends containing nylon-6,6 and the LC poly(ester-amide)s prepared did not show an enhancement in tensile modulus with respect to nylon-6,6 when the LCP contained long 12-methylene flexible spacer units. A modest enhancement in tensile modulus was observed for the blends which contained nylon-6,6 and a LC poly(ester-amide) having a shorter 6-methylene flexible spacer unit, which were melt-extruded at temperatures at which extensive interchange reactions did not appear to take place. A significant enhancement in tensile modulus was observed for blends containing nylon-6,6 and a LC poly(ester-amide) having a 6-methylene spacer unit, which were melt-extruded at 300°C, a temperature at which extensive molecular interchange appeared to occur. Because the blends were melt-extruded on small scales, the processing conditions were not optimized and the conclusions should be considered tentative.
LCPs containing a long flexible spacer unit may reduce polymer melting transitions such that polymers containing otherwise rigid segments can form liquid crystalline domains below the temperature of polymer degradation. However, the decoupling of the rigid segments by flexible spacer units may compromise the inherent stiffness of the entire polymer chain and lead to a compromise in mechanical properties which is not observed in all-aromatic liquid crystalline polymers.

**Future Work**

Nylon-6,6/poly(ester-amide) blends which were melt-extruded at 300°C showed a significant improvement in tensile modulus relative to nylon-6,6. The enhancement in tensile modulus was attributed to molecular interchange reactions. The deficiency of the method was perhaps the use of long flexible spacer units. However, the flexible spacer unit may serve to decouple the rigid-rod segments leading to a polymer having an inherent stiffness much less than that of all-aromatic LCPs. The length of the flexible spacer unit cannot be reduced without generating polymers having melting transitions above the onset of polymer degradation.

A possible approach is to prepare oligomers from terephthaloylbis(4-oxybenzoyl chloride) and N,N'-dimethylalkylenediamines having very short flexible spacer units. Oligomers would be expected to have significantly lower melting temperatures and could be melt-processed at temperatures where the rate of molecular interchange could be controlled.

One disadvantage of the N-methylated poly(ester-amide)s is the corresponding loss of interchain hydrogen bonding. The use of N-methylated imino groups may result in a compromise in mechanical properties. An
alternative approach could involve the preparation of low molecular weight polymers from terephthaloylbis(4-oxybenzoic acid) and hexamethylene diamine. The resulting oligomers could then be melt-extruded with nylon-6,6 at temperatures where the rate of molecular interchange could be systematically investigated. By using such a method, it is envisioned that a copolymer could be prepared containing rigid-rod units within the nylon-6,6 phase.

A possible molecular reinforcing agent for nylon-6,6 should not be limited to liquid crystalline polymers. The tensile properties and the dimensional stability of nylon-6,6 might be improved by the high temperature heating of a rigid-rod polymer with nylon-6,6 where molecular interchange reactions occur. Although molecular interchange reactions are known to occur, very little detailed information exists on how these reactions can be controlled. The preparation of copolymers having controlled block lengths from molecular interchange reactions could yield new polymers having a combination of advantageous properties.

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