Study of Liquid-Crystalline Behaviour of Aliphatic-Aromatic Polyamides Derived from Castor Oil Based Dimer Acid by DSC

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ABSTRACT
Aliphatic-aromatic polyamide of castor oil based dimer acid (DA) with p-phenylenediamine (PPD) was characterized by differential scanning calorimetry. This polyamide exhibited interesting liquid-crystalline behavior which was quite unexpected looked at the structure of dimer acid moiety.

Key words: Dimer Acid, Aliphatic-Aromatic Polyamide, p-Phenylenediamine, Differential Scanning Calorimetry.

1. INTRODUCTION
Polyamides occupy an important place in the world of polymers because they offer excellent physical and chemical properties, thermal and oxidative stability, flame resistance, and superior mechanical and dielectric properties [1, 2]. Aromatic polyamides are thermally stable polymers and possess several high-performance properties, with an attractive combination of excellent chemical, physical, and mechanical properties [3]. The applications of aromatic polyamides are often hampered by problems in their fabrication. The basic problems are the rigidity of backbone and strong hydrogen bonding in wholly aromatic polyamides results in higher melting temperature (Tm), glass transition temperature (Tg) and limited or poor solubility in most of the organic solvents. The high crystallinity and high stiffness of polymer backbone leads to difficulties in processing of aromatic polyamides.

For overcome these problems a lot of efforts have been made to synthesize structurally modified aromatic polyamides having improved solubility and processability with retention of their high thermal stability [4-17]. The introduction of flexible groups pendant to an aromatic backbone [18-21], the use of Non-symmetrical monomers with meta and ortho-linkages [22-29], synthesis of polyamides with noncoplanar units in the polymer chains [33], introduction of bulky side groups into the polymer chains, [30-33], Bridging groups like isopropylidene, hexafluoro-isopropylidene, oxygen, carbonyl and sulphonyl. Semi rigid cyclo aliphatic spacers [34] resulted in a number of modified polyamides.

New diamines bearing substituted 1,2,4-triazole and quinoxaline moieties with OCH₃ or Br units were successfully synthesized and used for preparation of novel polyamides (PAs) by direct polycondensation with aromatic and aliphatic dicarboxylic acids [35]. A series of HDA-based Nylon 636/Nylon 66 copolymers are synthesized by in situ polymerization [36]. The ecological impacts of using conventional flame retardants, thereby signifying the necessity to use eco-friendly agents [37]. The exponential growth of polymer applications has led to the development of new techniques for polymer characterization. However, no single technique has proved more useful than thermal analysis. To select the proper conditions of processing and usage of polymeric materials, it is necessary to know the specific behavior of polymers in crystalline, glassy and rubber-like states and regularities governing their transition from on state of aggregation into another [38]. In this regard, differential scanning calorimetry (DSC) is a widely used technique. Among its various potential applications, the study of transition peaks such as melting peaks is quite common.

Liquid crystalline polymers (LCP) are a subject of scientific interest because of their molecular self-orientation ability applicable for high performance materials. If the thermotropics LCP have double
bonds in the main chain, they can produce two-dimensional reinforced polymeric material through cross linking reaction [39]. The amide linkages have been rarely used to synthesize thermo tropic liquid crystalline polymers because the high degree of H-bonding associated with these groups increases intermolecular attraction to the point where the melting transition could be high enough and thermo tropic mesomorphism usually could not occur [40-42].

Nowadays, agro-based renewable materials are the subject of a growing number of academic and industrial research projects. Because of diminishing fossil resources combined with the global and increasing environmental concern of petroleum-based plastics [43]. Renewable resources such as vegetable oils are ideal alternatives to provide base chemicals for various materials as they are abundant throughout the world and contain several reactive chemical sites such as double bonds, allylic carbons, ester groups, and the alpha-carbons of the ester groups, all of which can be used for polymerization [44-49].

Castor oil contains Dimer acids (DA) are obtained by the polymerization of C18-acids such as oleic and linoleic acids. These environmentally friendly, commercially available products are cheap to produce, liquid at room temperature, non crystalline, biodegradable, and organo-soluble.

Dimer acid, a 36-carbon dicarboxylic acid (figure 1), possesses a cyclohexene ring from which four aliphatic chains originates, two of which terminate into carboxylic acid groups.

**Figure 1:** Chemical Structure of Dimer acid

Dimer acid can be a very good precursor for LCP in conjunction with aromatic amines. Dimer acid has been exploited for synthesis of many commercial polyamides with aliphatic diamines [50]. Nevertheless, to the best of our knowledge we reported the synthesis of dimer acid based polyamides incorporating aromatic diamines for the first time [51].

Characterization of these polyamides by IR, viscosity and solid conductance measurements revealed unusual properties for these polymers. This led us to correlate their behavior, which is incompatible for individual polymer chains, to supramolecular assembly. In the present communication, differential scanning calorimetric study of poly (p-phenylenediameramide) [PPD] is reported.

2. EXPERIMENTAL

2.1 Materials

The preparation of aromatic-aliphatic polyamide, poly (p-phenylenedimeraimide) [PPD] from dimer acid and p-phenylenediamines was reported in our earlier communication [51].

2.2 Measurement

Thermal analysis of PPD was done on a Ku point 2100 differential scanning calorimeter under inert atmosphere at a heating rate of 10 °C min⁻¹ in 20 to 600 °C range.

3. RESULTS AND DISCUSSION

Usually wholly aromatic polyamides are prepared by condensation of diacid and diamines in presence of triphenyl phosphate (TTP) and pyridine in DMF solution. However, due to solubility of PPD in DMF and pyridine it could not be precipitated from the reaction mixture. Polyamide could only be separated when DMF and pyridine were not taken in the reaction mixture. However, once the polyamide was separated from the reaction mixture and dried under vaccum, it could not be dissolved simply on mixing the solid product with the solvent. It was necessary of soften the sample by heating up to 80 °C and then mixing the solvent for dissolution. The softened sample formed fibres on stretching. The concentrated solution also produced fibrous structures on evaporation of solvent during transfer from one vessel to another. This indicated that the polyamide had semi crystalline structure in which the stacks of crystalline lamellae were alterned by amorphous layers (Fig.2).

**Figure 2:** Schematic presentation of structure of PPD
Different chains became mobile upon heating the polyamide sample. This facilitated their dissolution. The parallel alignment of different chains seems to be somewhat unusual for dimer acid unit with several methylene groups and a cyclohexene ring with two side chains because of the possibility of several conformations. Though, polyamides were expected to be insulating materials, they showed solid conductance in $10^{-10}$-$10^{-13}$ S cm$^{-1}$ range [51].

The elemental analysis data for these polyamides revealed a high water content, 4.3 water molecules per repeat unit in case of PPD. Upon heating at 80 °C in air oven for four hours the solid conductance increased from $7.8\times10^{-12}$ to $7.0 \times 10^{-9}$ S cm$^{-1}$. On heating PPD above 320 °C in air, 42.5% carbonaceous residue (char yield) was obtained. The aromatic unit contributed 11.7% only to the total weight of the repeat unit of the polyamide. This indicated that aliphatic segment also provided carbon to the char.

Thermotropic Liquid Crystal Polymers behaviour explained in details [52]. The DSC thermo gram of polyamide, PPD (Fig. 3) showed its LC behavior as three endothermic peaks were obtained. The glass transition temperature ($T_g$) was marked by a slight deflection in the baseline at 80 °C. It is well known that the magnitude of associated changes (e.g., heat capacity and expansion coefficient) occurring at $T_g$ decreases with decreasing amorphous content, consequently, $T_g$ is sometimes difficult to detect in highly crystalline polymers. In the present case, a high $T_g$ in comparison to nylon-6, probably indicated sufficient crystalline nature of this polyamide.

Although prediction of $T_g$ from structural information is difficult, a rough rule of thumb is available for those semi crystalline polymers which melt at $T_m$. Experimental data indicate that for a wide variety of polymers, the ratio $T_g/T_m$ generally falls between 0.50 and 0.75, if the temperature is compared in Kelvin [53]. For PPD upon taking $T_g$ as 80 °C (353 °K) and $T_m$ as 378.86 °C (651.86 °K) the ratio $T_g/T_m$ was calculated to be 0.54 well within the range. Shukla and Dixit [54] used the empirical relationship $T_g=1/2 \ T_m$ for symmetrical polymers and $T_g=2/3 \ T_m$ for unsymmetrical polymer, for the calculation of $T_g$ taking the melting point in °C. If this relationship is used to calculate the $T_g$ for PPD assymmetrical polymer, in the present study the value comes out to be 72.44 °C and a value as 252.6 °C is considered to an unsymmetrical polymer. A little inflection or the deviation from the baseline was observable at 280 °C. This second $T_g$ may be accounted for the high energy requirement for free rotation around bond axis for the aromatic units originating from the aromatic diamines moiety.

The side chains of Dimer acid may contribute towards the free volume resulting in reduction in steric hindrance between adjacent polymer chains. This may be qualitatively attributed to the fact for the very long alkyl chains possibility of close packing exists. This conclusion finds support from the DSC studies by Cameron and Sherrington [55] for highly porous elastomeric materials prepared.
from styrene, divinyl benzene and varying amounts of 2-ethylene-hexylacrylate or corresponding methacrylate. They concluded that Tg decrease as the chain length increase beyond a certain value, crystallization of side chain occurs and Tg start to increase once more. Branching of the alcohol chain restricts the rotation of the side chain bonds so Tg is raised.

Three endothermic peaks were observable in this polyamide, and in the case of a polymer which melts with multiple peaks, the melting point is generally reported as the temperature maxima of the final peak. The first and second endotherms at 144.88 °C and 197.07 °C respectively may be attributed to the phase transition because of the low energy requirements. The first endotherm corresponds to the crystal to smectic phase transition, the second endotherm, smectic to nematic phase transition, and the third endotherm highlights the phase transition from nematic to isotropization. Thus, a liquid crystalline nature may be inferred for this polyamide. The melting endotherm is followed by a series of exotherms due to cross linking and cyclization. However, there is no endotherm associated with covalent bond fission up to 500 °C indicating that this polyamide exhibited high resistance against degradation.

4. CONCLUSIONS
The polyamide poly(p-phenylene dimer amide ) [PPD] seems to possess thermal properties very appropriate for its use as a fibre. The characterization of PPD by DSC analysis indicated its semi-crystalline (liquid crystalline) nature. The polar amide groups contribute towards the strong secondary forces necessary for a fibre. Its Tm above 300 °C would make it useful for maintaining its physical integrity even on use at elevated temperatures. The polyamide is soluble in organic solvents which may facilitate its processing but once it is obtained in dry state it would not easily dissolve unless heated up to Tm, thus rendering it somewhat solvent resistant. Further, low but significant solid conductance value suggested its antistatic behavior.

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5. REFERENCES

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*Bibliographical Sketch

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