

## Synthesis of polyamide-imide and its mechanism of imidization

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### Abstract

A series of novel polyamide-imide acid (PAA) using two monomers of the trimellitic anhydride chloride (TMAc) and m-phenylenediamine (m-PDA) have been successfully prepared by solution polycondensation with a special catalyst. The polyamide-imide acid is imidized into polyamide-imide (PAI) by two methods of chemical imidization and thermal imidization. The resulting polymers are well soluble in some polar organic solvents such as Dimethylacetamide (DMAC), *N*-methylpyrrolidone (NMP), Dimethylsulfoxide (DMSO) and Dimethyl Formamide (DMF) on account of the presence of amide linkages in the main chains of PAI. Solid content and monomer ratio are studied by designing different polymeric formula to optimize the polymerization process. Then, thermal imidization of the PAA resin is performed to research the mechanism of imidization, obtaining the intrinsic viscosity and the degree of imidization under the different imidization conditions.

**Keywords:** Polyamide-imide, Synthesis, Imidization

### Introduction

By reason of their remarkable thermal stability, strength, modulus, dimensional stability and other excellent physical properties, linear aromatic polyimides are well known as a class of superior engineering materials. However, suffering handling process and troublesome properties have been become major problems due to high thermal deformation temperature, high melting temperature and poor solubility. To improve the drawback of the high performance materials, a long-term target has been pursued to balance thermo-mechanical properties and processing performance. Introducing amide linkages into the polyimide main chains can offer a superior material called polyamide-imide (PAI) which is given a new concept of ultra polymer. This special polyimide comes to a compromise between thermal stability and processability. It is noteworthy that the physical properties of PAI maintain high levels under the high temperature compared to other high-performing engineering plastics such as PPS, PEEK, PES and PEI. Solubility under polar solvents and thermoplasticity endow PAI widespread application value and prospect in films, coatings, polymer blends and alloys and composites.

Various polymerization approaches of polyamide-imides have been carried out successfully, for instance, bulk polymerization, solution polymerization, interfacial polymerization. Advantages and disadvantages simultaneously exist for the aforementioned polycondensation methods. Nevertheless, solution polymerization as a typical synthetic method of aromatic polymers is characterized of

simplification of polymerization installations, stability of polymerization process.

In this paper, we prepare polyamide-imide acid (PAA) by solution polycondensation of trimellitic anhydride chloride (TMAc) and m-phenylenediamine (m-PDA), and then PAA is imidized into PAI by thermal imidization. Synthesis and imidization are deeply researched for construction of the relationships between the properties of PAA/PAI polymers and the conditions of thermal imidization. This polymer has excellent solubility in polar solvents and high glass transition temperature. It is expected to have potential as ultra polymer for fibers, films and molding compounds.

## **Results and Discussion**

A series of polyamide-imide acid (PAA) by solution polycondensation of trimellitic anhydride chloride (TMAc) and m-phenylenediamine (m-PDA) using DMAc as solvent are synthesized, and then PAA is separated into powder from the PAA/DMAc solution. PAA powder is imidized into polyamide-imide (PAI) by thermal imidization under the given times and temperatures.

Except the influence of reaction temperature, solid content, the kind and ratio of monomer, polymerization process and sequential structure on the PAA/PAI performances such as intrinsic viscosity and glass transition temperature, imidization as a remarkable factor greatly affects the properties of PAI depending on the transformation of amic acid into imide and the chain extension resulting from unique amino/anhydride recombination.

In our work, the polymerization temperature is significant effect on the polymerization process with respect to the molecular weight of polymer. The higher the reaction temperature is, the larger the intrinsic viscosity is. However, the controllability and stability of polycondensation are poor with the increasing polymerization temperature. In fact, we find that the reaction temperature below 5°C enables the controllability and stability of polymerization to be optimized. Intrinsic viscosity decreases first and then increases with the change of solid content from 10% to 30%. When the solid content is over 30%, the failure of polymerization comes up, which results in the aggregation of polymers. In addition, the sequential structure of polymer chain called the structures of head-head, tail-tail and head-tail suffers the effect of the polymerization technique, and the sequential structures gives rise to various different properties of polymers.

The degree of imidization and the efficiency of imidization are significant consideration for optimizing the performance of PAI polymer. The different polymer structure and polymerization process generates diverse imidization conditions. Fourier transformation infrared spectrum (FT-IR) is an effective approach to characterize the mechanism of the imidization. The relationships of imidization temperature and the ratio of  $I_{1380}$  and  $I_{1500}$  at a certain temperature are shown in Figure 1. With the increasing imidization temperature, the  $I_{1380}/I_{1500}$  gradually increases. When the temperature increases to 350°C, the  $I_{1380}/I_{1500}$  reaches to a maximum value. And then with the increase of temperature continually, the  $I_{1380}/I_{1500}$  keeps stable. It is reasonable that the imidization temperature at 350°C is defined as complete imidization temperature. Figure 2 shows the relationship of imidization time and the  $I_{1380}/I_{1500}$ . Obviously, the degree of imidization reaches completion under the 30 min of imidization time.

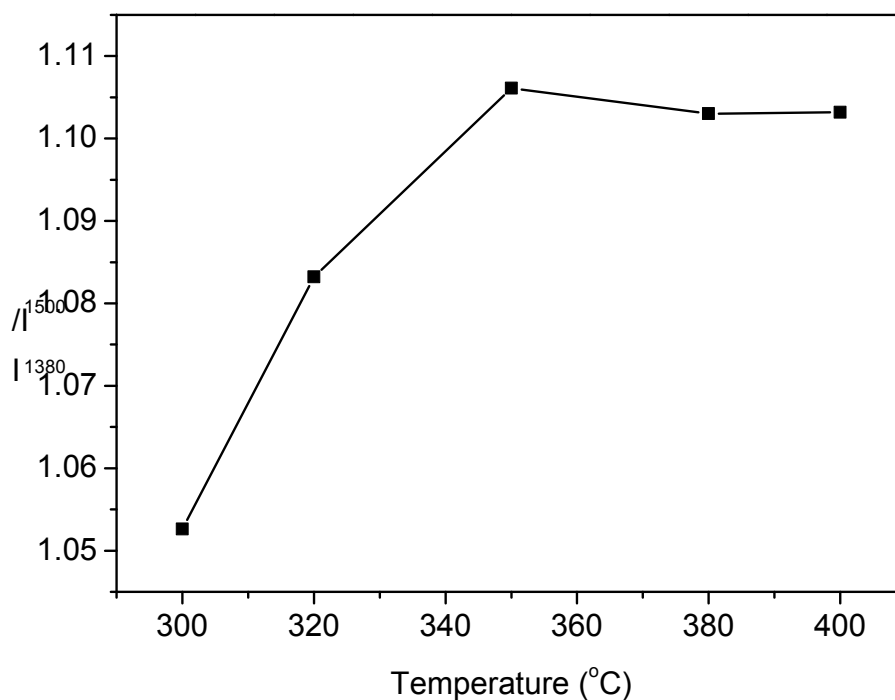


Figure 1. Temperature dependence of  $I_{1380}/I_{1500}$  obtained from FT-IR for PAI polymer.

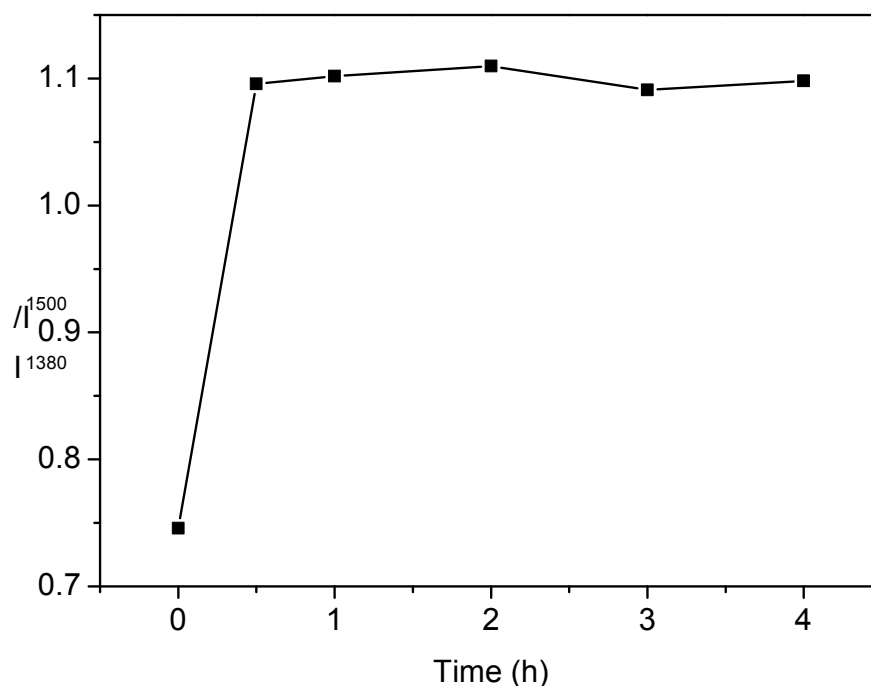


Figure 2. Time dependence of  $I_{1380}/I_{1500}$  obtained from FT-IR for PAI polymer.

The complex rule of the intrinsic viscosity is because of the influence on the imidization and chain extension simultaneously. Figure 3 shows the time dependence of intrinsic viscosity obtained from ubbelohde viscometer for PAI polymer. Below 190°C of imidization temperature, the intrinsic viscosity elevates with the increased imidization time. When the imidization time is over 4 h, the intrinsic viscosity arrives at a platform. The tendency is influenced by the evaporation of trace moisture and solvent and the enhanced chain extension of amino/anhydride recombination. When the imidization temperature increases to 220—280°C. Within the 2 h of imidization time, the intrinsic

viscosity of PAI enhances rapidly. After imidization time exceeds 2 h, the intrinsic viscosity maintains the same level. Further, there is no obvious difference about the intrinsic viscosity under the three imidization temperature of 220, 250 and 280°C, indicating that the chain extension of amino/anhydride recombination fails to strengthen with the elevated temperature from 220 to 280°C. It is attributed to the invariable rigidity of the polymer chain in the rising process of temperature causing the increase of the glass transition temperature of polymer. The imidization temperature at 310°C results in the increase of intrinsic viscosity rapidly. The imidization time fails to exceed 1.5 h at the imidization temperature of 340°C because of the insolubility of the PAI.

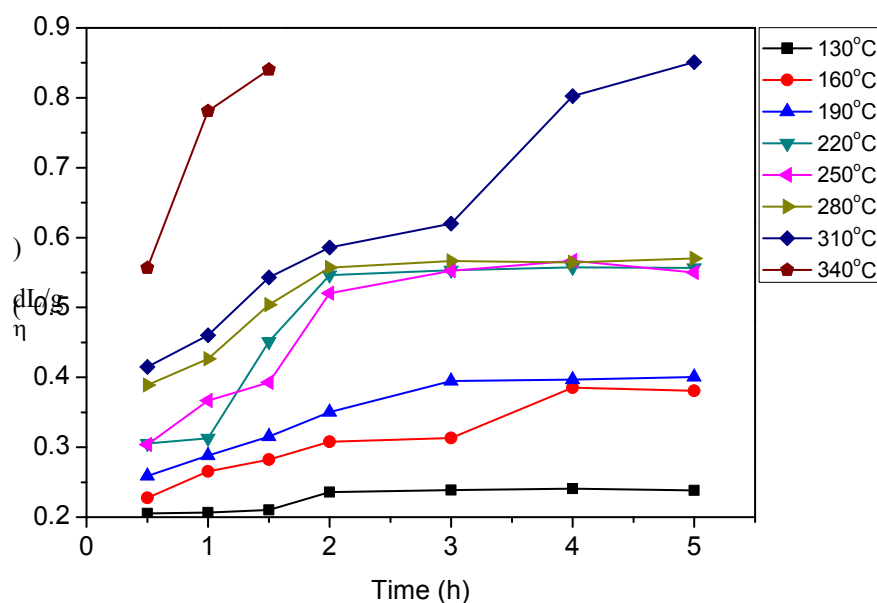


Figure 3. Time dependence of intrinsic viscosity obtained from ubbelohde viscometer for PAI polymer.

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