

# Synthesis, Characterization and Thermal Study of Polyimides Derived from Polystyrene

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## ABSTRACT

A novel polyimides of polystyrene with high thermal stability were prepared by the reaction of aminated polystyrene with Benzophenone tetracarboxylic dianhydride. The aminated polystyrene were prepared from the nitration of polystyrene followed by chemical reduction of its nitro groups. Infrared (FT-IR) spectra and thermogravimetric analysis (TGA) were used to characterize polymers . The prepared polymer exhibit good thermal and thermooxidative stability at polymer decomposition temperature greater than 550°C in air atmosphere . Another attractive feature is their high char yields 75% at 650°C in air atmosphere.

## Introduction

Polyimides are considered to be among the most important super-engineering materials because of their extraordinary dielectric and superior mechanical properties at elevated temperature due to their thermal stability (1-9). Recently much efforts has been devoted to developing high performance polyimide materials with excellent thermomechanical properties, and high optical transparency (10-12). In particular its excellent insulating properties ,together with radiation resistance, and fire resistance have made polyimide one of the favorite choice for applications in cable insulation ,electrical component seal assemblies, and component lead in nuclear power plants, military aircraft and space shuttles(13,14). Other applications include various electronic components such as flexible circuit. Semiconductor pads, microprocessor chip carries, coil insulation, magnetic wire insulating and solar arrays (15).

Polyimides as a thermally stable polymers have been received extensive interest in recent decades because of increasing demands for high temperature polymers as replacement metals or ceramics in automotive aerospace and microelectronic industries

(16). In general, it is difficult to process polyimides because of their poor solubility in a common organic solvents and high melting temperature in fully imidized form therefore, the processing is usually carried out with polyamic acid intermediate which can be converted into polyimide via vigorous thermal treatment or chemical treatment. The concept of this research is to incorporating the polystyrene into the backbone of aromatic polyimides to improve the toughness and increase the thermal stability so we started by nitration of polystyrene, then reduction of nitro group to poly(4-amino styrene), followed by the reaction of the resulting amino polymer with carboxylic dianhydride to prepare polystyrene polyamic acid then by cyclization process can afforded polyimides of polystyrene.

## Materials and Methods

Polystyrene was purchased from commercial sources. benzophenone tetracarboxylic dianhydride ,nitric acid (94%), tin (sn) 99% powder were obtained from Fluka ,N-methyl pyrrolidone purchase from BDH.

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## Measurements

The FTIR Spectra which was used to study the chemical structure of the polymer matrix were performed with Shemadzu FT-IR spectrometer model 8400s.

Thermogravimetric analysis (TGA) was recorded on (Rheometric A, Scientific, U.K) from ambient temperature to 700°C with heating rate of 10 °C/min.

## Preparation of Poly (p-nitrostyrene) (17):

Polystyrene was purified by dissolving in chloroform then precipitated into methanol, filtered and dried. 10gm of purified polystyrene powdered was added slowly in a portion wise to a 60ml of chilled concentrated nitric acid (96%) in a 250ml of 3-neck round bottom flask. The initial temperature during addition of polystyrene was kept below 5°C. The mixture was vigorously stirred by means of a magnetic stirrer, and the time of addition was limited 10-15 minutes.

First polymer turned black, then orange, when mixture become homogeneous, The temperature raised and heating continued for 1hour at 50 °C, at the end of the reaction , reddish yellow colored viscous liquid was obtained , it was poured into ice-cold water and stirred ,after sometime a yellow colored solid precipitate was obtained which was thoroughly washed several times with warm water and 10% NaHCO<sub>3</sub> till it was free from acid . The sample was then dried in vacuum oven at 60 °C for 12 hours. A sample has been characterized by FTIR.

## Preparation of poly (4-aminostyrene) (18):

10 g of poly(4-nitrostyrene) was added in 250 ml three neck round flask, and 60 ml of 37% HCl , and 50 ml of absolute ethanol , then 40 g of granular tin(Sn) was added and the mixture reflux for 9 h. The solid polystyrene amine hydrochloride was collected and washed with water, then the polystyrene amine hydrochloride was heated with 100 ml of 10% sodium hydroxide . The resulting free base was collected and washed with water.

The crude product (6.5 g ) give 65 % yield of pure poly(4-amino styrene). The prepared polymer was identified through FT-IR spectroscopy.

## Preparation the polyimide of polystyrene:

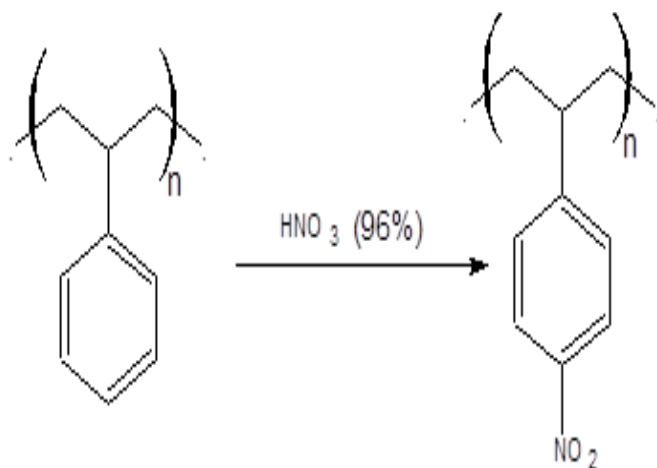
5g of poly (4-aminostyrene) was added to 25ml of N-methyl pyrrolidone(NMP) in a three-necked round bottom flask under nitrogen atmosphere and stirred for 2 hour until complete dissolution .Next a 5g of benzophenone tetra carboxylic dianhydride was dissolved in 15 ml of NMP then added to the solution of poly(4-amino styrene) in NMP solvent .The polycondensation reaction took place in NMP under hydrous conditions and nitrogen atmosphere. The resulting viscous solution of polyamic acid was stirred at room temperature for 24 hour, then it was heated at 150 °C for 3 hour for cyclization to polyimide structure .The water resulting from cyclization process was eliminated with a slow stream of nitrogen gas.

## Results and Discussion

### Nitration of polystyrene:

The nitration of polystyrene with concentrated nitric acid can be studied from the mechanism of the formation of nitronium ion which responsible for aromatic nitration as postulated by Ingold .

Nitration of polystyrene results in monomer disubstituted product depending on the conditions of the nitration experiment, but the nitration in o-position is slow and does not occur in this reaction due to steric hindrance.



#### FTIR-Spectrum of poly(4- nitrostyrene):

The chemical structure of poly(4- nitro styrene) was analyzed by FT-IR analysis in Fig(1) which confirmed the nitration of polystyrene as shown in fig. 1, the vibration band at  $3107\text{cm}^{-1}$  attributed for aromatic C-H stretching ,the band at  $2928,2854\text{ cm}^{-1}$  for aliphatic C-H stretching.  $1597, 1518\text{ cm}^{-1}$  for asymmetric (ArNO<sub>2</sub>) N=O stretching,  $1390$  for symmetric stretching N=O,  $1329\text{ cm}^{-1}$  for C—N stretching.

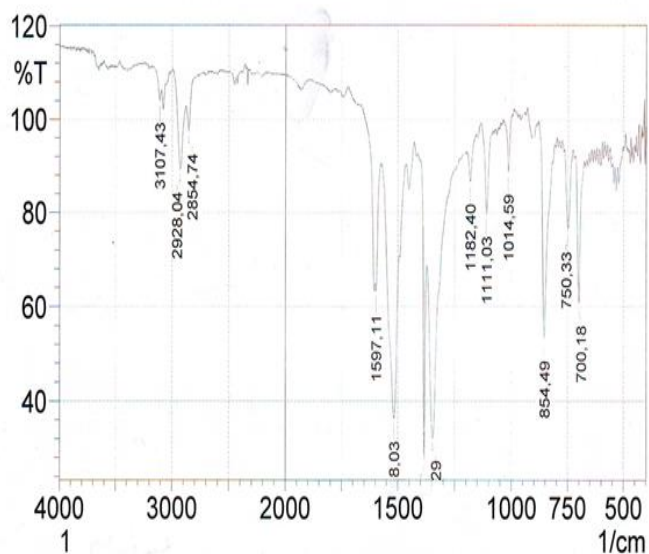
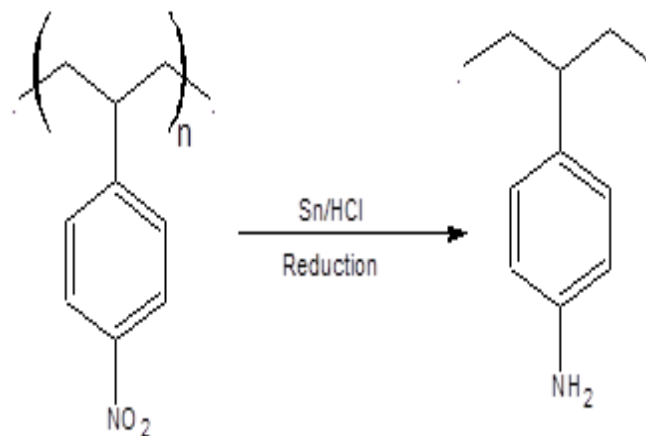


Figure (1) :FTIR Spectrum of poly(4- nitro styrene)

#### Amination of poly(4-nitrostyrene):

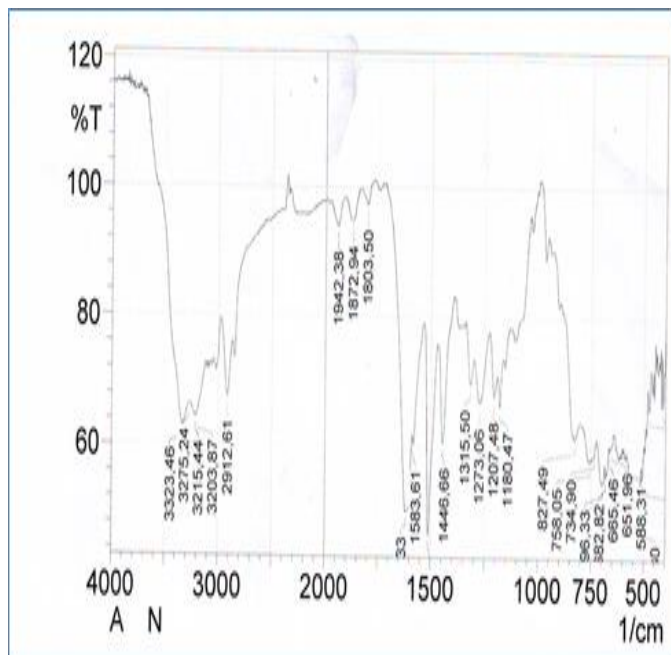
The second step was polystyrene nitro reduction by tin metals ,the nitro reduction of polynitrostyrene are synthetically important compounds acts as precursors to the synthesis of many interesting molecule and can be readily synthesized from polynitro styrene compound via reduction methods. The tin powder in concentrated HCl in ethanol it gives a yield of 67% .This process has been considered as effective method for the synthesis of polyamino styrene. However notable of disadvantages to these methods include high reaction temperatures and relatively long reaction times.



#### FTIR-Spectrum of poly(4- aminostyrene)

The polyaminostyrene was analyzed by FT-IR in Fig (2) ,there are two bands, the asymmetrical N-H stretch and symmetrical N-H stretch, located at  $3323, 3215\text{ cm}^{-1}$

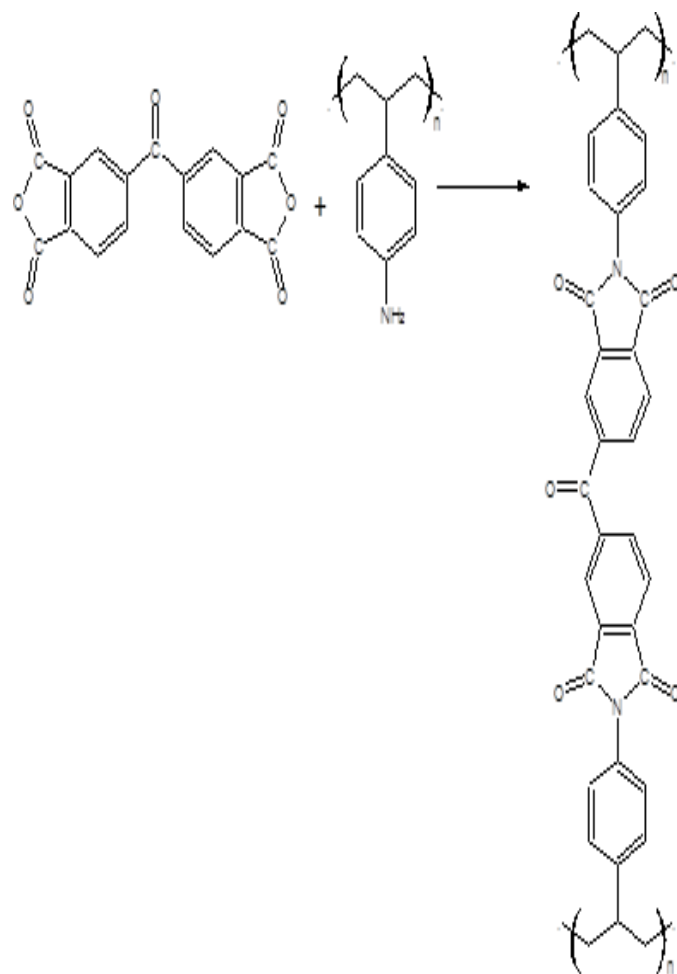
The N-H bending vibration for primary amines observed in the region  $1618, 1583\text{ cm}^{-1}$ . The C-N stretching vibration for aromatic amines is strong and in the region  $1315, 1273\text{ cm}^{-1}$ .



Figure(2):FTIR Spectrum of poly(4- aminostyrene)

### Reaction of poly(4-aminostyrene) with Benzophenone tetra carboxylic acid dianhydride:

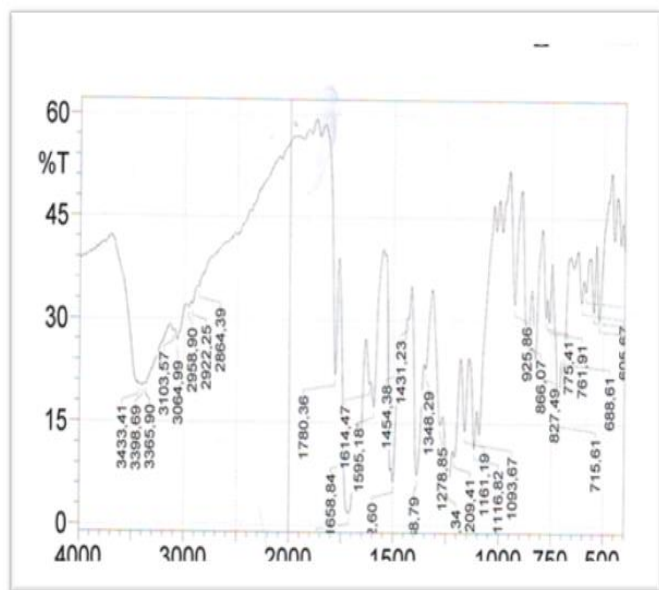
While the polyimides of polystyrene was prepared by the two step methods starting from reaction of polyamino styrene with Benzophenone tetra carboxylic acid dianhydrides in which first step was the formation of polyamic acid through ring opening poly addition reaction ,the polymerization proceeded homogeneously through out the reaction and afforded highly viscous polymer solution .The second imidization step was carried out via chemical cyclodehydration of polyamic acid as in scheme1 below .The formation of polyimide polystyrene was confirmed by means of FT-IR spectroscopy and TGA analysis .



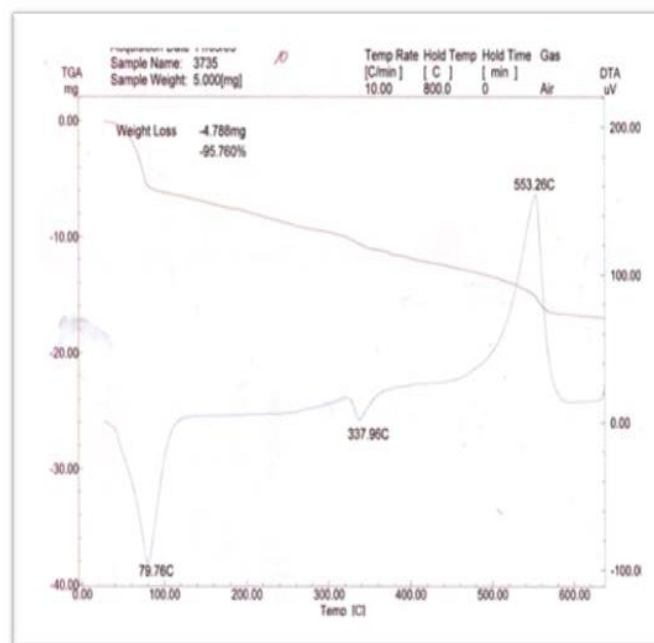
Scheme1:Reaction of Benzopenone tetracarboxylic dianhydride with poly(4-aminostyrene)

### FTIR Spectrum of polyimide polystyrene:

The FT-IR spectra for polyimides polystyrene as shown in Fig (3) was analyzed and showed that the absorbtion bands at  $1780\text{cm}^{-1}$  and  $1710\text{cm}^{-1}$  is due to asymmetric and symmetric stretching of C=O in five member ring imide ring indicates the imide ring remained intact in the polymerization , the imide group is also confirmed from the bands observed at  $1454(\text{Ar-N stretch})$ ,  $1388(\text{C-N stretch})$ ,  $1116\text{cm}^{-1}$  and  $775\text{cm}^{-1}$  .



Figure(3): FTIR Spectrum of polyimides/polystyrene



Figure(4): TGA thermogram of cured polyimides polystyrene

### Thermogravimetric Analysis

The thermal stability of new polyimides for polystyrene was evaluated by thermogravimetric. The presence of water was also evidence in TGA curve (Fig 4) which showed 5wt % weight losses in the range of 79 °C, assigned both to the loss of crystallization water to 100 °C, and coordination water (150-200 °C) removal. The thermal behavior of the polyimide was evaluated by thermogravimetric analysis. The polymers did not show significant weight loss below 300 °C, they began to decompose in the range of 300-550 °C and showed 5% weight loss in the range of 550-560 °C, one can assume that degradation process could begin in aliphatic segment of the back bone and then propagates to the entire structure, no significant weight loss was observed up to 300 °C.

### Conclusion

A novel polyimides were successfully prepared by nitration of polystyrene followed by reduction of nitro groups converting it to aminated polystyrene, the reaction of aminated polystyrene with benzophenone tetracarboxylic dianhydride get a polyimides which exhibit a good thermal and thermooxidative stability with high char yield in air atmosphere.

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## تحضير وتشخيص ودراسة الثباتية الحرارية لبوليمر البوليئيميد المشتق من البولي ستايرين

عبد السلام عبد الحسين شياح

### الخلاصة

تم تحضير بوليمر جديد ومستقر حرارياً من نوع البوليئيميد بولي ستايرين وذلك من خلال نترنة البولي ستايرين ثم أختزال المجاميع النيتروجينية الى مركباتها الامينية وتليها عملية تفاعل البولي امينوستايرين مع البنزوفينون تتراكاربوكسيلك أسيد داي انهيدرايد لتحضير البولي أيميدات لبوليمر البولي ستايرين. تم تشخيص هذه البوليمرات بجهاز ال (FT-IR) والتي أكدت صحة هذه المركبات الكيميائية المحضرة وكذلك فحصت بجهاز التحليل الوزني الذي أثبت الاستقرارية الحرارية لها . فهي تمتلك استقرار حراري أعلى من  $500\text{ C}^{\circ}$  في الهواء وهناك خاصية مميزة وهي أنها تعطي تقحم أعلى من 75% في درجة حرارة  $680\text{ C}^{\circ}$  في جو من الاوكسجين .