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SYNTHESIS AND THERMAL BEHAVIOUR OF SILICON CONTAINING POLY(ESTER IMIDE)S

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A series of silicon containing poly(ester imide)s [PEIs] were synthesized using novel vinyl silane diester anhydride (VSEA) and various aromatic and aliphatic dimines by two-step process includes ring-opening polyaddition reaction to form poly(amic acid) and thermal cyclo-dehydration process to obtain poly(ester imide)s. VSEA was synthesized by using dichloro methylvinylsilane and trimellitic anhydride in the presence of K_2CO_3 by nucleophilic substitution reaction. The PEIs were characterized by FTIR spectroscopy. The thermal properties of PEIs were investigated by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) methods. The prepared PEIs showed glass transition temperatures in the range of 320–350°C and their 5% mass loss was recorded in the temperature range of 500–520°C in nitrogen atmosphere. These had char yield in the range of 45–55% at 800°C.

Keywords: *aromatic diamine, cyclo-dehydration, poly(ester imide), thermal stability, vinyl silane diester anhydride VSEA*

Introduction

Polyimides are one of the most important classes of high performance polymers because of their outstanding thermal stability, resistance to chemicals, good mechanical and electrical properties. Due to these properties they have been widely used in aerospace, microelectronic, aviation, defence and separation industries [1–9]. However, they also have some disadvantages such as high water absorption, high dielectric constant, low contact angle and low optical properties. To overcome these disadvantages many attempts have been made by incorporating different moieties like fluorine, silicon and bulky side groups, etc. [9–19].

Among them, considerable attention has been devoted for the synthesis of silicon containing polyimides, which are well known for their low dielectric constant, low water absorption, good flame resistance and superior electrical properties [19–22]. On the other hand the incorporation of the ester groups into the macromolecular chain generally leads to improved thermoplasticity.

In this article, we have reported the synthesis and characterization of silicon containing poly(ester imide)s. A new vinyl silane diester anhydride (VSEA) was synthesized by using dichloro methylvinylsilane and trimellitic anhydride in the presence of K_2CO_3. VSEA was characterized by FTIR, ^{1}H NMR spectroscopy and elemental analysis methods. Poly(ester imide)s were synthesized using the above dianhydride and various aromatic diamines by two-step process. The spectral and thermal properties of PEIs are also discussed.

Experimental

Materials

Dichloro methylvinylsilane (from Aldrich, 99%) was used as received. Trimelletic anhydride was recrystallized from acetic anhydride. Diamino diphenyl methane (DDM), diamino diphenyl sulphone (DDS), oxydianiline (ODA) and *bis*(amino phenoxy) phenyl sulphone (BAPP) were recrystallized from ethanol before use. N,N-dimethylacetamide (DMAc) was purified by distillation under reduced pressure over phosphorous pentoxide and stored over 4 Å molecular sieves.

Synthesis of vinyl silane diester anhydride (VSEA)

In a typical reaction, trimellitic anhydride (0.02 mol), dichloro methylvinylsilane (0.01 mol) were dissolved in DMAc (50 mL) and toluene (20 mL) were taken in three-necked round bottom flask equipped with a stir bar, a Dean-Stark trap fitted with condenser and nitrogen inlet. Potassium carbonate (0.01 mol) was added and the reaction mixture was stirred at 130°C for 4 h followed by the removal of water azeotropically with toluene. After removing toluene by distillation under reduced pressure, the reaction mixture was refluxed under stirring for another 2 h. The reaction mixture was cooled to room temperature and then poured into 500 mL of dichloromethane resulted in a brown solid precipitate, which was collected under vacuum filtration. The crude product was recrystallized from acetic anhydride to afford off-white crystals. The reaction

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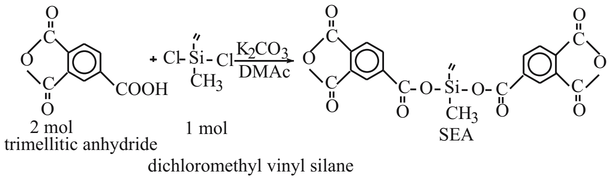


Scheme 1 Synthesis of monomer

procedure is shown in Scheme 1. Melting point (220°C) (by DSC); TLC: single point, F.W. ($C_{21}O_{10}H_{12}Si$): 452.30 g mol^{-1}, CHNS Anal.; Calcd. C (55.71), H (2.65); Found C (54.23), H (2.36).

Synthesis of poly(ester imide)s

Equimolar amounts of diamine and dianhydrides monomers were reacted in nitrogen atmosphere. A representative polymerization procedure is as follows.

A round-bottom flask equipped with a nitrogen inlet, a stir bar was charged with 0.01 mol of diamine (DDM) and 20 mL of DMAc. The solution was stirred until the diamine dissolved completely. 0.01 mol of dianhydride (VSEA) was added to this solution under effective stirring. The reaction mixture was stirred under magnetic stirring for 24 h at room temperature to obtain poly(amic acid) resin.

The poly(amic acid) resin was cast onto clean and dry glass plate by using a doctor blade. Then thermal imidization was carried out in an oven at 100°C for 1 h and at 150, 200, 250°C for 30 min at each temperature. The pale-yellow transparent films obtained by thermal imidization process. The other PEIs were prepared in similar manner from VSEA and other aromatic amines.

Measurements

The infrared spectra were recorded using Nicolet 750 Fourier transform infrared spectrophotometer. The inherent viscosities of the polymers were determined using Ostwald viscometer with 0.5 g dL DMAc solution at 30°C. Glass transition temperatures (T_g) were obtained using differential scanning calorimetry, using TA Instruments, USA (Model No. DSC 2910) at a heating rate of 10°C min^{-1} under N_2 atmosphere. The degradation temperatures (T_d) were recorded using Hi-Res TGA 2950 instrument at a heating rate of 20°C min^{-1} under N_2 atmosphere. Elemental analysis was made on a Vario-EL Elementar (CHNSO) Analyzer. The water uptake was determined by the change of the mass in vacuum dried film specimens before and after immersion in water at room temperature for 24 h.

Results and discussion

Characterization of VSEA

VSEA was synthesized by using dichloro methylvinylsilane and trimellitic anhydride in presence of potassium carbonate by nucleophilic substitution reaction. VSEA was characterized by FTIR spectroscopy, ^{1}H NMR spectroscopy.

Figure 1 shows the FTIR spectrum of VSEA. Absorption band at 1728 cm^{-1} was observed due to C=O anhydride stretching and C=C vinyl stretching was observed at 1581 cm^{-1}. The characteristic absorption band of Si–O stretching was observed at 1090 cm^{-1} and C–O–C interaction stretching was observed at 1260 cm^{-1}.

Figure 2 represents the ^{1}H NMR spectrum of VSEA. The vinyl protons were observed at δ= 4.5 ppm, methyl protons were observed at δ=2.7 ppm and multiplet due to aromatic protons was observed in the range of δ=6.5–7.4 ppm.

Imidization of poly(ester imide)s

The synthesis of PEIs was carried out via poly(amic acid) intermediate. The diamines were re-

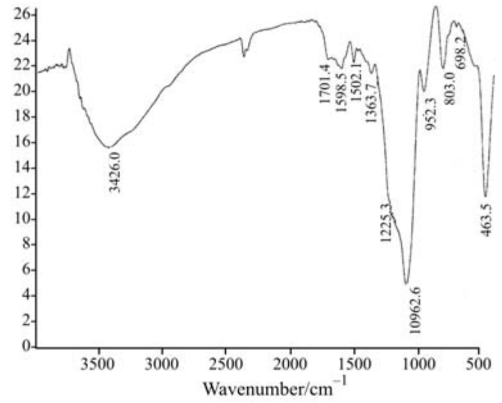


Fig. 1 FTIR spectrum of VSEA

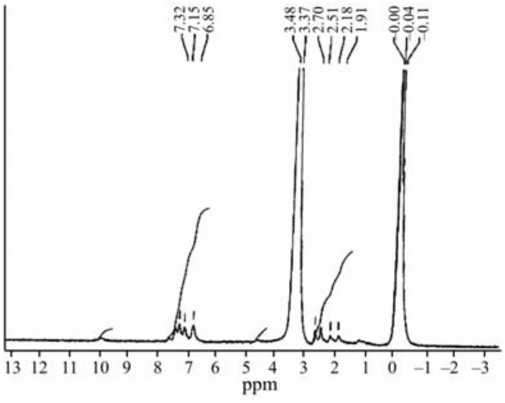
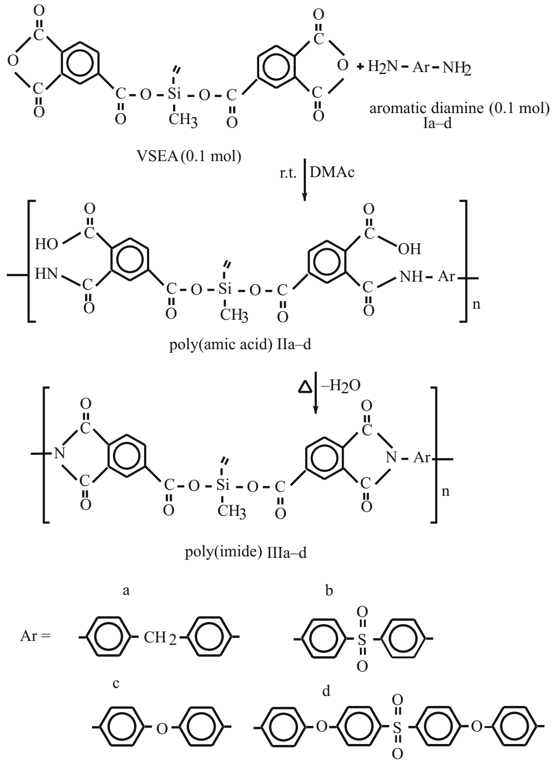


Fig. 2 ^{1}H NMR spectrum of VSEA

acted with equimolar amount of VSEA at room temperature. Initially, diamine was dissolved in measured amount of dry DMAc and then dianhydride was added portion wise to obtain poly(amic acid). The solid content of poly(amic acid) was achieved in the range of 12–15%. The inherent viscosity of poly(amic acid) was measured at concentration 0.5 g dL^{-1} in DMAc. The inherent viscosity of poly(amic acid)s was found in the range of 0.69–0.94 dL g^{-1}. The inherent viscosity represents the moderate molecular mass of poly(amic acid).

The poly(amic acid) solutions were cast on clean glass plates and heated through various stages upto 250°C to remove solvent and water formed during the process of imidization. The complete imidization was occurred at 250°C. The reaction procedure is shown in Scheme 2.



Scheme 2 Synthesis of silicon containing polyimide

FTIR spectroscopy allows monitoring of the imide ring formation during thermal imidization. From the spectra the characteristic absorption band of the imide ring was observed near 1780, 1723 (asymmetrical and symmetrical C=O stretching vibration), 1590 (C=C vinyl stretching), 1366 (C–N stretching vibration), 1094 (Si–O stretching) and those of amide and carboxyl groups in the region of 3000–3500 and 1500–1700 cm^{-1} disappeared, indicating a virtually completed conversion of the PAA precursor into PEI. A typical FTIR spectrum of poly(amic acid) and poly(ester imide) is shown in Fig. 3.

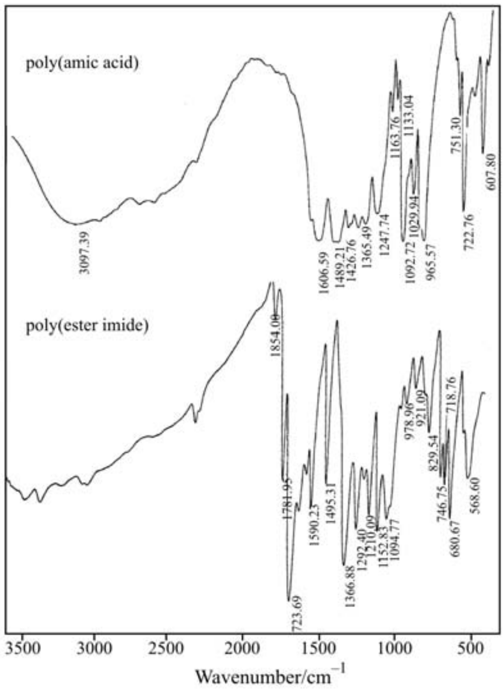


Fig. 3 FTIR spectra of poly(amic acid) and poly(ester imide) IIIa

Thermal behaviour of PEIs

The thermal behaviour of the poly(ester imides)s IIIa–d was evaluated by using the differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). Figure 4 shows that the DSC curves of PEIs. DSC measurements were conducted at a heating rate of 10°C min^{-1}. The glass transition temperatures (T_g) were taken as the midpoint of the change in slope of the baseline in DSC curve. The PEIs showed glass transition temperatures (T_g) in the range of 320–350°C. The thermoplastic nature of the present PEIs could be attributed to the presence of ester groups. The polyimide IIId had low T_g due to its two flexible ether groups in the main chain compare to other diamines. Figure 5 represents the TG plots of silicon containing PEIs. The decomposition temperatures (T_d) were recorded using TG measurements conducted at a heating rate 20°C min^{-1} in inert atmosphere. TG studies reveal that the prepared PEIs showed single step decomposition. From TG studies,

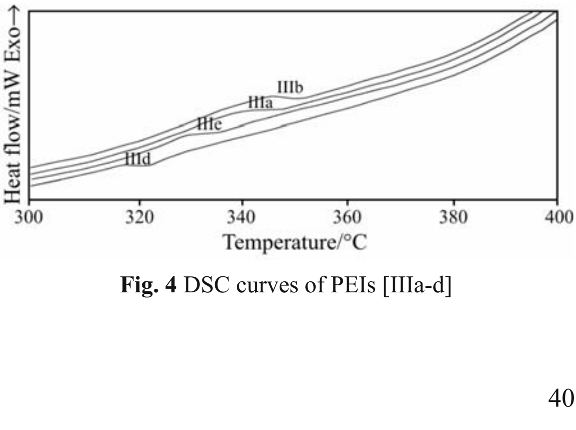


Fig. 4 DSC curves of PEIs [IIIa-d]

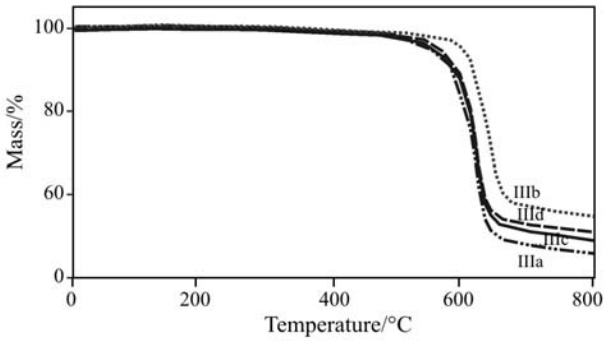


Fig. 5 TG plots of PEIs [IIIa-d]

the initial mass loss (IDT) was observed in the temperature range of 500–520°C and maximum loss (T_{max}) was observed in the temperature range of 530–550°C. The resulting PEIs had char yield 45–55% at 800°C in inert atmosphere.

Water uptake

Water uptake of the poly(ester imide) films was measured by immersing films into deionized water for 24 h at room temperature. Then the films were taken out, wiped with tissue paper and quickly weighed on a microbalance. The water uptake of the film was calculated from the following equation.

$$\text{water uptake (\%)} = \frac{W - W_0}{W_0} \cdot 100$$

where W_0 – is the initial mass of the PEI sample; W – is the mass of the PEI sample after immersion in water for 24 h.

The water uptake of PEIs was in the range of 0.54–0.75 mass%. They exhibited low water uptake values due to the presence of silicon group in the repeating unit. This is because of the silicon segments have a large steric effect and molar volume [23].

Conclusions

VSEA was synthesized by using dichloro methylvinylsilane and trimellitic anhydride in the presence of K_2CO_3 by nucleophilic substitution reaction. The structure of monomer was confirmed by spectral and elemental analysis. Poly(ester imide)s were synthesized using the above dianhydride (VSEA) and various aromatic diamines by two-step method. The synthesized poly(ester imide)s were characterized by FTIR spectroscopy and the thermal properties of the PEIs were investigated by using DSC and TG techniques. The prepared polyimides showed good thermal stability. The water uptake of PEIs was found in the range of 0.54 to 0.75 mass%.

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