An analysis of the structural, thermal and optical characteristics as well as the electrical resistivity of *tert*-butyldiphenylsilyl substituted poly(norbornene-dicarboximide)s

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ABSTRACT

A sequence of well controlled *tert*-butyldiphenylsilyl substituted poly(norbornene-dicarboximide)s with ascending molecular weights have been prepared using the Grubbs 1st generation catalyst in anhydrous chloroform. The kinetics of the polymerization was examined using nuclear magnetic resonance spectroscopy and gel permeation chromatography. By decreasing the Grubbs catalyst concentration, the polymer molecular weights increased linearly. The glass transition temperatures and thermal decomposition temperatures initially increased with polymer molecular weight, then reached a plateau. Regardless of molecular weight the polydispersities remained narrow. The polymers exhibited a predominantly *trans* microstructure and matrix-assisted laser desorption/ionization mass spectrometry was utilized to determine polymer end groups and to calculate the absolute molecular weights. The residual ruthenium content of the polymers was quantified using inductively coupled plasma mass spectrometry and the influence on the resistivity, refractive indices and thin film optical transmittance was evaluated.

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1. Introduction

Poly(norbornene-dicarboximides) are a well-researched type of living polymer which were originally prepared by ring opening metathesis polymerization (ROMP) in 1992 [1]. Since then, the polymers have been functionalized with numerous active groups, tailoring them to a varied range of applications [2–5]. As a consequence of their outstanding thermal features, superior optical transparency, effective film forming characteristics, low moisture absorption and robust mechanical properties they have been utilized as both the passive and active components in organic electronic and optical applications [6–8]. A central requirement for their utilization is a high purity. Polymers must be free from residual catalyst or other fragments associated with their synthesis as if impure a degradation in their thin film optical transparency, stability and a lower electrical resistivity may result. Important physical characteristics include the thermal decomposition temperature (T_d), glass transition temperature (T_g), resistivity (ρ) and

optical transparency. When incorporated into devices, polymers are often exposed to high operating temperatures and voltages for prolonged time periods, in such cases the presence of residual metal catalyst may reduce the device lifetime. Extensive efforts have been made to reduce the concentration of residual ruthenium in ROMP produced polymers, including by aqueous extraction [9], silica gel/activated carbon [10], the use of small molecule ruthenium scavengers and polymer supported catalysts [11].

In this manuscript we have synthesized a *tert*-butyldiphenylsilyl substituted norbornene-dicarboximide monomer. The *tert*-butyldiphenylsilyl group is a well-known bulky substituent in organic synthesis as well as being an excellent protecting group for alcohols, which can be easily removed by treatment with lithium acetate acting as a bifunctional Lewis acid–Lewis base catalyst [12] or by treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) [13]. The reactivity of this monomer was gauged by kinetic experiments which monitored the increase in polymer proton nuclear magnetic resonance (¹H NMR) signals and the reduction of monomer ¹H NMR signals. Gel permeation chromatography (GPC) was utilized to follow the growth in polymer molecular weight. After optimization of the polymerization conditions, a sequence of polymers was

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prepared with ascending molecular weights. This enabled an assessment of the living nature of the polymerization, the influence of the molecular weight on the thermal properties and an investigation of the impact of residual ruthenium on the optical properties and the resistivity. The polymer sequence was characterized using ¹H NMR, GPC and matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) to determine their absolute molecular weights and end groups. The molecular weights obtained by MALDI-MS were very similar to those measured by GPC and the ruthenium content of the polymers was quantified using inductively coupled plasma mass spectrometry (ICP-MS). The impact of this residual ruthenium on the refractive indices, thin film optical transmittance and electrical resistivity was evaluated. The synthesis of the precursors 1–4, monomer (5) and the polymer series (6a–j) is presented in Scheme 1.

2. Experimental

2.1. Techniques

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a JNM-LA400 spectrometer at 400 MHz and 125 MHz frequencies respectively in deuterated chloroform (CDCl₃) or dimethylsulfoxide (DMSO) with tetramethylsilane (TMS) as the internal standard. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed at a heating rate of 10 °C/min on an SII-TG/DTA 6200 and SII-DSC 6220 respectively,

with the samples being encapsulated in a standard aluminium DSC/TGA pan. To ensure a consistent measurement each sample was run twice, with the second run being quoted in the manuscript. For DSC analysis the samples were heated from 30 °C to 250 °C and for TGA measurement the samples were heated from 30 °C to 500 °C both under a nitrogen atmosphere. TGA measurements quoted correspond to the temperature at which 5% mass loss occurred. The polymer molecular weights were determined by gel permeation chromatography (GPC) calibrated against narrow polydispersity index polystyrene standards using a Shodex GPC K-804L column on a JASCO LC2000 instrument at 40 °C in chloroform with a flow rate of 1 mL/min. Positive-ion MALDI-MS analysis was undertaken on a JEOL JMS-S3000 Spiral TOF instrument in Spiral and Linear modes. The Spiral mode was used for accurate end group analysis. The Linear mode was used to measure the complete distribution. In both cases the samples were prepared by mixing the matrix trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) in THF (30 mg/mL), polymer in THF (30 mg/mL) and salt, NaI in methanol (30 mg/mL) in a ratio of 1:1:1. The residual ruthenium content of the polymers was determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) on an Agilent 7500cs instrument. The polymer sample (50 mg) was decomposed using a microwave decomposing device and was added to a 5 g mixture of HCl and HNO₃. UV−vis transmission (400−1000 nm) measurements were obtained on a Jasco V-670 spectrophotometer. Refractive index measurements were obtained using a Sairon Technology Inc. Prism Coupler SPA-4000 on slide glass at 1310 and
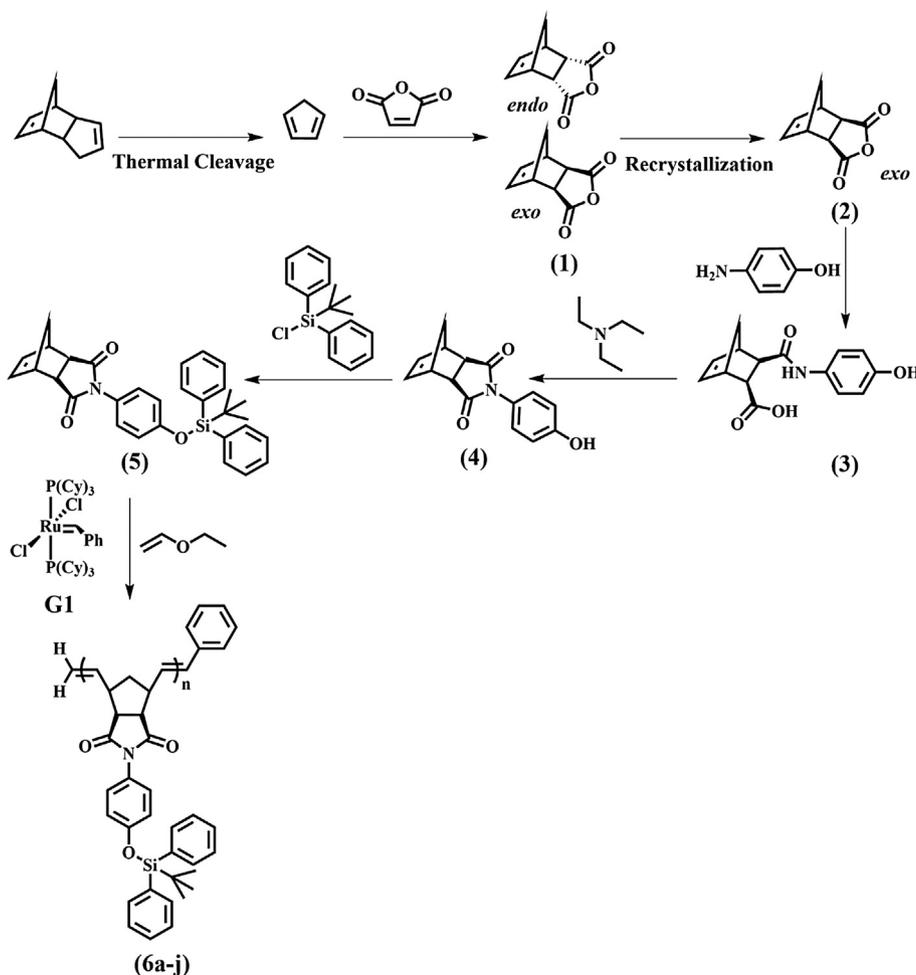
Scheme 1. Synthesis of compounds (1), (2), (3), (4), (5) and the polymer sequence (6a–j).