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Efficient method to prepare a new class of regioregular graft copolymer via click chemistry approach†

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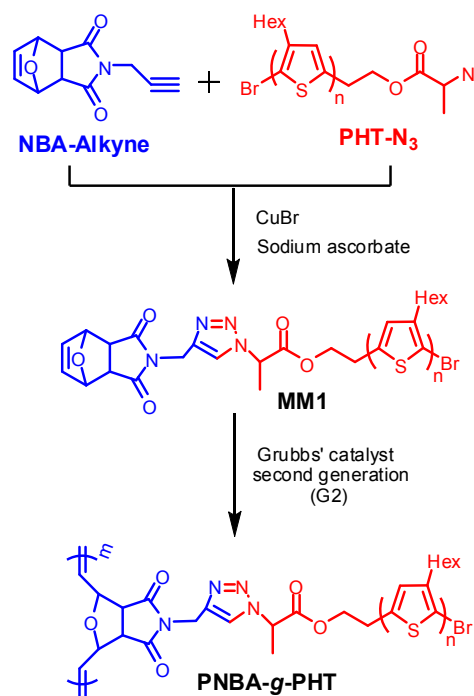
Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x
www.rsc.org/

We report the synthesis of a novel regioregular poly norbornene anhydride-*g*-(3-hexyl thiophene) (PNBA-*g*-PHT) graft copolymer. Grignard metathesis polymerization is used to make PHT homopolymer. Then, PHT-N₃ is prepared by chemical modification reaction of hydroxyl terminated PHT. A click chemistry approach is followed to synthesis MM 1. Finally ring opening metathesis polymerization (ROMP) of MM 1 produce the final copolymer. NMR and Cosy studies have clearly showed that the regioregularity is retained in the newly synthesized copolymer.

In recent trends in the literature, poly 3-hexyl thiophene (PHT) attracted interest of the researcher due to their highly optoelectronic properties such as photovoltaic and light emitting diode, solar cells.^{1,2} The synthesis of head to tail coupled regioregular poly (3-hexyl thiophene) polymer has been well established in the literature by McCullough and coworkers by using Grignard metathesis.³⁻⁵ However, regioregular PHTs still have issues, such as poor mechanical and processing properties relative to typical flexible polymer.⁶ Recently, block copolymer emerged as a interesting materials due to its self assembly properties, which under goes conventional superstructures as nanostructures.^{7,8} This problem shall be overcome by making copolymer of PHT with conducting polymer or oligomer units.⁹ Such a block copolymer could self-assemble into interesting morphologies, such as lamellar, spherical, cylindrical and vesicular structures.^{10,11} Most importantly, in the block copolymer, the π -conjugated segment helps to assemble novel morphologies, which enhances the mechanical as well as electronic properties of the polymeric materials.⁷ There are

reports where varieties of poly (3-hexyl thiophene) based block copolymers are synthesized via ATRP and RAFT polymerization techniques.^{1,3,8,11,12} Though, there are some limitations such as it is difficult to synthesize and purify. However, controlling the molecular weight as well as removal of catalysts are limitations associated with the existing procedure. So Ring opening metathesis polymerization (ROMP) is utilized in this work, because Grubbs' catalyst has a functional group tolerance.¹³⁻²⁰



Scheme 1: Synthesis scheme for (PNBA-*g*-PHT) copolymer.

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† Electronic Supplementary Information (ESI) available: details of synthesis procedure and other analytical data. See DOI: 10.1039/x0xx00000x

To overcome these problems, here we envisioned the simple synthesis route to prepare regioregular poly norbornene anhydride-*g*-(3-hexyl thiophene) (**PNBA-*g*-PHT**) graft copolymer by using ring opening metathesis polymerization¹⁶ and Grignard metathesis polymerization.^{21–23} Click chemistry approach was used to graft the PHT on norbornene backbone (Scheme 1).

First, we have synthesized regioregular vinyl-terminated poly (3-hexyl thiophene) (**PHT 1**) by Grignard metathesis method, using 1,3-Bis(diphenyl phosphino)propane Nickel (II) Chloride (Ni(dppp)Cl₂) as a catalyst.³ The formation of this product was confirmed by NMR spectroscopy. In ¹H NMR spectrum, the signal at δ 6.8 ppm indicated the presence of aromatic protons (Figure 1a) and also in solid state ¹³C CP-MAS NMR spectra, the signals at δ 10–40 ppm were ascribed for carbons of hexyl group and the signals at δ 130–145 ppm were responsible for aromatic thiophene ring (Figure 1b). A COSY spectrum showed a strong

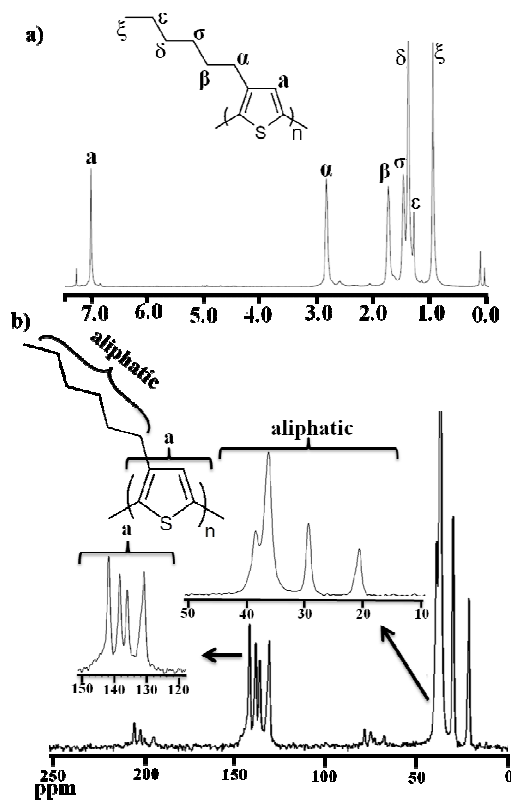


Figure 1. a) ¹H NMR spectrum for poly (3-hexyl thiophene); b) Solid state ¹³C CP-MAS spectra for poly (3-hexyl thiophene).

correlation between the HT α -CH₂ protons and the HT- β CH₂, which located as a broad peak at δ 1.69 ppm. The HT σ -CH₂ protons were also correlated with the HT ξ -CH₂ resonance at δ 1.20 (Figure S2 & S3). Also in the HMQC NMR spectrum, a broad signal at 2.81 ppm that overlapped with broad peak having lower intensity at 2.6 ppm (Figure S5). These results confirmed the regioregularity of poly 3-hexyl thiophene (Figure S1–S8). Then, PHT **1** was reduced by 9-BBN; followed by the reaction with 2-bromopropionyl bromides to get molecule **3** (Figure S10) and it was further functionalized to PHT-azide (**PHT-N₃**) (Figure S12).

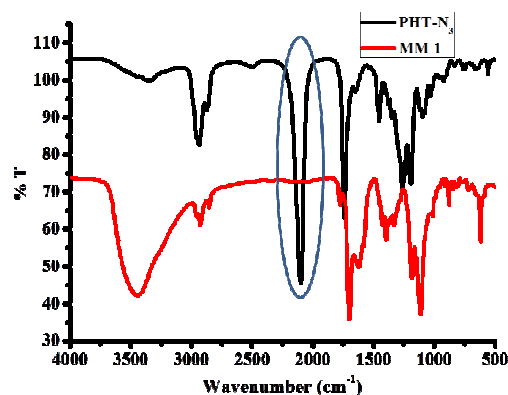


Figure 2. FT-IR spectra for PHT-N₃ (black) and macromonomer **MM 1** (red).

Next, the macromonomer (**MM 1**) was synthesized by click reaction between PHT-azide and norbornene-alkyne. The formation of the reaction was confirmed by FT-IR spectroscopy. In the FT-IR, the stretching frequency at 1633 cm⁻¹ was due to aromatic C=C and the stretching frequency at 2926 cm⁻¹ and 3329 cm⁻¹ were due to aliphatic and aromatic C-H stretching respectively. The stretching frequency for azide functional group at 2110 cm⁻¹ disappeared completely due to the formation of **MM 1** (Figure 2 and S14). Finally, the macromonomer (**MM 1**) was polymerized by ROMP technique using second-generation Grubbs' catalyst to yield poly norbornene anhydride-*g*-(3-hexyl thiophene) (**PNBA-*g*-PHT**) copolymer, that soluble in THF as well as chloroform. In the NMR spectroscopy, the appearance of new signal at δ 5.34 ppm confirmed polymer formation. The molecular weights of the macromonomer and polymers were obtained from GPC techniques using polystyrene as a standard and THF as a solvent. The observed molecular weight (M_n) was 20300 Da with polydispersity index 1.14 (Figure 3, S15 and Table 1).

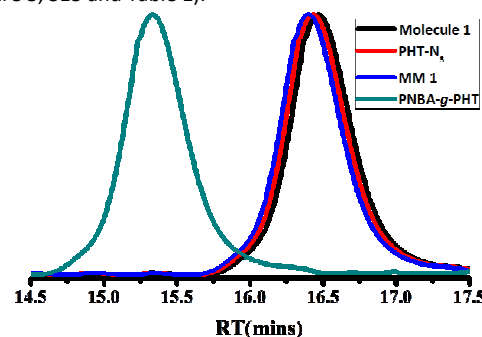


Figure 3. GPC traces for Molecule **1** (black), PHT-N₃ (red), Macromonomer **MM 1** (blue) and **PNBA-*g*-PHT** copolymer (pink).

Table 1: Molecular weights of the polymers. (GPC in THF solvent, calibration with polystyrene standards).

Sr. No.	Polymer	Molecular weight (M_n) by GPC (Da)	PDI
1	Molecule 1	5200	1.03
2	PHT-N ₃	5500	1.09
3	MM 1	5700	1.12
4	PNBA- <i>g</i> -PHT	20300	1.14

The electronic properties of the polymeric materials were studied by UV-vis spectroscopy, where the band at 449 nm was attributed

for thiophene segment; similar band was observed in copolymer as well (Figure S16-S17). Also the mechanical properties, for example, the thermal stability as well as rigidity of the polymer nature, were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Figure S18-S19) respectively. Finally, to study the morphology of the **PNBA-g-PHT** copolymer, atomic force microscopy (AFM) and scanning electron microscopy (SEM) was utilized. The **PNBA-g-PHT** copolymer solution in chloroform was prepared by spin coating method. The rod like nanostructured morphology was obtained by AFM (Figure 4a), which was further supported by SEM (Figure 4b).

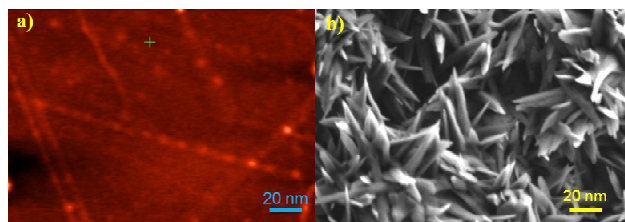


Figure 4. Morphology study of **PNBA-g-PHT** copolymer; a) AFM and b) SEM images.

In summary, we have successfully demonstrated the synthesis of novel regioregular poly norbornene anhydride-*g*-(3-hexyl thiophene) (**PNBA-g-PHT**) graft copolymer via Grignard metathesis polymerization and click chemistry approach followed by ring opening metathesis polymerization. The molecular weight of (**PNBA-g-PHT**) copolymer is observed by GPC with narrow polydispersity index. AFM as well as SEM confirms the rod morphology. To best our knowledge, this is the efficient report to prepare regioregular (**PNBA-g-PHT**) copolymer by metathesis polymerization in combination with click chemistry.

Acknowledgement

SRM thank CSIR, New Delhi for research fellowship and RS thanks DST, New Delhi for Ramanujan Fellowship, CARS/NPOL project for funding and IISER-Kolkata for the infrastructure and start up funding. We thank Dr. T. Mukundan and Ms. Shiny Nair (NPOL, Kochi) for valuable discussion.

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