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PAPER

Synthesis of [1]benzothieno[3,2-b][1]-benzothiophene pendant and norbornene random co-polymers via ring opening metathesis†

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2-Octyl-7-(11-(cis-5-norbornene-endo-2,3-dicarboxylicimide)undecane)[1]benzothienopheno[3,2-b]-benzothienophene (1) was synthesised and co-polymerised with varying amounts of 1-decyl(cis-5-norbornene-endo-2,3-dicarboxylic) imide (2) or norbornene, using a ruthenium catalyst, to produce a series of random co-polymers.

Introduction

Alkyl [1]benzothieno[3,2-b][1]benzothiophenes (BTBT) have attracted attention in recent years as a high performing organic transistor material,[1–3] with 2-tridecyl[1]benzothieno[3,2-b][1]-benzothiophene (C$_{13}$-BTBT) displaying hole mobilities as high as 17.2 cm^2 V^{-1} s^{-1} in polycrystalline thin films grown from solution.[4] Although there have been examples of polymers utilising this unit, coupled along a conjugated backbone,[5,6] there have been no examples of its incorporation as a side-chain, or "comb-shaped" polymer, where the unit is attached as a pendant group, via a flexible spacer chain to a polymer backbone. This would potentially allow enhanced processability and possible facile alignment of the BTBT units in a controlled way, as it is decoupled from the backbone where molecular motion is usually very restricted.[7–10]

Ring-opening metathesis polymerisation (ROMP)[11–14] was chosen as the preferred mechanism as it has proven tolerance with electron rich aromatic groups, due to the absence of radicals, and polynorbornene materials being used in plastic electronics for OLEDs[15,16] and OPVs[17] devices. The fast initiation rate of catalyst dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](benzylidene)bis(3-bromopyridine) ruthenium(II)[18] resulted in a lack of selectivity between the different norbornene monomers facilitating the synthesis of a random copolymer.[19]

Synthesis

BTBT was synthesised in a one step process from 2-chlorobenzaldehyde and sodium hydrosulfide hydrate, following

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literature procedures,[20] to produce 15 g of material in a yield typical for the reaction. Friedel–Crafts acylation of BTBT (3 g) with octanoyl chloride (Scheme 1) at low temperature produced the mono-addition product, [1]benzothieno[3,2-b]-[1]benzothiophene-2-octan-1-one (3), in very high yields.[21] The ketone was reduced using two and a half equivalents of aluminium chloride and lithium aluminium hydride to generate 2-octyl-[1]benzothieno[3,2-b][1]benzothiophene (4) quantitatively. These steps were repeated with 11-bromoundecanoic acid chloride, synthesised from 11-bromoundecanoic acid and oxalyl chloride, to produce 2-octyl-7-(11-bromoundecan-1-one)[1]benzothienopheno[3,2-b] benzothienophene (5) then

Scheme 1 Synthetic route to molecule 6. (a) 1.1 eq. C$_7$H$_{15}$COCl, 2.5 eq. AlCl$_3$, dry DCM, Ar, −78 °C, 4 h, 98%. (b) 2.5 eq. AlCl$_3$, 2.5 eq. 1 M LiAlH$_4$ in Et$_2$O, Ar, dry Et$_2$O and DCM, rt, O/N, 100/98%. (c) 1.4 eq. oxalyl chloride, cat. DMF, Ar, dry DCM, 1 h, 100%. (d) 2.5 eq. AlCl$_3$, dry DCM, Ar, −78 °C, 4 h, 88%.

Scheme 2 Synthesis of molecules 1 and 2. (a) 1 eq. NH$_4$OAc, AcOH, 140 °C, 16 h, 100%. (b) 1 eq. C$_8$BTBTC$_{11}$Br (0.5 g), 1.5 eq. K$_2$CO$_3$, 1 : 1 DMF : THF, reflux, 16 h, 96%. (c) 1 eq. 1-decylamine, 1 eq. triethylamine, Ar, dry toluene, reflux, 16 h, Dean–Stark app., 86%.
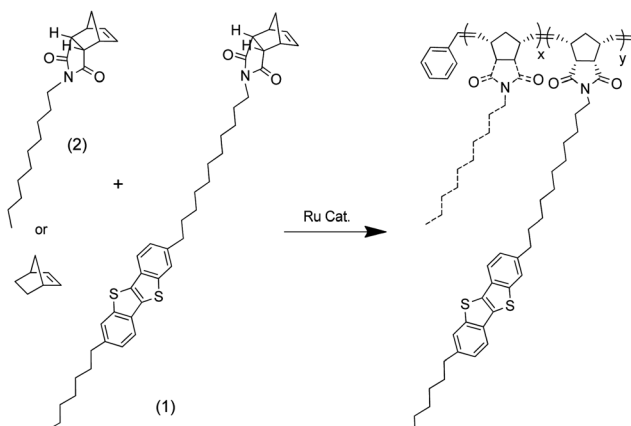
Scheme 3 Polymerisation of norbornene-BTBT with either norbornene or alkyl norbornene imide.

2-octyl-7-(11-bromoundecane) [1]benzothieno[3,2-b][1]benzothiophene (alkylbromo-BTBT) (6) in high yields.

The alkylbromo-BTBT underwent nucleophilic substitution with *cis*-5-norbornene-*endo*-2,3-dicarboxylic imide, synthesised from the anhydride and ammonium acetate,[22] to produce ROMP monomer 2-octyl-7-(11-(*cis*-5-norbornene-*endo*-2,3-dicarboxylicimide)undecane)[1]thienopheno[3,2-b] benzothiophene (BTBT

norbornene imide) (1) (Scheme 2). 1-Decyl(*cis*-5-norbornene-*endo*-2,3-dicarboxylic) imide (alkyl norbornene imide) (2) was also synthesised from the anhydride and 1-decylamine, using a Dean–Stark apparatus, to be used as a co-monomer.[23]

Norbornene-BTBT underwent ROMP polymerisation with bicyclo[2.2.1]hept-2-ene (norbornene) or the alkyl norbornene imide as co-monomers in different ratios using dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidasolidinylidene](benzylidene) bis(3-bromopyridine)ruthenium(II) as catalyst (Scheme 3) (Table 1). Attempts to synthesise a norbornene-BTBT homopolymer produced a material too insoluble to handle and was not further pursued.

Analysis

The table in Table 1 displays the number-averaged molecular weight (M_n), average molecular weight (M_w), theoretical average molecular weight (tM_n, see ESI for calculation), and the polydispersity index (PDI) of the corresponding polymers. Polymers with the norbornene co-monomer produced low M_n and large PDI, while polymers with the alkyl norbornene imide co-monomer produced a M_n very close to the tM_n and a small PDI. It is hypothesised that the rigidity of the norbornene unit compromises the polymer solubility, causing aggregation, and precipitation preventing high molecular weights from being formed while the copolymers incorporating alkyl chains on the norbornene imide had sufficient solubility to allow for propagation of the polymer chain.

NMR analysis[24] of the polymers show key hydrogen peaks that quantify the ratio of co-polymerisation between the monomers. Peaks at 7.7 ppm correspond to the aromatic hydrogens in the 3, 4, 8 and 9 positions of BTBT, integrating at 4 for every BTBT monomer, and give the most distinct signals for the monomer. p-BTBT1, 2 and 3 have distinct peaks at 5.2 and 5.3 corresponding to the respective Z and E polymer backbone alkenes formed from norbornene ring opening and peaks at 5.5 and 5.8 corresponding to the respective Z and E alkenes formed from norbornene-BTBT (Fig. 1). Due to the broadness of polymer ^{1}H NMR signals, accurate integration of the individual peaks is not possible so all were integrated together, from 5.1 to 5.8, to give the total number of vinyl backbone hydrogens *per* monomer. The ratio of co-monomers can then be measured; p-BTBT1 showed a poor incorporation of norbornene relative to the BTBT, roughly half of the expected amount, while p-BTBT2 and 3 had approximately the calculated

Table 1 Polymerisation of norbornene-BTBT

Polymer	Co-monomer & equivalents	Catalyst (eq.)	$M_n{}^a$ (kg mol^{-1})	$M_w{}^a$ (kg mol^{-1})	tM_n (kg mol^{-1})	PDI	Ratio^b
p-BTBT1	5 eq. norbornene	0.03	13	49	25	3.7	2.5 : 1
p-BTBT2	7.5 eq. norbornene	0.03	9.7	61	46	6.3	7 : 1
p-BTBT3	10 eq. norbornene	0.03	8.6	44	54	5.1	10 : 1
p-BTBT4	1 eq. alkyl-norbornene	0.015	69	89	65	1.3	1 : 1
p-BTBT5	2 eq. alkyl-norbornene	0.01	104	160	127	1.5	2 : 1

^{a} Determined by gel permeation chromatography in chlorobenzene relative to monodispersed polystyrene standards. ^{b} Ratio of co-monomers in polymer measured by ^{1}H NMR – (norbornene/alkyl-norbornene2): norbornene-BTBT.
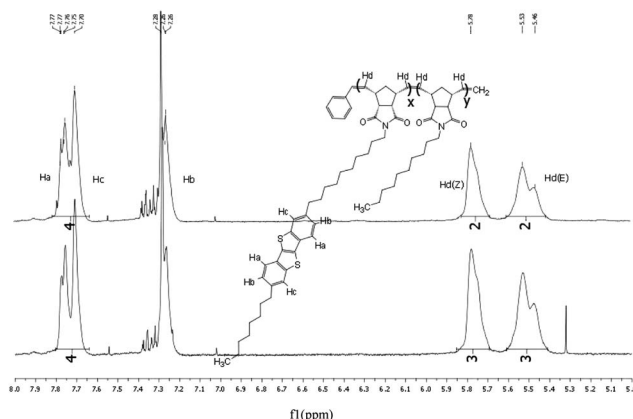
Fig. 1 Key proton peaks of p-BTBT1, 2, and 3.

Fig. 2 Key proton peaks of p-BTBT4, and 5.

Fig. 3 Typical UV-vis of ROMP polymers in solution and thin film.

ratio. It is suspected that this is the result of the same factors that caused the polymers to have a poor molecular weight, aggregation that prevented the polymerisation to proceed sufficiently.

Similarly, p-BTBT4 and 5 only have peaks at 5.5 and 5.8 as the co-monomers have the same polymerisable group (Fig. 2). The ratio between the aromatic and vinyl hydrogen peaks corresponds well with the predicted values given the ratio of co-monomers polymerised. Combined with the molecular weight data, the strategy of using co-monomers with an alkyl chain has been successful in producing polymers of the desired size and form.

Ultraviolet and visible spectroscopic (UV-vis) analysis spectra of BTBT ROMP polymers displayed a λ_{max} of 322 nm in solution and 322 nm, with a broadening of the signal, in the drop cast thin film typical for all five polymers. This red shift is too small to be head-to-tail, J-aggregation of the BTBT pendants[25-27] that would also create a narrowing of the signal. An absence of solvent–solute interactions is a likely explanation for this effect (Fig. 3).

Devices made using these materials produced no transistor performance. It is hypothesised that there is too much crowding of the BTBT by th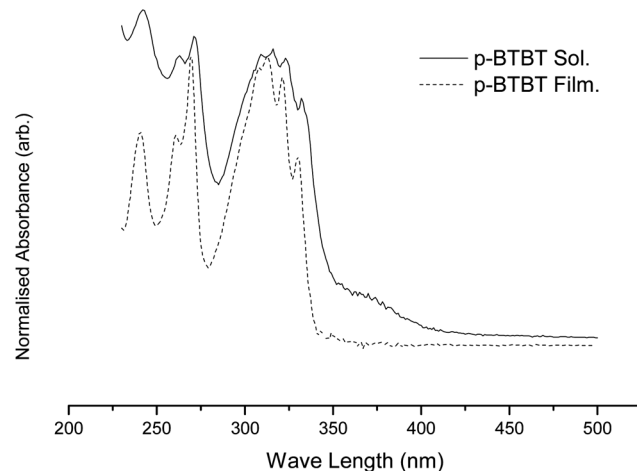e aliphatic poly-norbornene and alkyl chains, preventing a clear channel for hole transport through the material. This is corroborated with the UV-vis data that exhibits no indication of π-orbital overlap.

Conclusions

Pendant polymers of BTBT were synthesised utilising ROMP with varying success. Co-polymerisation with solubilising alkyl-pendants produced materials very close to theoretical predictions. However, the materials proved unsuccessful as transistor devices due to a lack of extended π-stacking. Further exploration of the ratio of aliphatic to aromatic is needed to ensure there is sufficient aromatic interactions for charge transport, while maintaining solubility. This could be achieved with a fine-tuning of the alkyl chain length and possible removal from one side of the BTBT pendant. ROMP materials have enormous potential for the controlled polymerisation of radical sensitive materials and provide interesting morphologies due poly-norbornene's backbone, justifying further interest.

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