Organic &
Biomolecular
Chemistry

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 6111

www.rsc.org/obc

PAPER

Block copolymers containing organic semiconductor segments by RAFT polymerization†‡

Ming Chen,* Matthias Häussler,* Graeme Moad* and Ezio Rizzardo

Received 21st February 2011, Accepted 9th June 2011
DOI: 10.1039/c1ob05276d

Approaches to the synthesis of block copolymers containing organic semiconductor segments (polythiophene, perylene diimide) by RAFT polymerization have been explored. A method involving transformation of a vinyl derivative to a macro-RAFT agent provides for the synthesis of block copolymers which are joined by a short non-hydrolysable linkage.

Introduction

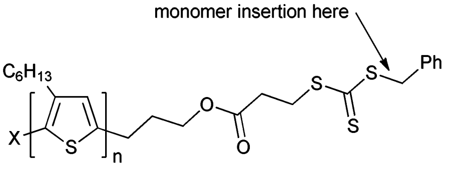
Control of radical polymerization with the addition of thiocarbonylthio compounds that serve as reversible addition fragmentation chain transfer (RAFT) agents was first reported in 1998.[1,2] Since that time much research carried out in these laboratories and elsewhere[3–11] has demonstrated that polymerization with reversible addition-fragmentation chain transfer is a reversible deactivation radical polymerization (RDRP);[12] an extremely versatile process that satisfies most of the established criteria for a living polymerization[13,14] It can be applied to form polymers with a narrow molecular weight distribution. These may be homopolymers or copolymers and can be formed from most monomers amenable to radical polymerization. A variety of architectures including stars, blocks, microgel and hyperbranched structures, and supramolecular assemblies are accessible.

While fully conjugated polymers, such as those that see use in organic semiconductors, cannot be directly made by RDRP methods (ATRP, NMP, RAFT), these methods can be used to form materials which comprise segments of these polymers either as blocks or as pendant units.[15–17]

Significant benefits of RAFT polymerization are the ability to form polymers with narrow molecular weight distributions and uniform compositions with the possibility of eliminating the low molecular weight "impurities" which can act as hole or electron traps in organic semiconductors while, at the same time, targeting the modest molecular weights that offer advantages in solubility, processing and film forming characteristics.

Block copolymers attract interest because of their ability to self-assemble to give nanophase separation into periodic domains. The dimensions of these domains can be in the range of 5–50 nm which encompasses that required for many semiconductor applications.[18–22] Block copolymers may also be added as a minor component and control the morphology of a blend by acting as a compatibiliser or structure director.[22–24] Recent reviews on the use of block copolymers in organic electronics include those by Segalman *et al.*,[25] Kim *et al.*,[19] Scherf *et al.*[26] and Darling.[22] The block copolymers containing conjugated segments are a sub-class of rod-coil polymers. Several relevant reviews have appeared on the use[15,25] and self-assembly[27] of such block copolymers.

There are three main processes whereby a RAFT synthesized polymer can be combined with fully conjugated polymers to form block copolymers. The post polymerization "grafting to" strategy involves coupling of a RAFT-synthesized polymer to a semiconductor segment. The "grafting through" strategy involves RAFT polymerization of a (macro)monomer with pendant semiconductor functionality. These strategies are included in our recent review.[15] This paper focuses on the "grafting from" strategy wherein macro-RAFT agents based on organic semiconductor or analogous oligomeric species are prepared by end-group modification of an organic semiconductor.



1a X=H
b X=Br

RAFT synthesized block copolymers based on poly(3-hexylthiophene) (P3HT) have been reported by Iovu *et al.*[28] Yang *et al.*[29] and Palaniappan *et al.*[30] These studies made use of the macro-RAFT agents **1a** or **1b** to form 'Z'-connected blocks where the thiocarbonylthio functionality in the product is positioned at the block linkage. This means that the block will be cleaved on

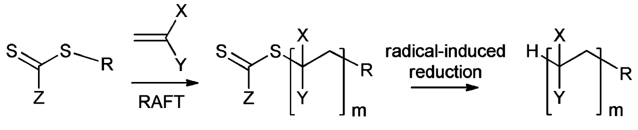
---

CSIRO Materials Science and Engineering, Bag 10, Clayton South, Victoria, Australia. E-mail: graeme.moad@csiro.au; Fax: +613 9545 2445; Tel: +613 9545 2509

† This paper is dedicated to the memory of Professor Athelstan L. J. Beckwith whose innovation and enthusiasm helped to inspire several generations of free radical chemists.

‡ Electronic supplementary information (ESI) available: ^{1}H NMR spectra. Synthesis of compounds **12** and **32**. Results of radical polymerizations performed in the presence of compounds **9–12**. Further details of RAFT polymerizations with **30**.

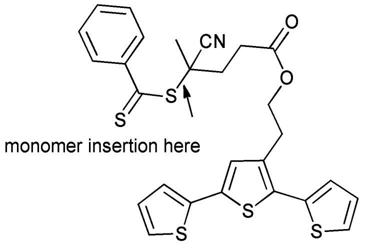
thiocarbonylthio group removal/transformation, for example, by radical induced reduction (refer Scheme 1).[11,31]



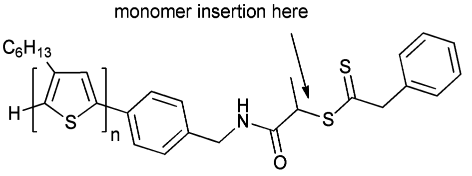
Scheme 1 Overall process for RAFT polymerization and thiocarbonylthio end-group removal.

This is of significance since the presence of the thiocarbonylthio group has been shown to be detrimental to some applications. For example, certain RAFT agents and macro-RAFT agents effectively quench the fluorescence of coumarone derivatives and acenaphthalene units.[32–34] No quenching is observed for the RAFT-synthesized polymers from which the thiocarbonylthio end-group had been removed, for example, by aminolysis[32] or radical-induced reduction.[33]

For 'R'-connected macro-RAFT agents, the thiocarbonylthio group remains at the chain end and the block linkage formed is a carbon-carbon bond so the structure should remain intact during processing.[35] Grande *et al.*[36] reported the terthiophene RAFT agent **2** which was used to form a polythiophene macro-RAFT agent by an electrodeposition process using cyclic voltammetry.



2



3

Rajaram *et al.*[24] made use of the 'R'-connected macro-RAFT agent **3** to form a P3HT block copolymer. The RAFT agents **2** and **3** possess a relative long connecting chain between the polythiophene chain and the thiocarbonylthio group and include a potentially hydrolysable ester or amide linkage. This linkage is retained at the block juncture in the RAFT synthesized polymer.

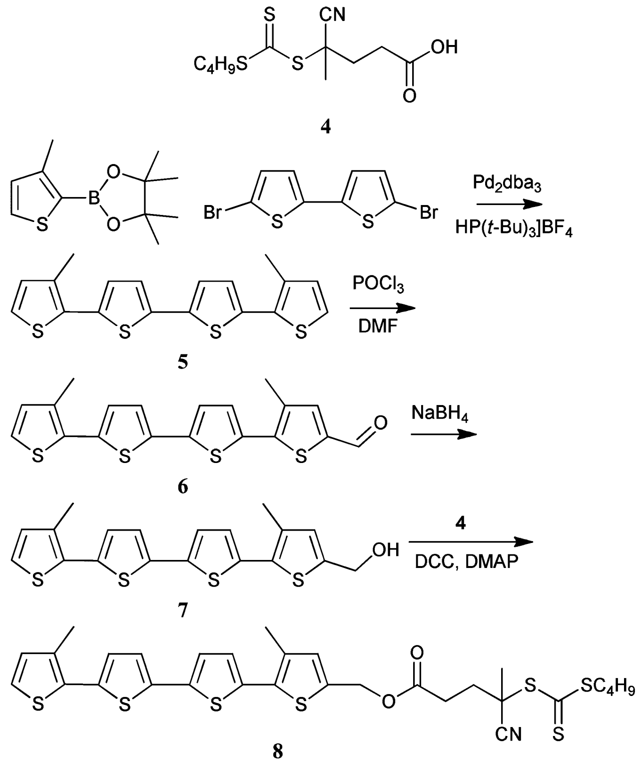
A method of synthesizing macro-RAFT agents suitable for forming 'R'-connected block copolymers involves the insertion of a single monomer unit into a RAFT agent structure to form a new macro-RAFT agent. Zard and coworkers[37–42] were the first to exploit this method when they applied xanthate transfer chemistry to selectively insert a single unit of a less-activated monomer such as a vinyl ester or a vinyl amide. The xanthate transfer process failed (by providing an oligomeric product) when applied to more activated monomers such as styrene (St) or acrylic monomers. We have previously used single unit monomer insertion with dithioester RAFT agents and appropriate St derivatives in preparing polymers for light harvesting applications.[33,35,43] McLeary, Klumperman and colleagues[44–50] observed that complete conversion of the initial RAFT agent to a species incorporating a single monomer unit is common to many well-behaved RAFT polymerizations including those of St[44,47] and methyl acrylate (MA)[46,49] with dithioester RAFT agents, and *N*-vinylpyrrolidone[48] and vinyl acetate[48] with xanthate RAFT agents. They termed this behaviour selective initialization. Moad *et al.*[51] proposed that the chain length dependence of propagation in radical polymerization ($k_p(1) \gg k_p(2)$) is such that, as long as the transfer constant of the RAFT agent is high ($C_{tr} > 10$), there will be substantial conversion to the single monomer "chain" before oligomerization to provide a two unit or longer chain. A further important consideration in minimizing byproducts is to select the 'R' group of the RAFT agent to be the same as the initiator derived radical. Thus, in the present work we use a cyanoisopropyl RAFT agent and use azobis(isobutyronitrile) (AIBN) as initiator.

The block juncture formed with use of this form of macro-RAFT agent is a carbon–carbon bond. In this paper we explore the use of this technology for the synthesis of block copolymers containing organic semiconductor segments.

Results and discussion

Synthesis and use of ester-linked macro-RAFT Agents

In initial studies, we prepared a macro-RAFT agent based on the tetrathiophene **5**[52] which was prepared by a palladium-catalyzed cross-coupling process'. The Vilsmeier–Haack reaction using one equivalent of $POCl_3$/DMF provided the monoaldehyde **6** in 52% isolated yield. This was transformed to a macro-RAFT agent **8** by the sequence of reactions shown in Scheme 2.



Scheme 2 Macro-RAFT agent synthesis from tetrathiophene.

This journal is © The Royal Society of Chemistry 2011

Table 1 Polymerizations with tetrathiophene macro-RAFT agent **8**[a]

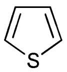
Reactant mole ratio								
Monomer		**8**	AIBN	Time/h	Conv.[b] (%)	M_n[c] (calc)	M_n[d]	$Đ$[f]
St	1577	8.2	1	16	41	8900	12,000	1.10
MMA	1640	8.2	1	16	91	18900	11,000	1.20
MA	1907	8.2	1	16	76	15900	23,900	1.24
AA	2278	8.2	1	6	26	5900	11,400[e]	1.11

[a] Bulk polymerization at 70 °C. [b] Conversions estimated from ^{1}H NMR spectrum. [c] Theoretical molecular weights calculated using the expression M_n(calc) = ([monomer]/[RAFT agent]) × fractional conversion × MW of monomer + MW of RAFT agent. [d] Molecular weights from GPC in polystyrene equivalents. [e] GPC after esterification of PAA segment with diazomethane.[4] Estimated molecular weight of free acid is 9500. [f] Molecular weight dispersity = M_w/M_n.

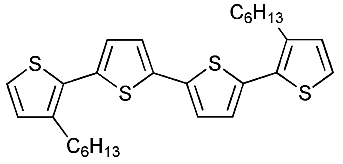
Bulk polymerizations of St, methyl methacrylate (MMA), MA, and acrylic acid (AA) were carried out at 70 °C. The macro-RAFT agent **8** provided good control over the molecular weight dispersity ($Đ$)[53] as shown in Table 1. However, the correspondence between found (GPC) and calculated molecular weights is poor. Higher than calculated molecular weights can often be attributed to either incomplete usage of the RAFT agent (*i.e.*, a low transfer constant, in this case $Đ$ should also be high) or the RAFT agent concentration being lower than expected (*i.e.*, an impure RAFT agent). Lower than expected molecular weights suggest there is a source of chain ends other than the RAFT agent. The polystyrene equivalent molecular weights for poly(MA) and poly(AA) are expected to be significantly lower than actual molecular weights.[54] The oligothiophene block may also affect elution behaviour.

The monomer conversions shown in Table 1 were also lower than expected for the reaction conditions. This suggested some interference of the oligothiophene on the course of polymerization. To test this hypothesis a series of control polymerizations of St, MA and MMA were conducted in the presence of thiophene and thiophene-containing compounds (**9–12**). The addition of compounds **9–11** provided a lowering of molecular weight *vs.* the control and significant retardation manifest as a reduced conversion of monomer to polymer. Moreover, analysis by GPC with diode array detection showed that some of the thiophene derivative was incorporated into the polymer. The effect was most profound with the acrylate (MA) and was small with MMA. This order correlates with the intrinsic activity of the corresponding propagating radicals.[55,56] Compound **12** in which the 2- and 5-positions of the thiophene are substituted appeared to be substantially less reactive (some lowering of molecular weight was observed but no retardation). Details of these experiments are provided in the ESI.‡

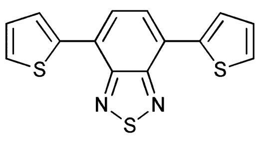
The procedure used by McCullough and coworkers[57] for the preparation of an ATRP macro-initiator was adapted as shown in Scheme 3 to provide a bis-macro-RAFT agent based on P3HT. Thus, regioregular P3HT (M_n, = 4094, X_n = 18), synthesized by the Grim process with a mixture of end-groups (**13**, X = H or Br), was debrominated by Grignard metathesis and quenched with water to yield **14**. The Vilsmeier–Haack reaction provided the telechelic polymer with α,ω-aldehyde groups which were reduced to hydroxymethyl end-groups with $LiAlH_4$. The P3HT **16** was converted to the bis-macro-RAFT agent **17** by esterification. The transformation to the bis-RAFT agent was followed by NMR.



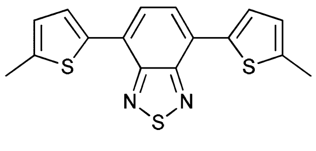
9



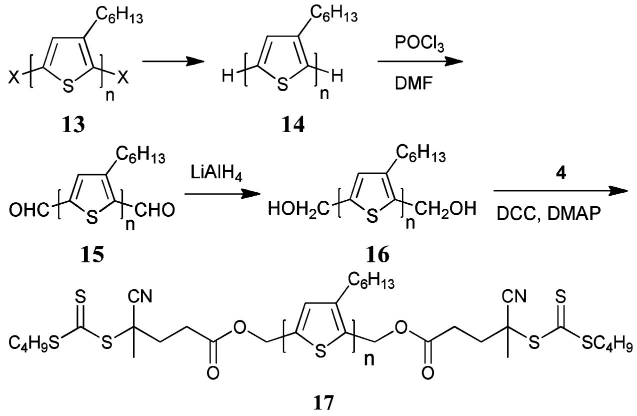
10



11



12



Scheme 3 Macro-RAFT agent synthesis from poly(3-hexylthiophene) derivative.

Solution polymerizations of St, MMA, MA, and AA were carried out at 70 °C in the presence of the P3HT bis-macro-RAFT agent **17**. Polymerization conditions and outcome are shown in Table 2. Good control (low $Đ$) was observed for MMA polymerization. Only low conversion was obtained for polymerization of St. Polymerization of MA gave a poly(MA) with a high dispersity and a lower than expected molecular weight. Attempted polymerization of AA provided an insoluble product which was not characterized. The results with MA and AA suggest interference of the P3HT block on the course of their polymerization.

Synthesis and use of carbon-linked macro-RAFT Agents

While **8** and **17** are effective RAFT agents, they (like **2** and **3**) have the disadvantage that the polythiophene segment is connected by a long, potentially hydrolysable, linkage. We therefore chose to evaluate single unit monomer insertion. The experimental protocol was first tested on 5-methyl-2-vinylthiophene (**20**).

There are a number of reports of radical polymerization of vinylthiophene derivatives.[58–63] This work demonstrated that the double bonds of vinylthiophene derivatives are highly reactive[58] and also suggested that it was important to block the 5-position to avoid side reactions such as transfer to monomer and crosslinking.[63] RAFT polymerization of 2- and 3-vinylthiophene and of 2,5-dibromo-3-vinylthiophene was reported by Mori *et al.*[64] Polymerization of the 2- or 3-vinylthiophene with or without

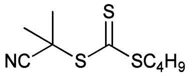
Table 2 Polymerizations with P3HT bis-macro-RAFT agent **17** (M_n,4094)[a]

Reactant mole ratio							
Monomer		17	AIBN	Conv.[b] (%)	M_n[d] (calc)	M_n[e]	Đ[f]
St	24400	45	12.2	8.6	8900	15100	1.16
MMA	7300	13.5	3.66	76.2	45300	54500	1.21
MA	7300	13.5	3.66	87.3	44700	73000	1.45
AA	6900	11.5	3.47	[c]	—	—	—

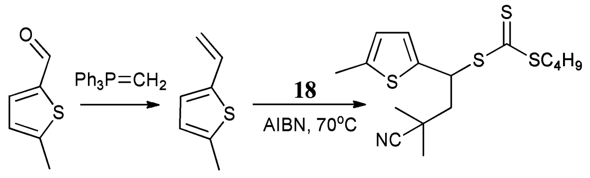
[a] Solution polymerization at 70 °C for 16 h. Chlorobenzene (CBz) was used as solvent for St (687 mg with 300 mg CBz), MMA (660 mg with 1 g CBz) and MA (568 mg with 1 g CBz). A mixture of 1 : 1 (w/w) of CBz and acetonitrile was used for AA (475 mg with 1 g solvent). [b] Conversions estimated from ^{1}H NMR. [c] Not determined (polymer precipitated during polymerization). [d] Theoretical molecular weights calculated were using the expression M_n(calc) = ([monomer]/[RAFT agent]) × fractional conversion × MW of monomer + MW of RAFT agent. [e] Molecular weights from GPC in polystyrene equivalents. [f] Molecular weight dispersity = M_w/M_n.

RAFT agent gave only low molecular weight polymers. RAFT polymerization of 2,5-dibromo-3-vinylthiophene was successful providing a low dispersity polymer. The result again indicates the importance of blocking the 2 and 5 positions of the thiophene unit to radical attack.

The RAFT agent (**21**) was synthesized from the vinylthiophene **20** and butyl cyanoisopropyl trithiocarbonate **18** as shown in Scheme 4 to provide a 68% isolated yield.

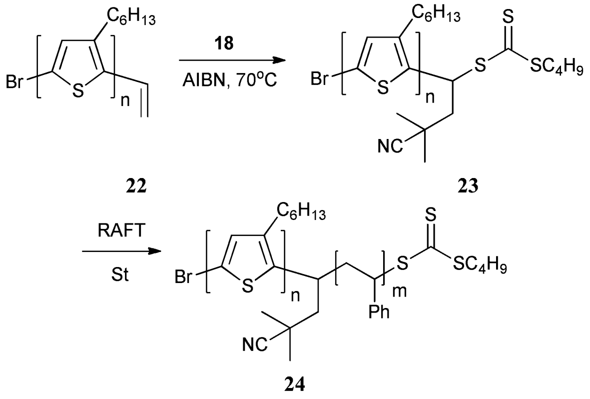


18



Scheme 4 RAFT agent synthesis from vinylthiophene.

A P3HT macro-RAFT agent **23** was synthesized by an analogous procedure as shown in Scheme 5. Vinyl terminated P3HT **22** (M_n (GPC) 2400 polystyrene equivalents, Đ 1.39, M_n (NMR) ~5000) was synthesized by Grignard metathesis polymerization.[65,66] The single unit monomer insertion was conducted in chlorobenzene solvent with a two-fold excess of **18**. This reaction gave ~90% conversion of **22** (based on the ^{1}H NMR spectra, Fig. 1) and provided at 36% isolated yield of the P3HT macro-RAFT agent (the low isolated yield is partly a consequence of the small scale of the reaction and losses during precipitation). Very high conversion for the single unit monomer insertion step is important since **22** and **23** are not readily separated by chromatography or other means. The experimental conditions also provided a component twice the molecular weight of the precursor P3HT (**23**) (Fig. 2a). This component appeared inert in the subsequent RAFT polymerization and is therefore thought to be an impurity (**25**) formed by termination by combination. Residual **22** and other impurities formed by termination by disproportionation (**26**, **27**) or cross-combination with cyanoisopropyl radicals (**28**) most likely account for a peak in the GPC chromatogram of the P3HT-*block*-PSt with molecular weight similar to the P3HT macro-RAFT agent (**23**) (Fig. 2b). The amounts of these impurities might be minimized by optimization of the reaction conditions. A balance needs to be achieved between the need for high conversion of **22** and minimization of by-products from termination reactions. Up to two moles of the termination products is expected for each mole of AIBN decomposed.



Scheme 5 Macro-RAFT agent synthesis from poly(3-hexylthiophene) macromonomer and use in RAFT polymerization to form poly(3-hexylthiophene)-*block*-polystyrene.

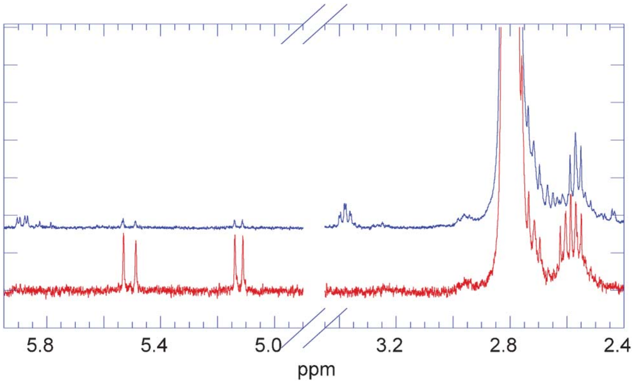
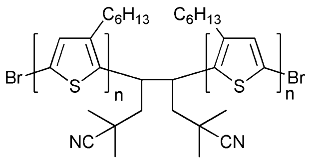
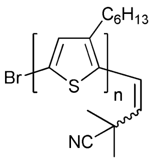


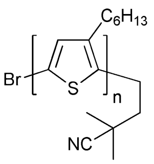
Fig. 1 Regions 2.4–3.4 and 4.9–5.9 ppm of ^{1}H NMR spectra of vinyl-P3HT (**22**) (lower trace) and (impure) P3HT macro-RAFT agent (**23**) (upper trace). Signal assignments for **22** δ 5.51 (=C*H*H), 5.25 (=CH*H*), 2.60 (t, vinyl-Tp-CH_2), 2.55 (t, Br–Tp–CH_2). Signal assignments for **23** δ 5.88 (m, Tp–CH–S), 3.38 (m, S–CH_2C$_3$H$_7$), 2.8 (t, Tp–CH_2), 2.55 (t, Br–Tp–CH_2) (Tp = thiophene).



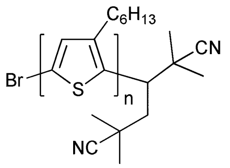
25



26



27



28

This journal is © The Royal Society of Chemistry 2011

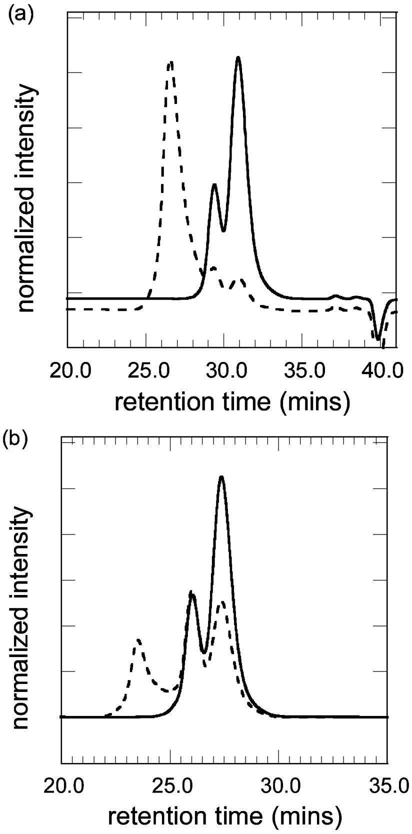


Fig. 2 Gel permeation chromatogram (GPC) obtained with (a) refractive index detection and (b) UV detection with wavelength 530 nm of macro-RAFT agent **23** (—) and P3HT-*block*-polystyrene **24** (- - - -) (see Experimental and Table 4).

Table 3 Bulk styrene polymerizations with RAFT agent **21**[a]

Reactant mole ratio								
St	21	AIBN	Temp./°C	Time/h	Conv. (%)	M_n[b] (calc)	M_n[c]	$Đ$[d]
500	10	1	70	16	0	—	—	—
5000[e]	10	1	70	16	22	11800	11800	1.10
5000[e]	10	1	70	16	17	9210	12600	1.11
5000[f]	10	0	110	16	41	21700	24000	1.11

[a] Bulk polymerization at 70 °C. [b] Theoretical molecular weights calculated using the expression M_n(calc) = ([monomer]/[RAFT agent]) × fractional conversion × MW of monomer + MW of RAFT agent. [c] Molecular weights from GPC in polystyrene equivalents. [d] Molecular weight dispersity = M_w/M_n. [e] Duplicate experiments. [f] Thermal initiation.

Table 4 Solution styrene polymerization with macro-RAFT agent **23** (M_n,~5000)[a]

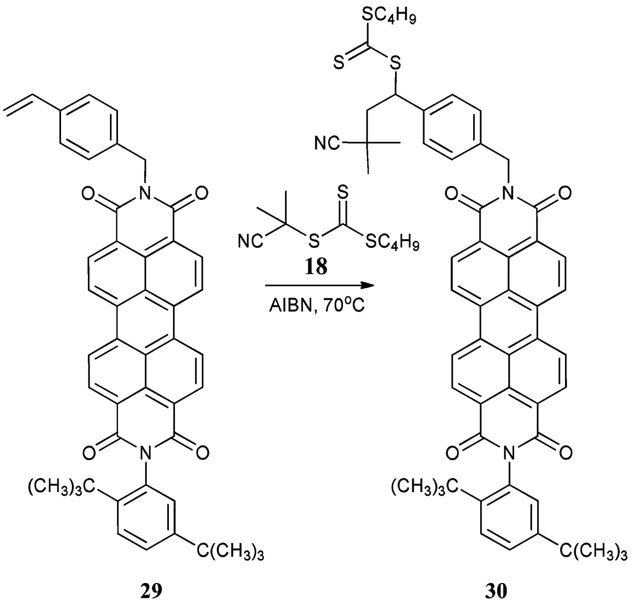
Reactant mole ratio							
St	23	AIBN	Temp./°C	Time/h	Conv. (%)	M_n[b]	$Đ$[c]
2000	4[d]	1	70	20	57	86600	1.12

[a] Solution polymerization (687 mg St with 300 mg chlorobenzene) at 70 °C for 16h. [b] Molecular weights from GPC in polystyrene equivalents. [c] Molecular weight dispersity = M_w/M_n of P3HT-*block*-polystyrene component (refer Fig. 1a). [d] impure RAFT agent (see text).

The RAFT agents **21** and **23** were evaluated in St polymerization (Table 3 and Table 4 respectively). Marked retardation was seen for high concentration of **21**. Conversions obtained with lower concentrations **21** were consistent with those obtained in styrene polymerization with other RAFT agents under the conditions indicated.[54,67]

The impure macro-RAFT agent **23** (contaminated with **25–28**) was used in RAFT polymerization. The GPC chromatograms of both the macro-RAFT agent **23** and P3HT-*block*-PSt **24** are shown in Fig. 2. The assignment of the peak attributed to the P3HT block copolymer was confirmed by UV-visible spectrophotometry and GPC with photodiode array detection (Fig. 2b) which showed that the high molecular weight peak contained both P3HT and polystyrene while the two low molecular weight peaks contained only P3HT (see discussion above). Pure P3HT-*block*-PSt **24** was isolated by recycle GPC.

The perylene diimide macro-RAFT agent **30** was prepared from the styrene derivative **29** by single unit monomer insertion into RAFT agent **18** (Scheme 6). The reaction was performed with 1 : 1 : 0.05 ratio of **29** : **18** : AIBN. The single unit monomer insertion appeared to be quantitative based on **29** and provided a 92% isolated yield after chromatography. This crystalline product **30** was not contaminated by dimers as might be formed by radical-radical termination.



Scheme 6 RAFT agent synthesis from perylene diimide derivative.

The macro-RAFT agent **30** was evaluated in the polymerization of the triarylamine monomer (**31**) and the benzobisthiadiazole derivative (**32**) We have previously reported on the design of **31** and the RAFT homopolymerization of this monomer.[68] There also are several reports on RAFT polymerization of related triarylamine-based monomers in the literature.[69–73] The position of the diphenylamine group *meta* to the styrene double bond and blocking the *para* positions of the phenyl substituents are important in minimizing side reactions during polymerization.[68] The GPC showed that the macro RAFT agent was completely consumed during polymerization, confirming the purity of the

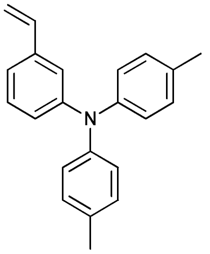
Table 5 Polymerizations with perylene diimide macro-RAFT agent **30**[a]

Reactant mole ratio							
Monomer		**30**	AIBN	Conv.[b] (%)	M_n[c] (calc)	M_n[d]	Đ[e]
31	50	1	0.1	40	6900	8400	1.3
32	20	1	0.1	40	4500	3200	1.2

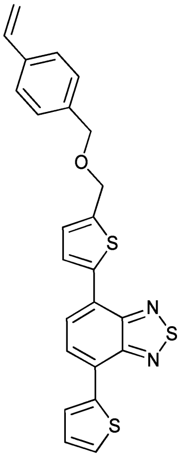
[a] Solution polymerization at 70 °C for 16 h (500 mg **26** with 1.17 g chlorobenzene; 1.0 g **27** with 2.0 g chlorobenzene). [b] Conversions estimated from ^{1}H NMR. [c] Theoretical molecular weights calculated were using the expression M_n(calc) = ([monomer]/[RAFT agent]) × fractional conversion × MW of monomer + MW of RAFT agent. [d] Molecular weights from GPC in polystyrene equivalents. [e] Molecular weight dispersity = M_w/M_n.

RAFT agent, and a high transfer constant for **30** in the polymerization is indicated by the relatively low dispersity obtained (Đ 1.3, Table 5).

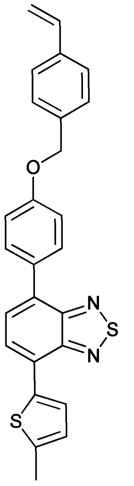
For polymerization of **32** while the dispersity of the block copolymer was also low (Đ 1.2), the molecular weight distribution obtained was distinctly bimodal. Moreover, a contaminant containing the perylene diimide chromophore and with molecular weight similar to **30** is observed by GPC. These observations can be seen as indicative of side reactions involving **32** and again emphasizes the importance of protecting the 2- and 5 positions of thiophene units. The possibility of such side reactions was also indicated in the model studies with compounds **11** and **12** (*vide infra*). The successful RAFT homopolymerization of suitably substituted monomers containing the benzobisthiadiazole unit (*e.g.*, **33**) has been reported elsewhere.[68]



31



32



33

Conclusions

Transformation of a vinyl compound to a macro-RAFT agent provides a route to 'R'-connected block copolymers where the block linkage is short and does not contain hydrolysable ester or amide groups. The method is applicable to vinylthiophene and to St derivatives and has been demonstrated with the preparation of block copolymers containing organic semiconductor segments.§

Organic semiconductors by their nature may be reactive towards radicals. The present work also provides another demonstration of the high reactivity of thiophene units in radical polymerization and the importance of substituting both the 2- and 5-positions of thiophene units in derived (macro)RAFT agents and monomers to minimize side reactions during radical polymerization.

Experimental

Materials and instruments

AIBN (TCI) was recrystallized from methanol. 2-(3-Methylthien-2-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane,[74] 5,5′-dibromo-2,2′-bithiophene,[75] were prepared according to published literature methods. The RAFT agents, 4-(butylthiocarbonothioylthio)-4-cyanopentanoic acid (**18**) and butyl 2-cyanopropan-2-yl-carbonotrithioate (**4**), were synthesized by the method of Thang and coworkers.[76,77] Monomers St, MMA and MA were filtered through basic alumina and flash distilled immediately before use. Catalysts tris(dibenzylideneacetone)dipalladium (Pd_2dba_3) and HP(*t*-Bu)$_3$]BF_4 were obtained from Strem. The *N*,*N*-di-*p*-tolyl-3-vinylaniline (**31**) was prepared as previously described.[68] All other starting materials were obtained from Aldrich and used as received.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Av400 spectrometer (^{1}H 400.13 MHz; ^{13}C 100.63 MHz) at 25 °C in deuterated solvents as stated. Chemical shifts are expressed as parts per million downfield from (external) tetramethylsilane. High resolution Positive ion Electron Impact mass spectra (HRMS-EI) were obtained with a ThermoQuest MAT95XL mass spectrometer using an ionization energy of 70 eV. Accurate mass measurements were obtained with a resolution of 5000-10000 using perfluorokerosene as the reference. High resolution positive ion electrospray mass spectra (HRMS-ESI) were acquired with a Micromass Q-TOF II mass spectrometer using a cone voltage of 50V and a capillary voltage of 3.0kV. The sample was introduced by direct infusion at a rate of 5 μl min^{-1} using NaI as an internal calibrant. Molecular weights were determined by gel permeation chromatography (GPC) performed with tetrahydrofuran (THF, 1.0 mL min^{-1}) as eluent at 30 °C using a Waters GPC instrument equipped with a Waters 2414 refractive index detector, and a Waters 2996 diode array detector, a series of four Polymer Laboratories PLGel columns (3 × Mixed-C and 1 × Mixed-E each 30 cm × 7.5 mm), and Empower Software. The GPC was calibrated with low dispersity polystyrene standards (Polymer Laboratories EasiCal, M_p from 264 to 256000) and molecular weights are reported as polystyrene equivalents. Recycling preparative GPC was performed with a JAI LC-9201 Separations Module equipped with a RI-50s Refractive Index Detector, a UV-3740 Single Wavelength Detector and 2 JAI preparative columns (JAIGEL-2H (20 × 600 mm) and JAIGEL-2.5H (20 × 600 mm)) connected in series at room temperature (~22 °C) with chloroform (3.5 mL min^{-1}) as eluent. Thin layer chromatography (TLC) was performed with silica gel 60 F254 sheets (Merck) and eluting solvent as indicated. Melting points were obtained with a Buchi B-545 melting point apparatus. Ultraviolet-visible absorption spectra (UV) were obtained for solutions in 1 cm path-length quartz cuvettes using a Cary 5E spectrophotometer.

---

§ The synthesis of the RAFT agents **8**, **17**, **20**, **23** and **30** was previously described in a patent application[35] and are mentioned in a recent review.[15]

(3,3‴-Dimethyl-[2,2′:5′,2″:5″,2‴-quaterthiophen]-5-yl)methyl 4-(((butylthio)carbonothioyl)thio)-4-cyanopentanoate (8)

3,3‴-Dimethyl(2,2′:5′,2″:5″,2‴-quaterthiophene) (5). A solution of 5,5′-dibromo-2,2′-bithiophene (2.7 g, 8.3 mmol) and 4,4,5,5-tetramethyl-2-(3-methylthiophen-2-yl)-1,3,2-dioxaborolane (4.1 g, 18.3 mmol) in toluene (100 mL) and *N*,*N*-dimethylformamide (DMF) (80 mL) was carefully degassed by purging with nitrogen. A solution of tripotassium phosphate monohydrate (12.6 g, 55 mmol) in 70 mL water was then added. The resulting emulsion was degassed, and the catalyst system (Pd_2dba_3 [186.6 mg, 0.18 mmol], $[HP(t\text{-Bu})_3]BF_4$ [105 mg, 0.36 mmol]) was added. Afterwards, the mixture was stirred at room temperature overnight. After removal of the toluene solvent under reduced pressure, the mixture was poured into water (300 mL) and was extracted with chloroform (3 × 40 mL). The organic phase was washed with water (30 mL), dried over magnesium sulfate, and the solvent evaporated. Purification by flash chromatography on silica gel [hexane : ethyl acetate = 4 : 1 (v/v)] followed by recrystallization from hexane/dichloromethane yielded yellow crystals of **5** (2.6 g, 87.5%). ^{1}H NMR ($CDCl_3$): δ 7.15 (d, J = 5.2 Hz, 2H, 5,5‴-*H*), 7.13 (d, J = 3.8 Hz, 2H, 3′,4″-*H*), 7.05 (d, 2H, J = 3.8 Hz, 4′,3″-*H*), 6.89 (d, J = 5.2 Hz, 2 H, 4,4‴-*H*), 2.43 (s, 6H, -CH_3). The ^{1}H NMR spectrum was consistent with that reported.[52]

3,3‴-Dimethyl-[2,2′:5′,2″:5″,2‴-quaterthiophene]-5-carbaldehyde (6). Phosphorus oxychloride (1.04 g, 6.8 mmol) was slowly added into a solution of **5** (2.41 g, 6.73 mmol) and DMF (0.51 mL, 6.8 mmol) dissolved in 50 mL dichloromethane. The mixture was stirred for 15 min at room temperature and then heated at 70 °C for 2 h. The dark red solution was then cooled and poured into ice water and neutralized (pH = 7) through the addition of potassium hydroxide. The organic layer was separated and the water phase three times extracted with dichloromethane (30 mL). The combined organic phases were consecutively washed with sodium bicarbonate and brine solution and dried over $MgSO_4$. Purification by silica gel column chromatography with n-hexane : ethyl acetate in a ratio 4 : 1 (v/v) gave red crystals of **6** (1.35 g, 52%). ^{1}H NMR ($CDCl_3$): δ 9.81 (s, 1H, -CHO), 7.54 (s, 1H, 3-*H*), 7.24 (d, J = 3.8 Hz, 1H, 3′-H), 7.17 (m, 3H, 4′,4″,5‴-*H*), 7.06 (d, J = 3.9 Hz, 1H, 3″-*H*), 6.90 (d, 1H, J = 5.1 Hz, 4‴-*H*), 2.48 (s, 3H, 4-CH_3), 2.43 (s, 3H, 3‴-CH_3).

(3,3‴-Dimethyl-[2,2′:5′,2″:5″,2‴-quaterthiophen]-5-yl)methanol (7). To a suspension of **6** (1.35 g, 3.5 mmol) in 30 mL dry ethanol was added 265 mg (7 mmol) sodium borohydride in small portions. The reaction mixture quickly changed colour from orange to yellow and the stirring was continued for 30 min. Removal of the solvent under reduced pressure followed by purification with flash silica gel column chromatography using chloroform as eluent yielded yellow crystals of **7** (1.32 g, 97.2%). ^{1}H NMR ($CDCl_3$): δ 7.15 (d, J = 5.2 Hz, 1H, 5‴-H), 7.13 (dd, J = 3.8 Hz, 2H, 3′,4″-*H*), 7.05 (d, 1H, J = 3.8 Hz, 4′-*H*), 7.02 (d, 1H, J = 3.8 Hz, 3″-*H*), 6.89 (d, J = 5.2 Hz, 1H, 4‴-*H*), 6.81 (s, 1H, 3-*H*), 4.77 (s, 2H, -OCH_2), 2.43 (s, 3H, 3‴-CH_3), 2.38 (s, 3H, 4-CH_3).

(3,3‴-Dimethyl-[2,2′:5′,2″:5″,2‴-quaterthiophen]-5-yl)methyl 4-(((butylthio)carbonothioyl)thio)-4-cyanopentanoate (8). A mixture of **4** (0.53 g, 1.81 mmol) and DCC (0.41 g, 1.98 mmol) was dissolved in dichloromethane (10 mL). After stirring for 15 min, a solution of **7** (0.64 g, 1.65 mmol) and DMAP (8 mg, 0.07 mmol) in dichloromethane (10 mL) was added dropwise. A precipitate was formed immediately. After 4 h, the precipitate was filtered and washed with dichloromethane (5 mL). The filtrate was concentrated by rotary evaporation. The red crude product was further purified by silica gel column chromatography with ethyl acetate : n-hexane = 1 : 4 (v/v) as the eluent to afford the title compound (**8**) as a yellow viscous oil (1.05 g, 96.3% yield). TLC ($CHCl_3$) R_f 0.66. ^{1}H NMR ($CDCl_3$): δ 7.15 (d, J = 5.2 Hz, 1H, 5‴-H), 7.13 (dd, J = 3.8 Hz, 2H, 3′,4″-*H*), 7.05 (dd, 2H, J = 3.8 Hz, 4′,3″-*H*), 6.89 (d, J = 5.2 Hz, 1H, 4‴-*H*), 6.88 (s, 1H, 3-*H*), 5.22 (s, 2H, -OCH_2), 3.33 (t, 2H, J = 7.5 Hz, -SCH_2), 2.67 (m, 2H, C(O)CH_2), 2.56 (m, 1H, CH_2CMeCN), 2.43 (s, 3H, 3‴-CH_3), 2.41 (m, 1H, CH_2CMeCN), 2.38 (s, 3H, 4-CH_3), 1.87 (s, 3H, C(CN)CH_3), 1.68 (m, 2H, SCH_2CH_2), 1.43 (m, 2H, SCH_2CH_2CH_2), 0.93 (t, 3H, J = 7.5 Hz, $SCH_2CH_2CH_2$CH_3). ^{13}C NMR ($CDCl_3$): δ 13.6, 15.5, 22.1, 24.8, 29.7, 29.8, 33.8, 36.7, 46.3, 61.0, 77.2, 119.0, 123.4, 123.8, 124.0, 126.1, 126.3, 130.8, 131.5, 132.6, 132.9, 133.8, 134.2, 134.9, 135.0, 135.8, 136.4, 137.0, 171.2, 216.9 (C=S). HRMS (EI) Found 661.0400 Calculated for $C_{30}H_{31}NO_2S_7$ 661.0394.

α,ω-Dihydroxymethyl-poly(3-hexylthiophene) (16)

α,*ω*-Dihydroxymethyl-poly(3-hexylthiophene) (X_n = 18 by ^{1}H-NMR) was prepared according to procedure of Liu *et al.*[57] the polymer was purified by Soxhlet extraction with methanol (~16 h) and chloroform (~16 h).

α,ω-Bis(((4-(((butylthio)carbonothioyl)thio)-4-cyanopentanoyl)oxy)methyl)-poly(3-hexylthiophene) (17)

A mixture of RAFT agent **4** (0.291 g, 1.0 mmol) and dicyclohexyl carbodiimide (0.25 g, 1.2 mmol) was dissolved in dichloromethane (120 mL). After stirring for 15 min, a solution of **16** (0.3 g, 0.1 mmol) and 4-dimethaminopyridine (4 mg, 0.04 mmol) in dichloromethane (10 mL) was added dropwise. This solution was stirred at room temperature overnight and afterwards concentrated by rotary evaporation. The concentrated solution was precipitated into methanol (100 mL) and a brown solid was obtained, which was filtered and washed with additional methanol (3 × 20 mL) and dried in a vacuum oven until constant weight (0.31 g, 93.9% yield). Due to the additional purification steps and the removal of oligomeric P3HT, X_n as estimated from ^{1}H NMR increased to 21, which was used to calculate the molecular weight of the macro-RAFT agent used in the polymerization (M_n, = 4094). ^{1}H NMR ($CDCl_3$): δ 6.89 (s, Tp-*H*), 5.25 (s, -OCH_2), 3.33 (t, -SCH_2), 2.79 (TpC$H_2C_5H_{11}$), 2.67 (m, C(O)CH_2), 2.56 (m, CH_2CMeCN), 2.41 (m, CH_2CMeCN), 1.87 (s, C(CN)CH_3), 1.70 (m, $TpCH_2$C$H_2C_4H_9$ and SCH_2CH_2),1.43 (m, $TpC_2H_4C_3$$H_6$$CH_3$ and SC_2H_4CH_2), 0.93 (m, Tp-C_5H_{11}-CH_3 and $SCH_2CH_2CH_2$CH_3) (Tp = thiophene).

2-Methyl-5-vinylthiophene (20)

13.9 mL butyl lithium (1.6 M solution in hexane) was added to a solution of methyltriphenylphosphonium bromide (8.5 g, 23.8 mmol) in THF (40 mL). The resulting solution was stirred for 3 h when of 5-methylthiophene-2-carbaldehyde (**19**) (2.0 g, 15.9 mmol) in THF (10 mL) was added. The reaction mixture was stirred overnight then poured into 500 mL ice water. The product was extracted with diethyl ether and the extracts washed with brine and dried over magnesium sulphate. Flash column chromatography on silica gel eluting with hexane/chloroform (5 : 1) gave 2-methyl-5-vinylthiophene (**20**) (0.38 g, 19.1%). ^{1}H NMR ($CDCl_3$): δ 6.74 (d, 1H, *J* = 3.5 Hz, 3 Tp-H), 6.72 (dd, 1H, J = 17.1 and 10.8 Hz, Tp-CH =), 6.60 (d, 1H, *J* = 2.5 Hz, 2 Tp-H), 5.43 (d, 1H, *J* = 17.3 Hz, = C*H*H), 5.04 (d, 1H, *J* = 10.8 Hz, = CH*H*), 2.45 (s, 3H, CH_3).

Butyl (3-cyano-3-methyl-1-(5-methylthiophen-2-yl)butyl) carbonotrithioate (21)

2-Methyl-5-vinylthiophene (**20**) (375 mg, 3.02 mmol), butyl 2-cyanopropan-2-yl-carbonotrithioate **18** (705 mg, 3.02 mmol) and AIBN (5 mg, 0.03 mmol) were placed in an ampoule and the solution degassed through three freeze-pump-thaw cycles. The ampoule was sealed under vacuum and heated in a constant-temperature oil bath at 70 °C for 20 h. The crude product was purified by silica gel flash column chromatography with hexane/chloroform (5 : 1 v/v) as the eluent to provide **21** (730 mg, 67.6%). TLC (hexane/$CHCl_3$ 3 : 1 v/v) R_f 0.16. ^{1}H NMR ($CDCl_3$): δ 6.91 (d, 1H, *J* = 3.4 Hz, 4 Tp-H), 6.60 (d, 1H, 3.4 Hz, 3 T-H), 5.64 (dd, 1H, J = 10.4 and 4.3 Hz, Tp-C*H*CH$_3$), 3.35 (t, 2H, *J* = 7.35, S-CH$_2$), 2.45 (s, 3H, Tp-CH$_3$), 2.33 (m, 2H, Tp-CHC*H*$_2$), 1.67 (m, 2H, S-CH$_2$C*H*$_2$), 1.42 (s, 6H, C(CN)(CH$_3$)$_2$), 1.30 (s, 2H, C*H*$_2$CH$_3$), 0.93 (t, 3H, *J* = 7.3 Hz, CH$_2$C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 13.6, 15.5, 22.0, 26.7, 27.7, 29.9, 31.8, 36.6, 46.3, 47.6, 123.7, 125.1, 127.1, 138.5, 140.7, 221.9 (C═S). HRMS (ESI) Found 380.0592 Calculated for $C_{16}H_{23}NS_4Na^+$ 380.0611.

Synthesis of P3HT-Macro-RAFT agent (23)

A polymerization tube was charged with vinyl-end-functionalized P3HT (**22**)[65,66] (M_n (GPC) 2400, $Đ$ 1.39, 120 mg, 2.44×10^{-5} mol) of butyl 2-cyanopropan-2-yl-carbonotrithioate (11.4 mg, 4.9×10^{-5} mol), AIBN (0.082 mg, 5×10^{-7} mol), and chlorobenzene (1.35 mL). The mixture was degassed through three freeze-pump-thaw cycles, sealed under vacuum and heated in a constant-temperature oil bath at 70 °C for 20 h. The macro-RAFT agent (**23**) was precipitated three times from a large excess of methanol, filtered, washed with methanol, and dried under vacuum to constant mass (45 mg, 36%). ^{1}H NMR ($CDCl_3$): δ 6.98 (s, Tp-H), 5.88 (m, Tp-CH), 3.38 (m, S-CH$_2$), 2.8 (t, Tp-CH$_2$), 2.55 (t, Br-Tp-C*H*$_2$), 1.71 (m, Tp-CH$_2$C*H*$_2$), 1.44 and 1.35 (m, CH$_2$ of hexyl and butyl groups), 0.94 (m, CH$_3$ of hexyl and butyl groups). Expansions of the NMR spectrum are shown in Fig. 1. The GPC chromatogram is shown in Fig. 2.

N′-(Di-2,5-*tert*-butylphenyl)-*N*-(4-vinylbenzyl)perylene diimide (29)

A mixture of *N*-(di-2,5-*tert*-butylphenyl)perylene diimide**[78]** (1.0 g, 1.7 mmol), 4-vinylbenzyl chloride (0.40 g, 2.6 mmol) in t K_2CO_3 (2.3 g, 17.5 mmol) in DMF (20 mL) was heated for 16 h at 70 °C. Purification by flash silica gel column chromatography, using dichloromethane as the eluent, yielded red crystals of **29** (0.95 g, 80%) m.p. 233–235 °C. ^{1}H NMR ($CDC1_3$): δ 8.61 (d, 2H, *J* = 8.0 Hz, perylene-H), 8.30 (dd, 4H, *J* = 8.0, 5.3 Hz, perylene -H), 8.12 (d, 2H, *J* = 8.2 Hz, perylene -H), 7.60 (d, 1H, *J* = 8.7 Hz, Ph-H), 7.47–7.53 (m, 3H, Ph-H), 7.36 (d, 2H, *J* = 8.2, Ph-H), 7.33 (d, 1H, *J* = 2.3 Hz, Ph–H), 6.73 (dd, 1H, J = 17.6 and 10.9 Hz, ═C*H*H), 5.76 (d, 1H, *J* = 17.6 Hz, ═CH*H*), 5.31 (s, 2H, St-C*H*$_2$-*N*-), 5.25 (d, 1H, *J* = 10.9 Hz, C*H*═CH$_2$), 1.36 (s, 9H, -C(C*H*$_3$)$_3$), 1.29 (s, 9H, -C(C*H*$_3$)$_3$). ^{13}C NMR ($CDCl_3$) δ 31.3, 31.8, 34.4, 35.5, 43.5, 114.0, 122.8, 122.9, 123.7, 125.7, 126.1, 126.3, 126.4, 128.0, 128.7, 129.5, 129.6, 131.0, 131.5, 132.6, 134.1, 134.2, 136.4, 136.6, 137.1, 143.7, 150.3, 162.9, 164.2. UV (dichloromethane): λ_{max} 528, 489, 457 nm. HRMS (EI) Found 694.2804 Calculated for $C_{47}H_{38}N_2O_4$ 694.2826.

Perylene diimide based macro-RAFT agent (30)

A solution of above monomer (**29**) (0.50 g, 0.7 mmol) **18** (0.16 g, 0.7 mmol) and AIBN (6 mg, 0.035 mmol, ~5 mol%) in chlorobenzene (3 mL) was placed in an ampoule which was degassed through three freeze-thaw evacuate cycles then heated 16 h at 70 °C. The product was purified by flash column chromatography on silica gel with dichloromethane as the eluent to yield red crystals of **30** (0.60 g, 92%) m.p. 217–219 °C. TLC ($CHCl_3$) R_f 0.07. ^{1}H NMR ($CDC1_3$): δ 8.67 (b, 2H, perylene-H), 8.46 (b, 4H, perylene-H), 8.33(b, 2H, perylene-H), 7.20 (b, 1H, Ph-H), 5.42 (m, 1H, -S-C*H*(Ph)-CH2-), 5.35 (s, 2H, Ph-C*H*$_2$-*N*-), 3.26 (t, 2H, *J* = 7.45 Hz, -CH$_2$-C*H*$_2$-S-), 2.34 (m, 2H, -CH(Ph)-C*H*$_2$-C-), 1.36 (s, 9H, -C(C*H*$_3$)$_3$), 1.34 (s, 6H,–C(CN)(C*H*$_3$)$_2$), 1.29 (s, 9H, -C(C*H*$_3$)$_3$), 0.86 (t. 3H, *J* = 7.3 Hz, -CH$_2$C*H*$_3$). ^{13}C NMR ($CDCl_3$) δ 13.5, 22.0, 27.1, 27.6, 29.9, 31.2, 31.7, 31.9, 34.3, 35.5, 36.6, 43.3, 45.2, 51.6, 123.0, 123.1, 123.7, 123.9, 126.1, 126.4, 127.9, 128.5, 128.8, 129.1, 129.7, 130.0, 131.3, 131.7, 132.6, 134.4, 134.5, 137.3, 138.2, 143.7, 150.2, 163.1, 164.3, 221.7. UV (dichloromethane): λ_{max} 528, 482, 462, 313 nm. HRMS (ESI) Found 950.3038 Calculated for $C_{24}H_{18}N_2OS_3Na^+$ 950.3096.

RAFT Polymerization

Prior to polymerization the monomers were flash distilled. The monomer, AIBN, RAFT agent and solvent (concentrations as indicated in Table 1–Table 5) were combined in an ampoule which was degassed through three freeze-pump-thaw cycles, sealed under vacuum and heated in a thermostatted oil bath for the stated time. Polymerization was terminated by rapidly cooling the ampoule. A small sample of the reaction mixture was retained to determine the monomer conversion by ^{1}H NMR spectroscopy. The polymers were precipitated three times by addition into a rapidly stirred large excess of non-solvent (methanol for St and n-hexane for MA and MMA), filtered, washed with non-solvent, and dried in vacuum to constant mass. The conditions, conversions and molecular weights of the polymers obtained are shown in Table 1–Table 5.

Notes and references

1 J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo and S. H. Thang, *Macromolecules*, 1998, **31**, 5559–5562.
2 T. P. Le, G. Moad, E. Rizzardo and S. H. Thang, Polymerization with living characteristics, DuPont/CSIRO, WO9801478, 1998.
3 G. Moad, E. Rizzardo and S. H. Thang, *Polymer*, 2008, **49**, 1079–1131.
4 G. Moad, E. Rizzardo and S. H. Thang, *Acc. Chem. Res.*, 2008, **41**, 1133–1142.
5 G. Moad, E. Rizzardo and S. H. Thang, *Aust. J. Chem.*, 2005, **58**, 379–410.

This journal is © The Royal Society of Chemistry 2011

6 G. Moad, E. Rizzardo and S. H. Thang, *Aust. J. Chem.*, 2006, **59**, 669–692.

7 G. Moad, E. Rizzardo and S. H. Thang, *Aust. J. Chem.*, 2009, **62**, 1402–1472.

8 A. Favier and M.-T. Charreyre, *Macromol. Rapid Commun.*, 2006, **27**, 653–692.

9 S. Perrier and P. Takolpuckdee, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 5347–5393.

10 C. Boyer, V. Bulmus, T. P. Davis, V. Ladmiral, J. Liu and S. Perrier, *Chem. Rev.*, 2009, **109**, 5402–5436.

11 G. Moad, E. Rizzardo and S. H. Thang, *Polym. Int.*, 2011, **60**, 9–25.

12 A. D. Jenkins, R. I. Jones and G. Moad, *Pure Appl. Chem.*, 2010, **82**, 483–491.

13 T. R. Darling, T. P. Davis, M. Fryd, A. A. Gridnev, D. M. Haddleton, S. D. Ittel, R. R. Matheson Jr., G. Moad and E. Rizzardo, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 1706–1708.

14 R. P. Quirk and B. Lee, *Polym. Int.*, 1992, **27**, 359–367.

15 G. Moad, M. Chen, M. Häussler, A. Postma, E. Rizzardo and S. H. Thang, *Polym. Chem.*, 2011, **2**, 492–519.

16 M. Sommer, S. Huettner and M. Thelakkat, *J. Mater. Chem.*, 2010, **20**, 10788–10797.

17 C. Brochon and G. Hadziioannou, *ACS Symp. Ser.*, 2009, **1023**, 243–256.

18 C. Park, J. Yoon and E. L. Thomas, *Polymer*, 2003, **44**, 6725–6760.

19 H.-C. Kim, S.-M. Park and W. D. Hinsberg, *Chem. Rev.*, 2010, **110**, 146–177.

20 I. Botiz and S. B. Darling, *Mater. Today*, 2010, **13**, 42–51.

21 F. S. Bates and G. H. Fredrickson, *Annu. Rev. Phys. Chem.*, 1990, **41**, 525–557.

22 S. B. Darling, *Energy Environ. Sci.*, 2009, **2**, 1266–1273.

23 K. Sivula, Z. T. Ball, N. Watanabe and J. M. J. Fréchet, *Adv. Mater.*, 2006, **18**, 206–210.

24 S. Rajaram, P. B. Armstrong, B. J. Kim and J. M. J. Frechet, *Chem. Mater.*, 2009, **21**, 1775–1777.

25 R. A. Segalman, B. McCulloch, S. Kirmayer and J. J. Urban, *Macromolecules*, 2009, **42**, 9205–9216.

26 U. Scherf, A. Gutacker and N. Koenen, *Acc. Chem. Res.*, 2008, **41**, 1086–1097.

27 B. D. Olsen and R. A. Segalman, *Mater. Sci. Eng., R*, 2008, **62**, 37–66.

28 M. C. Iovu, C. R. Craley, M. Jeffries-El, A. B. Krankowski, R. Zhang, T. Kowalewski and R. D. McCullough, *Macromolecules*, 2007, **40**, 4733–4735.

29 C. Yang, J. K. Lee, A. J. Heeger and F. Wudl, *J. Mater. Chem.*, 2009, **19**, 5416–5423.

30 K. Palaniappan, N. Hundt, P. Sista, H. Nguyen, J. Hao, M. P. Bhatt, Y.-Y. Han, E. A. Schmiedel, E. E. Sheina, M. C. Biewer and M. C. Stefan, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 1802–1808.

31 Y. K. Chong, G. Moad, E. Rizzardo and S. H. Thang, *Macromolecules*, 2007, **40**, 4446–4455.

32 J. P. S. Farinha, P. Relogio, M.-T. Charreyre, T. J. V. Prazeres and J. M. G. Martinho, *Macromolecules*, 2007, **40**, 4680–4690.

33 M. Chen, K. P. Ghiggino, E. Rizzardo, S. H. Thang and G. J. Wilson, *Chem. Commun.*, 2008, 1112–1114.

34 A. D. Kitchin, S. Velate, M. Chen, K. P. Ghiggino, T. A. Smith and R. P. Steer, *Photochem. Photobiol. Sci.*, 2007, **6**, 853–856.

35 M. Chen, G. Moad, E. Rizzardo, R. A. Evans and M. Haeussler, Conducting and Semiconducting Organic Materials, CSIRO, WO2009155657A1, 2009.

36 C. D. Grande, M. C. Tria, G. Jiang, R. Ponnapati and R. Advincula, *Macromolecules*, 2011, **44**, 966–975.

37 S. Z. Zard, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 672–685.

38 B. Quiclet-Sire and S. Z. Zard, *Top. Curr. Chem.*, 2006, **264**, 201–236.

39 B. Quiclet-Sire and S. Z. Zard, *Chem.–Eur. J.*, 2006, **12**, 6002–6016.

40 B. Quiclet-Sire and S. Z. Zard, *Org. Lett.*, 2008, **10**, 3279–3282.

41 F. Lebreux, B. Quiclet-Sire and S. Z. Zard, *Org. Lett.*, 2009, **11**, 2844–2847.

42 B. Quiclet-Sire, G. Revol and S. Z. Zard, *Tetrahedron*, 2010, **66**, 6656–6666.

43 M. Chen, K. P. Ghiggino, A. W. H. Mau, E. Rizzardo, W. H. F. Sasse, S. H. Thang and G. J. Wilson, *Macromolecules*, 2004, **37**, 5479–5481.

44 J. B. McLeary, F. M. Calitz, J. M. McKenzie, M. P. Tonge, R. D. Sanderson and B. Klumperman, *Macromolecules*, 2004, **37**, 2383–2394.

45 J. B. McLeary, F. M. Calitz, J. M. McKenzie, M. P. Tonge, R. D. Sanderson and B. Klumperman, *Macromolecules*, 2005, **38**, 3151–3161.

46 J. B. McLeary, J. M. McKenzie, M. P. Tonge, R. D. Sanderson and B. Klumperman, *Chem. Commun.*, 2004, 1950–1951.

47 J. B. McLeary, M. P. Tonge and B. Klumperman, *Macromol. Rapid Commun.*, 2006, **27**, 1233–1240.

48 G. Pound, J. B. McLeary, J. M. McKenzie, R. F. M. Lange and B. Klumperman, *Macromolecules*, 2006, **39**, 7796–7797.

49 E. T. A. van den Dungen, H. Matahwa, J. B. McLeary, R. D. Sanderson and B. Klumperman, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 2500–2509.

50 E. T. A. van den Dungen, J. Rinquest, N. O. Pretorius, J. M. McKenzie, J. B. McLeary, R. D. Sanderson and B. Klumperman, *Aust. J. Chem.*, 2006, **59**, 742–748.

51 G. Moad, Y. K. Chong, R. Mulder, E. Rizzardo and San H. Thang, *ACS Symp. Ser.*, 2009, **1024**, 3–18.

52 P. A. Chaloner, S. R. Gunatunga and P. B. Hitchcock, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1597–1604.

53 R. G. Gilbert, M. Hess, A. D. Jenkins, R. G. Jones, P. Kratochvíl and R. F. T. Stepto, *Pure Appl. Chem.*, 2009, **81**, 351–353.

54 Y. K. Chong, J. Krstina, T. P. T. Le, G. Moad, A. Postma, E. Rizzardo and S. H. Thang, *Macromolecules*, 2003, **36**, 2256–2272.

55 G. Moad and D. H. Solomon, *The Chemistry of Radical Polymerization*, Elsevier, Oxford, 2006, pp. 11–48.

56 H. Fischer and L. Radom, *Angew. Chem., Int. Ed.*, 2001, **40**, 1340–1371.

57 J. Liu, E. Sheina, T. Kowalewski and R. D. McCullough, *Angew. Chem., Int. Ed.*, 2002, **41**, 329–332.

58 J. C. Bevington, T. N. Huckerby, M. G. Liu and F. G. Thorpe, *Eur. Polym. J.*, 1987, **23**, 95–97.

59 M. E. Randazzo, L. Toppare and J. E. Fernandez, *Macromolecules*, 1994, **27**, 5102–5106.

60 R. M. O'Malley, M. E. Randazzo, J. E. Weinzierl, J. E. Fernandez, L. M. Nuwaysir, J. A. Castoro and C. L. Wilkins, *Macromolecules*, 1994, **27**, 5107–5113.

61 D. L. Trumbo, *Polym. Bull.*, 1996, **36**, 463–469.

62 M. Melucci, M. Zambianchi, A. Zanelli, N. Camaioni, M. Gazzano, A. Bongini and G. Barbarella, *ChemPhysChem*, 2007, **8**, 2621–2626.

63 M. Melucci, G. Barbarella, M. Zambianchi, M. Benzi, F. Biscarini, M. Cavallini, A. Bongini, S. Fabbroni, M. Mazzeo, M. Anni and G. Gigli, *Macromolecules*, 2004, **37**, 5692–5702.

64 H. Mori, K. Takano and T. Endo, *Macromolecules*, 2009, **42**, 7342–7352.

65 M. Jeffries-El, G. Sauvé and R. D. McCullough, *Macromolecules*, 2005, **38**, 10346–10352.

66 M. C. Iovu, M. Jeffries-El, E. E. Sheina, J. R. Cooper and R. D. McCullough, *Polymer*, 2005, **46**, 8582–8586.

67 J. Chiefari, R. T. A. Mayadunne, C. L. Moad, G. Moad, E. Rizzardo, A. Postma, M. A. Skidmore and S. H. Thang, *Macromolecules*, 2003, **36**, 2273–2283.

68 M. Häussler, P. Lok, M. Chen, J. Jasieniak, R. Adhikari, S. King, S. Haque, C. M. Forsyth, K. Winzenberg, S. E. Watkins, E. Rizzardo and G. J. Wilson, *Macromolecules*, 2010, **43**, 7101–7010.

69 M. Zorn, W. K. Bae, J. Kwak, H. Lee, C. Lee, R. Zentel and K. Char, *ACS Nano*, 2009, **3**, 1063–1068.

70 M. Zorn and R. Zentel, *Macromol. Rapid Commun.*, 2008, **29**, 922–927.

71 P. E. Williams, A. O. Moughton, J. P. Patterson, S. Khodabakhsh and R. K. O'Reilly, *Polym. Chem.*, 2011, **2**, 720–729.

72 D. Kessler, M. C. Lechmann, S. Noh, R. Berger, C. Lee, J. S. Gutmann and P. Theato, *Macromol. Rapid Commun.*, 2009, **30**, 1238–1242.

73 M. C. Lechmann, D. Kessler and J. S. Gutmann, *Langmuir*, 2009, **25**, 10202–10208.

74 J. Cremer, E. Mena-Osteritz, N. G. Pschierer, K. Mullen and P. Bauerle, *Org. Biomol. Chem.*, 2005, **3**, 985–995.

75 P. Bauerle, F. Pfau, H. Schlupp, F. Wurthner, K.-U. Gaudl, M. B. Caro and P. Fischer, *J. Chem. Soc., Perkin Trans. 2*, 1993, 489–494.

76 S. H. Thang, Y. K. Chong, R. T. A. Mayadunne, G. Moad and E. Rizzardo, *Tetrahedron Lett.*, 1999, **40**, 2435–2438.

77 G. Moad, Y. K. Chong, E. Rizzardo, A. Postma and S. H. Thang, *Polymer*, 2005, **46**, 8458–8468.

78 H. Langhals and S. Saulich, *Chem.–Eur. J.*, 2002, **8**, 5630–5643.