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Monotelechelic poly(*p*-phenylenevinylene)s by ring opening metathesis polymerisation†

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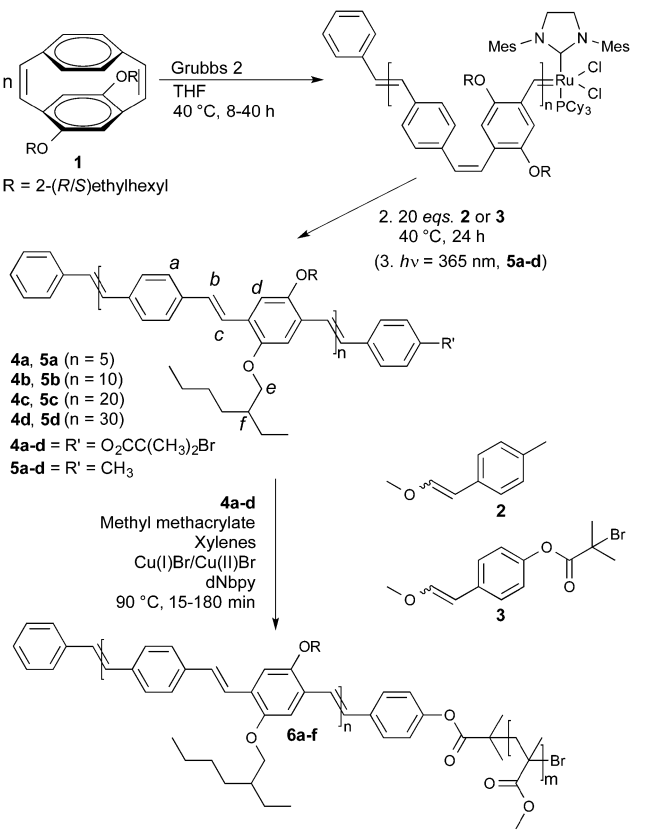
Poly(*p*-phenylenevinylene)s (PPVs) with single reactive end groups have been prepared with high molecular weights, narrow polydispersities ($Đ_M$) and excellent end functionality (*f*). PPVs functionalised with α-bromoester end groups are effective macroinitiators in the atom transfer radical polymerisation (ATRP) of methyl methacrylate (MMA).

The use of π-conjugated polymers as the active layer in electronic devices has been the subject of intense research over the past 20 years.[1] Precise control of both the backbone microstructure and end groups in this important class of polymers is a considerable challenge, principally due to a scarcity of well-controlled routes for their synthesis. Current notable examples include nickel catalysed Grignard metathesis polymerisation to give poly(thiophene)s and palladium catalyst transfer Suzuki–Miyaura polycondensation to give poly(fluorene)s and poly(*p*-phenylene)s.[2] End group control afforded by such routes can lead to improved stability and optimisation of the photophysical and electronic properties, *e.g.* elimination of reactive groups, minimisation of charge trapping and tuning of the band gap.[3] Reactive end groups also provide access to block copolymers *via* the 'grafting to' and 'grafting from' methodologies.[4] The structure-driven self-assembly of block copolymers (containing one or more π-conjugated segments) holds great promise in organic electronics, where the thin-film morphology of the active material has a dramatic influence on the overall device performance.[5]

PPVs remain a popular choice of π-conjugated polymer in organic electronic devices due to their favorable electronic and optical properties.[6] Synthetic routes to PPVs, while numerous, are usually uncontrolled; giving broad $Đ_M$, poorly defined end groups and non-conjugated defects.[7] Controlled polymerisations to PPVs are restricted to precursor routes or limited by the achievable molecular weight.[8] The exception is the ROMP of substituted cyclophanedienes and cyclophanetrienes, which provides a direct route to defect-free, structurally defined PPVs of predetermined M_n and narrow $Đ_M$.[9] Conjugated diblock copolymers with two different phenylenevinylene segments have also been prepared *via* this route.[10] In an extension of this work, we report the preparation of monotelechelic PPVs bearing α-bromoester and tolyl end groups. The α-bromoester end functionalised PPVs have further been used as macroinitiators in ATRP, giving a series of PPV-*b*-PMMA copolymers that retain the desirable optical properties (Scheme 1).



Scheme 1 Synthesis of α-bromoester and tolyl functionalised monotelechelic PPVs **4a–d** and **5a–d** and the corresponding PPV-*b*-PMMA diblock copolymers **6a–f**.

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† Electronic supplementary information (ESI) available: Synthesis of cyclophanediene **1**, vinyl ether **3**, polymers **4a–d**, **5a–d** and **6a–f**. MALDI-TOF-MS of polymer **5b**, molecular weight distribution of polymers **4a–d**, **5a–d**, and GPC chromatograms of block copolymers **6a–f**. See DOI: 10.1039/c4cc05118a

The monomer 4,7-diethylhexyloxy-[2.2]paracyclophane-1,9-diene (**1**) was prepared by a modification of the previously reported procedure.[11] The ROMP of cyclophanediene **1** was initiated using the Grubbs 2 complex in THF at 40 °C. The number average degree of polymerisation (x_n) was effectively controlled by changing the [**1**]/[Grubbs 2] ratio, as expected for a living polymerisation. In previous reports, quenching of the active ruthenium carbene chain end with an excess of ethyl vinyl ether resulted in each PPV chain containing a vinyl and a phenyl end group.[9a] Monotelechelic PPVs with one functional end group should therefore be prepared by quenching the polymerisation with vinyl ethers carrying the desired functionality. The ROMP of cyclophanediene **1** is efficiently quenched on addition of 20 eq. of either α-bromoester functionalised vinyl ether **2** or tolyl functionalised vinyl ether **3**, at 40 °C for 24 hours. α-Bromoester functionalised polymers **4a–d** and the corresponding tolyl terminated homopolymers **5a–d** were isolated as orange films in excellent yields (83–90%), after purification by multiple precipitations onto a short methanol/Celite column and extraction with hot chloroform. ^{1}H NMR spectroscopy of polymer **4b** confirmed the incorporation of the α-bromoester group with a sharp singlet at 2.09 ppm corresponding to the two CH_3 groups of the ester (Fig. 1(a)). The OCH_2 of the main polymer chain are observed at 3.49 and 3.98 ppm, corresponding to adjacent vinylene bonds in the *Z* and *E* stereochemistry, respectively (other key signals are assigned in Fig. 1(a)).[12] The end group functionalisation (f) was calculated by integration of the two CH_3 groups of the terminal α-bromoester group against H–*f*. For example in polymer **4b** the expected integrals from the ratio of [**1**]/[Grubbs 2] are 6.0 : 20.0 and the observed integrals are 6.0 : 20.7, indicating a value for *f* of 97%. All values of *f* are above 90% for polymers **4a–d** and above 85% for polymers **5a–d** (Table 1). Typically in ROMP *f* is determined by integration of key signals associated with each end group, however in this instance signals for the phenyl end group (derived from the Grubbs 2 initiating species) are obscured due to overlap with signals of the polymer backbone.[13] Only one vinylene bond of cyclophanediene **1** is subject to metathesis, so the expected polymer backbone microstructure should consist of alternating *E*/*Z*-vinylene bonds.[9a] Surprisingly, and conveniently, polymers **4a–d** were isolated with the all *E*-vinylene stereochemistry (97% as determined by ^{1}H NMR spectroscopy), probably due to isomerisation during work-up. Polymers **5a–d** were obtained in the all *E*-vinylene stereochemistry after photoisomerisation.[10]

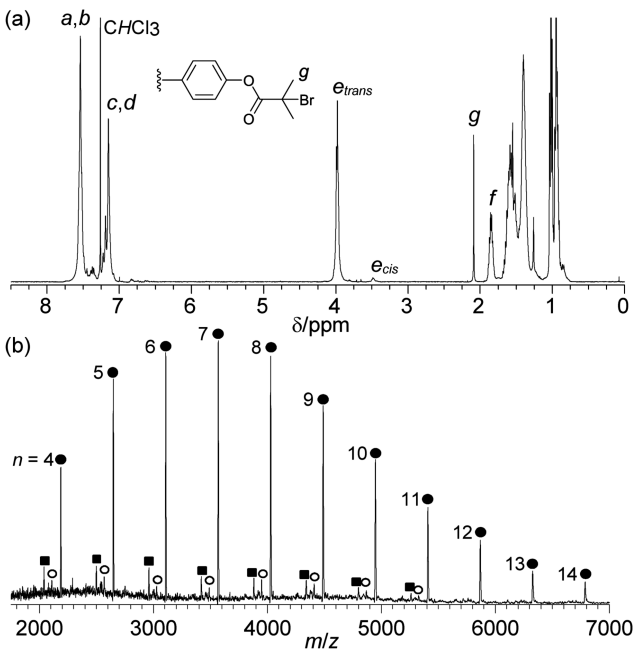

Fig. 1 (a) ^{1}H NMR spectrum of polymer **4b**, (b) MALDI-TOF-mass spectrum of polymer **4b** (x_n indicated).

Matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry (MALDI-TOF-MS) of the isolated polymer **4b** exhibited one major series corresponding to polymer chains with both α-bromoester and phenyl end groups (●), with the major series of peaks separated by the mass of the polymer repeat unit (461 Da) (Fig. 1(b)). Two additional minor series were observed; corresponding to polymers with a phenol end group, derived from the cleavage of the terminal ester bond (■) and a vinyl end group by elimination of hydrogen bromide (○).[14] The relative intensity of these two series was observed to increase with increasing laser power, suggesting that they result from fragmentation during the MALDI experiment (ESI†). For polymer **4b** no species were observed with a carbonyl end group, resulting from the decomposition of the ruthenium carbene chain end or polymers with a methyl vinyl ether end group. Species resulting from secondary metathesis were observed to occur in low abundance, as has previously reported.[10]

Gel permeation chromatography (GPC) analysis of polymers **4a–d** and **5a–d** exhibited a linear correlation between the M_n and the [**1**]/[Grubbs 2] ratio, indicating no loss of control during the polymerisation or importantly during the termination reaction (ESI†). Polymers **4a–d** were isolated with unimodal distributions and $Đ_M$ in the range of 1.36–1.51. As polymers **4a–d** were isolated predominantly in the all *E*-vinylene stereochemistry, an increase in the hydrodynamic volume of the chains over that of a simple random coil is observed. The apparent M_n values are approximately two times greater than that of the predicted M_n, when measured against the polystyrene calibration standards.

The controlled radical polymerisation of activated vinyl monomers using ATRP gives well-defined polymers (*e.g.* PMMA), that are not easily accessible using ROMP.[15] Block copolymers can be prepared using this polymerisation technique by the use of a suitably functionalised macroinitiators. Polymers **4a–d** were found to be effective macroinitiators for ATRP of MMA, resulting in PPV-*b*-PMMA block copolymers (**6a–f**) with excellent control of both segments. Although polymers **4a–d** are readily soluble in dilute solutions of solvents such as THF, $CHCl_3$, CH_2Cl_2, they are not fully soluble at the concentrations typically used in ATRP. Hence the synthesis of the diblock copolymers was performed with concentration of polymers **4a–d** of between 1.7–11.1 mM, using a solution of [MMA] : [xylenes] : [Cu(I)Br] : [Cu(II)Br_2] : [dNbpy] = [800] : [800] : [1] : [0.05] : [2] at 40 °C. The polymerisation was initiated by heating to 90 °C, with longer reaction times required to obtain polymers with higher molecular weight PMMA segments.

ATRP was terminated by exposure to air and the polymeric products purified by precipitation into methanol, followed by reprecipitation into diethyl ether from chloroform. The desired

Table 1 Summarised molecular weight data, values of *f* and optical properties of polymers; **4a–d**, **5a–d** and **6a–f**

Polymer	x_n[a] (PPV)	M_n[a] (kg mol^{-1})	x_m[b] (PMMA)	M_n (kg mol^{-1})	$Đ_M$[c]	f[b] (%)	λ_{max} (nm)	λ_{em}[d] (nm)	PLQY[d]
4a	5	2.6	—	4.7[c]	1.36	92	—	—	—
4b	10	5.0	—	9.0[c]	1.51	97	—	—	—
4c	20	9.6	—	22.8[c]	1.44	100	—	—	—
4d	30	14.1	—	39.0[c]	1.45	93	—	—	—
5a	5	2.5	—	3.7[c]	1.50	95	470	525	0.58
5b	10	4.8	—	8.8[c]	1.51	94	476	526	0.64
5c	20	9.4	—	18.8[c]	1.47	85	482	527	0.65
5d	30	14.0	—	37.4[c]	1.30	88	484	528	0.65
6a	5	—	800	82.7[b]	1.19	—	466	525	0.59
6b	10	—	750	79.9[b]	1.33	—	476	528	0.58
6c	20	—	450	54.5[b]	1.32	—	481	529	0.63
6d	20	—	800	87.6[b]	1.28	—	483	529	0.64
6e	20	—	1350	143.6[b]	1.31	—	483	529	0.67
6f	30	—	800	90.1[b]	1.31	—	486	529	0.66

[a] Calculated from the [**1**]/[Grubbs 2] ratio, inc. expected end groups. [b] Determined by ^{1}H NMR spectroscopy. [c] Determined by GPC with RI detection (calibrated against narrow $Đ_M$ polystyrene standards). [d] λ_{Ex} = 470 nm, against fluorescein standards (0.1 M sodium hydroxide$_{(aq)}$), in DCM.

diblock copolymers **6a–f** were isolated as bright orange powders.

The ^{1}H NMR spectrum of diblock copolymer **6c** obtained from the corresponding macroinitiator **4c**, (Fig. 2(a)) clearly displays peaks associated with both the PPV and PMMA segments. ^{1}H NMR spectroscopy was used to determine the x_n of the PMMA segment by integration of the OCH_3 of PMMA against the OCH_2 of the PPV segment. For the diblock copolymer **6c** a x_m = 450 for the PMMA segment was calculated, resulting in an assigned structure of PPV$_{20}$-*b*-PMMA$_{450}$.

Representative GPC chromatograms for macroinitiator **4c** and the corresponding diblock copolymer **6c** are shown in Fig. 2(b). The $Đ_M$ was observed to decrease from 1.44 for macroinitiator **4c** to 1.32 for polymer **6c**, with an apparent M_n = 46.0 kg mol^{-1} and is consistent with a controlled chain growth polymerisation. As PPV is strongly absorbing in the ultraviolet-visible region and PMMA is not, use of GPC equipped with both a UV-Vis detector (set at 450 nm) and a refractive index (RI) detector allowed for the detection of any residual macroinitiator **4c** and for possible side reactions during the ATRP. The GPC trace for block copolymer **6c** (Fig. 2(b)) shows no residual macroinitiator **4c** and concurrent unimodal distributions on both the RI and UV-Vis detectors. The absence of macroinitiator **4c** indicates a high degree of initiation in addition to the selective precipitation of the diblock copolymer **6c**. No evidence for termination by radical–radical coupling was observed, which would result in PPV-*b*-PMMA-*b*-PPV triblock copolymers. Slight tailing on the low molecular weight side, in particular to the UV-Vis chromatogram can be attributed to a small contribution from competing termination reactions, which are commonly observed in ATRP. The discrepancy between the apparent M_n from GPC and the M_n calculated from ^{1}H NMR spectroscopy is due to the hydrodynamic volume of the diblock copolymer **6c** being dominated by the rigid PPV segment.

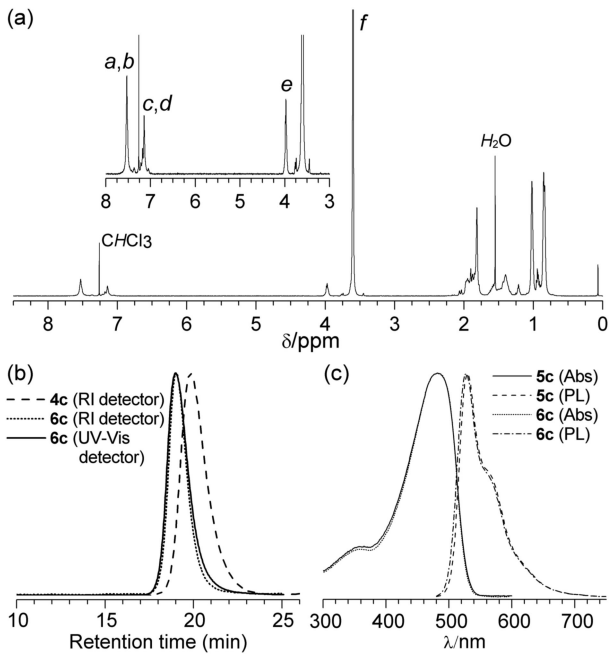

Fig. 2 (a) ^{1}H NMR spectrum of polymer **6c**, (b) GPC chromatograms of polymer **4c** and diblock copolymer **6c**, (c) UV-Vis absorption and PL spectra of diblock copolymer **6c** and the corresponding homopolymer **5c**.

The influence of the relative block lengths of the PPV-*b*-PMMA copolymers on the solution-phase optical properties, was studied by preparation of a series of polymers, **6a–f**, with varying PPV (*n*) and PMMA (*m*) block lengths. The UV-Vis and photoluminescence (PL) spectra and photoluminescence quantum yields (PLQY) were measured (molecular weight data in Table 1, *n* values were determined from [**1**]/[Grubbs 2] ratio, *m* values are rounded to the nearest 50 for ease of comparison). As expected, a red shift in the λ_{max} of the polymers was observed on increasing the conjugation length of the PPV block.

The length of the PMMA block has no discernible influence on the position of the maximum absorption (Table 1). Only a slight increase in the PLQY with increasing x_n of the PPV segment was observed and no significant variation with increasing x_n of the PMMA segment. For comparison, a series of polymers **5a–d** with similar PPV block lengths to each of the block-copolymers were also studied. Fig. 2(c) shows the UV-Vis and PL spectra of block copolymer **6c** and homopolymer PPV$_{20}$. It highlights the very close similarity of the absorption and emission profiles of the block copolymer and the corresponding homopolymer. Furthermore, there were no significant differences in PLQY between the diblock

copolymers and homopolymers, providing further evidence that the PPV conjugated backbone is not degraded by the ATRP reaction conditions.

In summary high molecular weight poly(*p*-phenylenevinylene-2,5-diethylhexyloxy-*p*-phenylenevinylene)s with functional end groups can be prepared by the termination of a living ROMP of cyclophanedienes with suitably functionalised vinyl ethers. Excellent control of the molecular weight, narrow $Đ_M$ and a high *f* are possible using this route. Functionalisation with α-bromoester groups results in PPVs which are effective macroinitiators for the ATRP of methyl methacrylate. PPV-*b*-PMMA diblock copolymers were obtained with unimodal distributions, narrow $Đ_M$, which are free from any residual PPV homopolymer. The solution-phase self-assembly and solid-state morphologies of these diblock copolymers are currently under investigation.

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