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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 (Dn) 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 polythiophenes and palladium-catalyst transfer Suzuki–Miyaura polycodensation to give poly(fluorenes) and poly(p-phenylenevinylene)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 DMn, 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 Mn and narrow Dn.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.

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 (xn) 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.12 Monotelechelic PPVs with 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 eqs. 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. 1H NMR spectroscopy of polymer 4b confirmed the incorporation of the α-bromoester group with a sharp singlet at 2.09 ppm corresponding to the terminal ester bond (Fig. 1, (b)). The OC\(^{-}\)-bonding to isomerisation during work-up. Polymers 5a-d were obtained in the all E-vinylene stereochemistry after photoisomerisation.\(^{10}\) 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(O).\(^{14}\) 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 (supplementary information). 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.\(^{15}\)

Fig. 1.  (a) 'H NMR spectrum of polymer 4b, (b) MALDI-TOF-mass spectrum of polymer 4b (\(\delta_n\) indicated).

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\(_2\)Cl\(_2\), 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]\(_2\):[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 diblock copolymers 6a-f were isolated as bright orange powders.
The 1H 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. 1H NMR spectroscopy was used to determine the $x_m$ 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. 2b. The $D_n$ 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 1H NMR spectroscopy is due to the hydrodynamic volume of the diblock copolymer 6c being dominated by the rigid PPV segment.

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 1H NMR spectroscopy, determined by GPC with RI detection (calibrated against narrow $D_n$ polystyrene standards), $\lambda_{max} = 470$ nm, against fluorescein standards (0.1 M sodium hydroxide, in DCM).

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 $x_m$ of the PPV segment was observed on increasing the conjugation length of the PPV block.

### Table 1. Summarised molecular weight data, values of $f$ and optical properties of polymers; 4a-d, 5a-d and 6a-f.

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<th>Polymer</th>
<th>$x_m$ (PPV)$^a$</th>
<th>$M_n$ (kg mol$^{-1}$)$^a$</th>
<th>$x_m$ (PMMA)$^a$</th>
<th>$M_n$ (kg mol$^{-1}$)$^a$</th>
<th>$D_n$</th>
<th>f (%)</th>
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$^a$ Calculated from the [1]/[Grubbs 2] ratio, inc. expected end groups, $^a$ determined by 1H NMR spectroscopy, $^a$ determined by GPC with RI detection (calibrated against narrow $D_n$ polystyrene standards), $^{λ_{max}} = 470$ nm, against fluorescein standards (0.1 M sodium hydroxide, in DCM).

### Fig. 2. (a) 1H 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 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 $x_m$ of the PPV segment was observed on increasing the conjugation length of the PPV block.
observed and no significant variation with increasing $x_b$ 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 6e and homopolymer PPV 3b. 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 PLOY 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-diethyloxy-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 $D_M$ and a high $f$ are possible using this route. Functionalisation with α-bromooester groups results in PPVs which are effective macroinitiators for the ATRP of methyl methacrylate. PPV-b-PMMA diblock copolymers obtained were unimodal distributions, narrow $D_M$, 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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Notes and references

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† Electronic Supplementary Information (ESI) available: [Synthesis of cyclophanediene I, vinyl ether J, 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/b000000xv].


