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The ring opening metathesis polymerisation (ROMP) of three *n*-octyl subsitutued [2.2]paracyclophane-1,9-dienes, initiated by Grubbs ruthenium carbene complexes is reported. The molecular weight of the resulting alkyl-subsituted poly(*p*-phenylene vinylene)s is determined by the monomer to initiator ratio and the polymers are isolated with relatively narrow polydispersities and control of the end groups. Only the pseudo-geminal isomer of the tetra-alkyl subsitutued [2.2]paracyclophane-1,9-diene was susceptible to ROMP. The optical properties of the two series of polymers was investigated.

Introduction

π-Conjugated organic polymers show unique optical and electronic properties, leading to their use as active materials in: fluorescence imaging, field effect transistors, photovoltaic cells, light emitting diodes, and chemical and biological sensors.[1-6] Poly(*p*-phenylene vinylene)s (PPVs), have attracted significant interest since Holmes *et al*. published their use in the emissive layer of the first polymeric organic light emitting diode.[7] PPVs remain of interest due to their favourable optical properties and have found recent application in fluorescence imaging.[8-11]

Unsubstituted PPV with a backbone of alternating vinylene bonds and phenylene groups is completely insoluble, and this prevents direct processing of this material from solution.[12] Solubilisation of PPVs has traditionally been achieved through the attachment of alkoxy chains on to the phenylene rings of the backbone. However, this functionalisation increases the electron density on the conjugated backbone, decreasing the band gap and leads to a red shift of the optical properties.[13, 14] Further, decreased photostability of these polymers is observed.[15] Solubilisation through attachment of alkyl chains to the phenylene rings results in minimal change to the energy of the band gap and the optical properties are very similar to those observed for the unsubstituted PPV.[7, 16]

Synthetic routes to alkoxy-substituted PPVs have been extensively described in the literature; however, the corresponding routes to the alkyl-substituted polymers are limited.[5, 17] This is primarily due to difficulties encountered in introducing alkyl chains on to the monomers. Alkyl-substituted PPVs have been prepared through precursor syntheses, including; Gilch (bischloromethyl benzenes), Wessling (sulfonium salt benzenes) and the sulfinyl route.[16, 18-21] Direct routes to alkyl-substituted PPVs include the acyclic diene metathesis (ADMET) of alkylated divinylbenzenes and the Stille coupling between bis-stannylethene and dialkyl aryl dihalides.[22-24] These methods proceed either through an uncontrolled chain growth or step growth polymerisation. These approaches result in poor control of molecular weight, reduced end group functionality, non-conjugated backbone defects and generally give poor yields of isolated polymers.

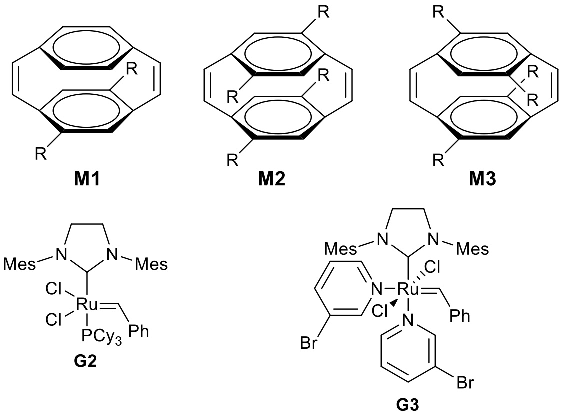

Figure 1. Alkyl substituted [2.2]paracyclophane-1,9-dienes **M1**, **M2** and **M3**, and ruthenium carbene initiators **G2** and **G3**, R = *n*-octyl.

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Electronic Supplementary Information (ESI) available: Additional research data supporting this publication are available as supplementary information accompanying this publication [Synthesis and ^{1}H NMR spectra of polymers; **P1a-d**, **P2a-b**, **P3a-c** and **P4**, GPC chromatogram of **P4**, ^{1}H NMR spectra and GPC chromatograms of attempted reaction of **M3** with **G2** and **G3**, procedure for calculation of PLQY of all polymers]. See DOI: 10.1039/x0xx00000x

Ring opening metathesis polymerisation (ROMP) of alkoxy substituted [2.2]paracyclophane-1,9-dienes, initiated with Grubbs ruthenium carbene complexes (*e.g.* **G2** and **G3**), has proven to be a valuable route towards well-defined, soluble PPVs (Fig. 1).[25-30] The polymers obtained from this route exhibit narrow polydispersities ($Đ_m$), high end-group functionality, a backbone free from non π-conjugated defects and predetermined molecular weights.

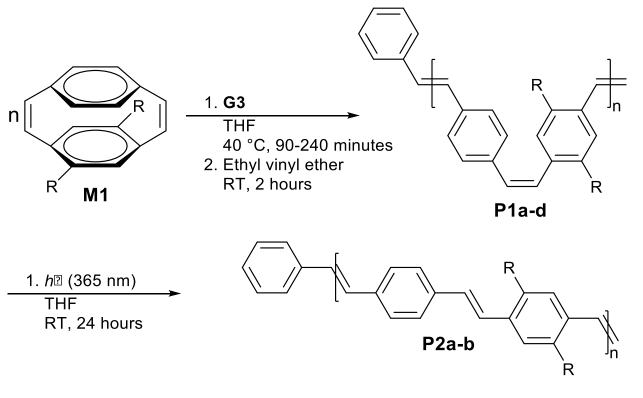
This contribution describes the preparation of alkyl-substituted PPVs by the ROMP of three [2.2]paracyclophane-1,9-dienes substituted with two and four *n*-octyl chains. The optical properties of the well-defined alkyl substituted poly(*p*-phenylene vinylene) have been investigated.

Results and discussion

Poly(*p*-phenylenevinylene-2,5-dioctyl-*p*-phenylenevinylene)s

In previous reports on the ROMP of alkoxy-substituted cyclophanedienes, initiated with **G2**, extended reaction times and high temperatures were required to achieve complete monomer conversion.[25, 31] This was a consequence of the oxygen atom in the *ortho* position of the benzylidene ring coordinating to the ruthenium metal displacing the tricyclohexylphosphine.[32] This strong interaction leads to a reduced rate of propagation and has recently been observed for similarly substituted cyclophanedienes by Zentel *et al.*[28] The [2.2]paracyclophane-1,9-dienes; **M1**, **M2** and **M3** are substituted with *n*-octyl chains and therefore no coordination of the side chains to the ruthenium metal is possible.

Initially the ROMP of **M1** was initiated with Grubbs second generation catalyst (**G2**) with a [**M1**]/[**G2**] of 10/1, using THF as a solvent at 40 °C, followed by quenching of the reactive ruthenium carbene chain end with ethyl vinyl ether. As expected the polymerisation was rapid with complete monomer consumption observed after 3 hours. The polymer was obtained as a green film after precipitation on to a Celite/methanol pad, followed by washing with methanol and extraction with chloroform.



Scheme 1. ROMP of **M1** initiated with **G3**, and photoisomerisation of *cis/trans*-vinylene polymers **P1a-b** to all *trans*-vinylene polymers **P2a-b**.

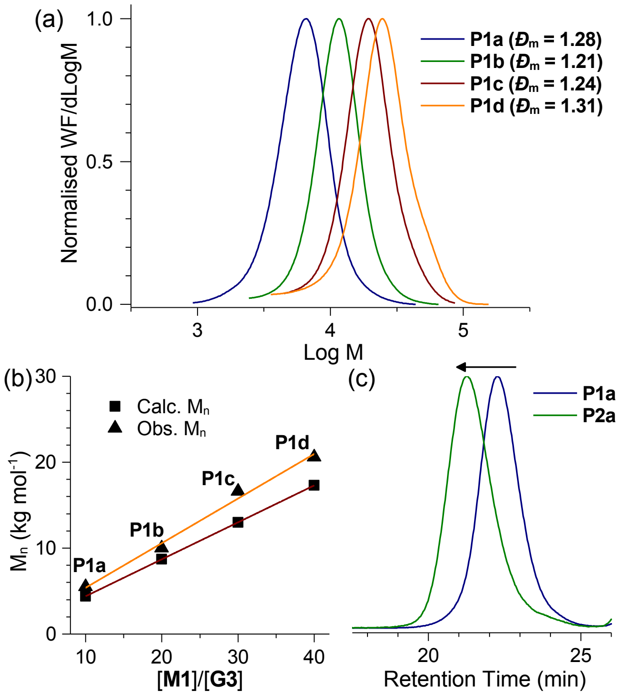


Figure 2. (a) Molecular weight distribution of polymers **P1a-d**, (b) dependence of the M_n of polymers **P1a-d** on the [**M1**]/[**G3**] ratio, (c) GPC chromatograms of *cis/trans*-vinylene polymer **P1a** and *trans*-vinylene polymer **P2a**.

The polymer exhibited a broad $Đ_m$ of 1.81 and a M_n of 4.3 kg mol^{-1} (expected M_n = 4.4 kg mol^{-1}) as determined from gel permeation chromatography (GPC) with a refractive index (RI) detector. This broad $Đ_m$ value was attributed to a slow and incomplete initiation by the initiator, **G2**. Complex **G3**, with two 3-bromopyridine ligands, has been reported to exhibit a faster rate of initiation in comparison to **G2**.[33] The ROMP of **M1** was repeated using **G3**, in THF at 40 °C, to complete monomer conversion ([**M1**]/[**G3**] = 10/1, **Scheme 1**). The isolated polymer **P1a** exhibited a much narrower $Đ_m$ value of 1.28 and a M_n of 5.5 kg mol^{-1} (calibrated against polystyrene standards). To investigate if the M_n could be modulated through variation of the [**M1**]/[**G3**] ratio, polymers with expected degree of polymerisation (x_n) of 20, 30 and 40 were synthesised. All polymers **P1a-d** displayed unimodal distributions with relatively narrow $Đ_m$ values of between 1.21-1.31 (**fig 2.(a)**). Comparison of the [**M1**]/[**G3**] ratio with the apparent M_n gave a linear correlation, which is indicative of a well-controlled chain growth polymerisation (**fig 2.(b)**).

As only one of the vinylene bonds of **M1** is subjected to metathesis the resulting polymers **P1a-d** are isolated with an alternating *cis/trans*-vinylene backbone. Isomerisation to the all *trans*-vinylene polymers **P2a-b** was performed by exposure of polymers **P1a-b** to light of wavelength 365 nm, in degassed THF, for 24 hours. The attempted isomerisation of polymers **P1c-d** was not successful due to the insolubility of the partial isomerised polymers. Isomerisation to the all *trans*-vinylene polymers results in a significant increase in the hydrodynamic volume, which is evident through GPC where an apparent increase in the M_n is observed (**fig. 2c**). For example the apparent M_n of polymer **P1a** increases from 5.5 to 9.6 kg mol^{-1} after isomerisation.

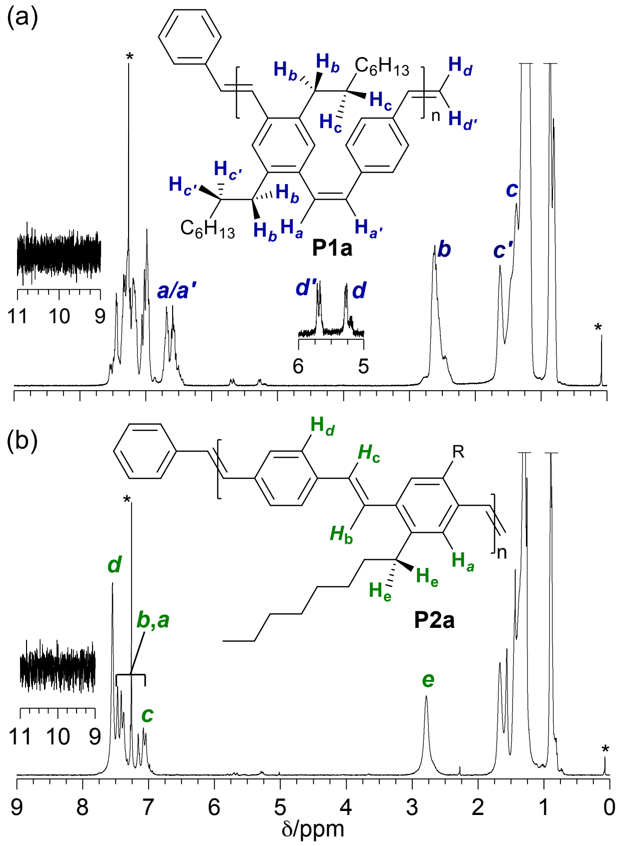


Figure 3. ^{1}H NMR spectra (CDCl$_3$) of (a) *cis/trans*-vinylene polymer **P1a** and (b) all *trans*-vinylene polymer **P2a**.

The ^{1}H NMR spectra of polymer **P1a** and **P2a** are shown in **Fig. 3.** A complex aromatic/vinylene region is observed for polymer **P1a** between 7.63-6.41 ppm, however, the hydrogens of the *cis*-vinylene bond (H_b and $H_{b'}$) are distinct in the region between 6.80-6.41 ppm. The complex nature of this region is due to **M1** containing both an unsubstituted and a substituted phenylene ring. Consequently head-head, tail-tail and tail-head couplings of **M1** can occur along the polymer backbone. Signals associated with the phenyl end group are additionally observed in this region. As observed previously for alkoxy-substituted PPVs, prepared by ROMP, two different environments exist for the hydrogens in the β-position of the side-chain.[31] This can be explained by the hydrogens of the *n*-octyl chain, adjacent to a *cis*-vinylene bond, being magnetically shielded by the adjacent phenylene ring and hence appear at a lower chemical shift. The hydrogens of the methylene group in the β-position of the chain are apparent as two signals, centred at 1.62 and 1.37 ppm. The hydrogens of the methylene group bonded to the phenylene rings are an apparent broad multiplet between 2.87-2.30 ppm. Two signals would be expected for these inequivalent hydrogens, however, they are coincidental in polymer **P1a** and are not resolved in the ^{1}H NMR spectrum. The hydrogens of the vinyl end group are visible as two sets of multiplets at 5.75-5.62 and 5.35-5.16 ppm. Negligible carbonyl defects were observed (see inset in **fig. 3a**). Polymer **P2a** exhibits a much simpler aromatic and vinylene region between 7.79-6.89 ppm (**fig. 3b**). The signals associated with the *cis*-vinylene bonds are no longer observed, showing that isomerisation is essentially complete. A downfield shift of the methylene hydrogens (H_e in **fig. 3b**) adjacent to the polymer backbone is observed to between 3.04-2.50 ppm. Again, minimal carbonyl defects were observed after photoisomerisation (see inset in **fig. 3b**). Fourier transform infrared (FT-IR) spectroscopy confirmed the isomerisation of the *cis*-vinylene bonds of polymer **P1a** to the all *trans*-vinylene polymer **P2a** (**fig. 4**). Absorbances associated with the C-H out-of-plane (OOP) bend of the *cis* and *trans* vinylene bonds of polymer **P1a** are observed at 959 cm^{-1}, and at 909 and 838 cm^{-1}, respectively. In polymer **P2a** only the C-H OOP bend of the *trans*-vinylene bond was observed at 957 cm^{-1}.

Matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry (MALDI-TOF-MS) of **P1a** (**Fig. 5**) showed one major polymer series corresponding to the expected linear polymer with vinyl and phenyl end groups (■). The peak separation of this series was equal to the mass of the monomer repeat unit (429 Da). Very small signals associated with additional series are observed due to intramolecular secondary metathesis occurring between the ruthenium carbene chain end and the unhindered *cis*-vinylene bonds of the polymer backbone. These species include: (i) cyclic oligomers with an equal number of repeat units and/or an additional unsubstituted or substituted phenylene ring, and (ii) linear polymers with vinyl and phenyl end groups and either an extra unsubstituted phenylene ring or substituted phenylene ring.

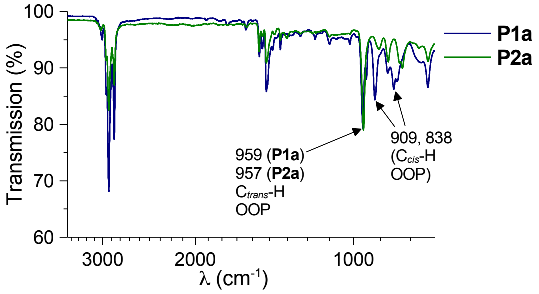


Figure 4. FT-IR spectra of *cis/trans*-vinylene polymer **P1a** and *trans*-vinylene polymer **P2a**.

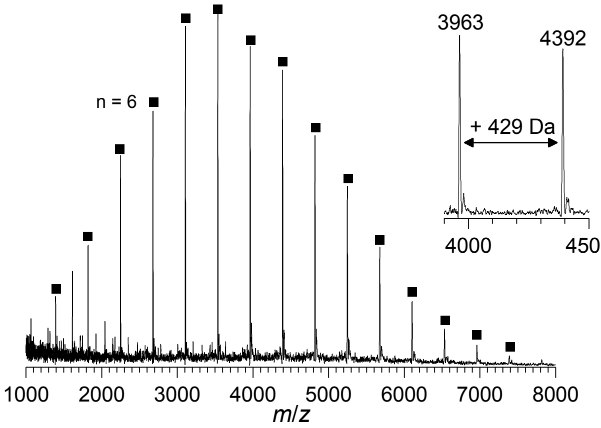


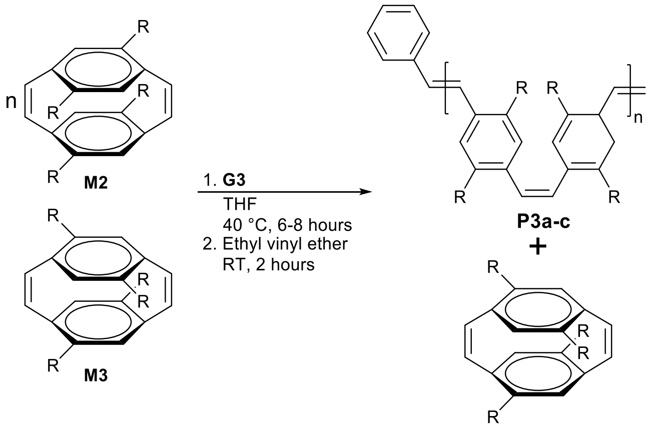
Figure 5. MALDI-TOF-mass spectra of polymer **P1a**.

There was no evidence of intermolecular secondary metathesis reactions in these mass spectra.

Poly(2,5-dioctyl-*p*-phenylenevinylene)s

The tetraoctyl substituted cyclophanedienes were isolated as an inseparable mixture of **M2** and **M3** (ratio of 17:83).[34] As previously reported for the ROMP of 4,7,12,15-tetraoctyloxy-[2.2]paracyclophane-1,9-diene and 5,8,12,15-tetraoctyloxy-[2.2]paracyclophane-1,9-diene, only the former isomer, with the long alkoxy chains in the pseudo-*geminal* positions, can be successfully polymerised.[35] Conversely, Zentel *et al*. found that reducing the alkoxy chain length to a methoxy group and refluxing in toluene resulted in polymerisation of the pseudo-*ortho* isomer.[28] ROMP of the mixture of **M2** and **M3**, was initiated with **G3**, assuming that only **M2** is reactive towards metathesis. An initial [**M2**]/[**G3**] ratio of 10/1 was used and the polymerisation was quenched by the addition of ethyl vinyl ether, after complete monomer conversion (Scheme 2). The polymer **P3a** was isolated as a green film after precipitation on to a Celite/acetone column, followed by washing with acetone and extraction with hot chloroform. Polymer **P3a** exhibited a M_n = 7.3 kg mol^{-1} (expected M_n = 6.6 kg mol^{-1}) and a relatively narrow $Đ_m$ of 1.25. The unreacted cyclophanediene **M3** was isolated from the acetone washing by column chromatography.

Further modulation of the [**M2**]/[**G3**] ratio to obtain expected x_n of 20, 30 and 40 was investigated. Polymers **P3b-c** with expected x_n of 20 and 30 exhibited unimodal distributions and $Đ_m$ values in range of 1.40-1.50 (**Fig. 6a**). The polymerisation with an expected x_n of 40 resulted in incomplete conversion of **M2**, even after an extended reaction time of 20 hours. However, the M_n of polymers **P3a-c** followed a linear correlation with the [**M2**]/[**G3**] ratio, indicating that the molecular weight could be controlled within this range of composition (**Fig. 6b**).



Scheme 2. ROMP of mixture of cyclophanedienes **M2** and **M3**, initiated with **G3**, R = *n*-octyl.

Photoisomerisation of the *cis*/*trans*-vinylene polymers **P3a-c** to the corresponding all *trans*-vinylene polymers was unsuccessful due to reduced solubility of the products during the isomerisation reaction. The reduced solubility of linear alkyl-substituted, all *trans*-vinylene PPVs, with increasing molecular weight has previously been reported.[24, 36, 37]

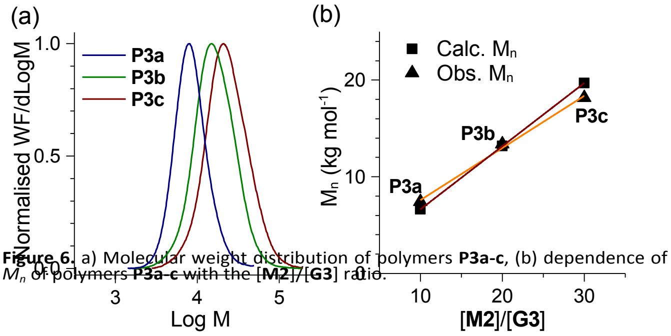


Figure 6. a) Molecular weight distribution of polymers **P3a-c**, (b) dependence of M_n of polymers **P3a-c** with the [**M2**]/[**G3**] ratio.

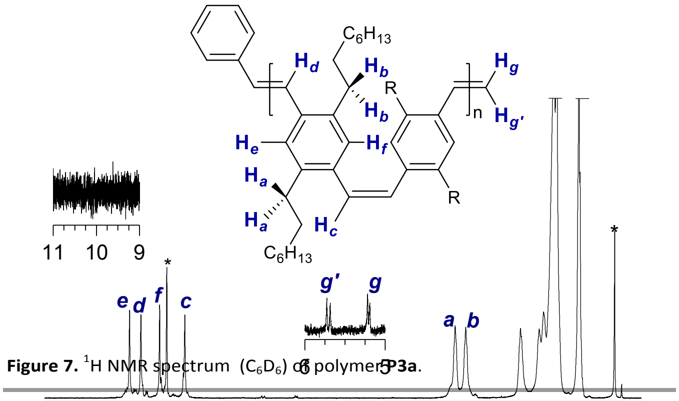


Figure 7. ^{1}H NMR spectrum (C_6D_6) of polymer **P3a**.

As both phenylene rings of **M2** are substituted with two alkyl groups there are no regiochemical isomers possible in the polymer backbone. Consequently a much simpler aromatic and vinylene region is observed in the ^{1}H NMR spectrum of *cis/trans*-vinylene polymer **P3a (fig. 7)**, when compared to that found for polymer **P1a (fig. 3a)**. The *cis*-vinylene hydrogens are observed at 6.86 ppm, the aromatic hydrogens adjacent to a *cis*-vinylene bond at 7.27 ppm, the *trans*-vinylene hydrogens at 7.55 ppm and 7.72 ppm for the aromatic hydrogens adjacent to a *trans*-vinylene. Unlike polymer **P1a** the two hydrogen environments of the methylene group bonded to the phenylene ring appear as two separate signals at 2.67 and 2.45 ppm.

MALDI-TOF-MS of polymer **P3a** showed a series of peaks that correspond to the desired polymer with phenyl and a vinyl end groups (■) (Fig. 8). The peak separation of this series was equal to the mass of the monomer repeat unit. Signals associated with secondary metathesis were present in low abundance, presumably due to the four *n*-octyl chains preventing reaction of the ruthenium carbene chain end with the *cis*-vinylene bonds of the polymer backbone. The increasing $Đ_m$ values on increasing x_n, the inability to reach full monomer conversion at x_n = 40 and the lower than expected intensity of the vinyl end groups in the ^{1}H NMR spectra suggest that carbene chain ends in these polymerisations are not living.

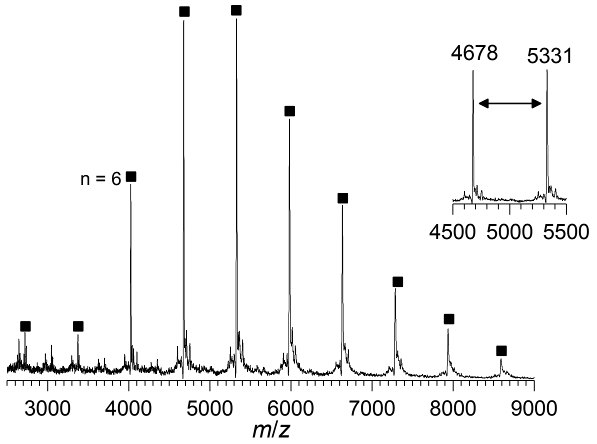


Figure 8. MALDI-TOF-mass spectrum of polymer **P3a**.

The reactivity of **M3** towards ROMP was investigated with both **G2** and **G3**, with a [**M3**]/[**G2**/**G3**] ratio of 5/1. A reaction temperature of 60 °C was used, with a reaction time of 20 hours. ^{1}H NMR spectroscopy and GPC chromatography of the crude reaction material showed no polymerisation of **M3** under any reaction conditions (see ESI). The unreactive nature of **M3** is thought to be a consequence of the four *n*-octyl chains, in the pseudo-*ortho* arrangement, preventing coordination of the vinylene bond to the ruthenium centre.

Optical properties

The optical properties of polymers **P1a-d**, **P2a-b**, **P3a-c** and **P4** were recorded in dilute chloroform at ambient temperature (**Table 1**). The absorption maxima (λ_{max}) of polymers **P1a-d** are observed between 370-373 nm, no red-shift was observed on increasing the x_n, indicating that all polymers were above the effective conjugation length of these polymers.[38]

The fluorescence emission maxima (λ_{em}) were identical for all polymers **P1a-d** at 482 nm (**Fig. 9a**). This is expected as the emission occurs from the segment of the polymer chain containing the most conjugated chromophores. A blue shift in the λ_{max} for absorption is observed when compared to that for the analogous alkoxy substituted poly(*p*-phenylenevinylene-2,5-diethylhexyloxy-*p*-phenylene vinylene), prepared by ROMP. These polymers show a λ_{max} between 462-467 nm.[26] The blue shift of the λ_{max} of alkyl substituted PPVs is expected due to the reduced electron donation of the alkyl substituents into the π-conjugated backbone. The photoluminescence quantum yield (PLQY) of polymers **P1a-d** increased with increasing x_n from 0.53 to 0.64. Isomerisation to the all *trans*-vinylene polymers **P2a-b** resulted in a red shift of the absorption maxima (λ_{max}) to 428 nm for both polymers. This is a consequence of the increased conjugation length in the all *trans*-vinylene configuration. The fluorescence spectra of **P2a-b** show a maximum emission at 483 nm and a secondary peak at 512 nm. A slight increase in the PLQY was observed, with values of 0.59 and 0.57 obtained for polymers **P2a-b**, respectively. The absorption spectra of polymers **P3a-c** show identical absorption maxima at 372 nm, comparable to the λ_{max} of polymers **P1a-d** and consistent with the negligible electron donating effect of the alkyl chains. The fluorescence spectra of polymers **P3a-c** all exhibited a maximum emission at 491nm, red shifted from the emission of polymers **P1a-d** by 10 nm.

α-Bromoester functionalised monotelechelic poly(*p*-phenylene vinylene-2,5-dioctyl-*p*-phenylenevinylene)

The ability to functionalise the end-groups of the alkyl-substituted PPV was investigated by quenching the polymerisation of **M1** with **G3** using a functionalised vinyl ether.[27] Block copolymers containing an alkyl substituted PPV segment are limited within the literature and only low molecular weight PPV oligomers have been reported.[39, 40] Consequently, incorporation of an α-bromoester group on to the terminus of the polymer chain generates macroinitiators, that are suitable for the growth of a second polymeric block by atom transfer radical polymerisation (ATRP). The terminal functionalization was achieved by quenching the ROMP of **M1** (expected x_n = 10), with an α-bromoester functionalised vinyl ether (see ESI).[27]

Table 1. Molecular weight data and optical data of polymers **P1a-d**, **P2a-b**, **P3a-c** and **P4**.

Polymer	x_n [a]	M_n (kg mol^{-1})[b]	M_n (kg mol^{-1})[c]	$Đ_m$ [c]	λ_{max} (nm)[d]	λ_{em} (nm)[d][e]	PLQY[d][e]
P1a	10	4.4	5.5	1.28	373	482	0.53
P1b	20	8.7	10.0	1.21	371	482	0.55
P1c	30	13.0	16.6	1.24	372	482	0.60
P1d	40	17.3	20.6	1.31	370	482	0.64
P2a	10	-	9.6	1.38	428	483	0.59
P2b	20	-	16.6	1.53	428	483	0.57
P3a	10	6.6	7.3	1.25	372	491	0.62
P3b	20	13.2	13.4	1.40	372	491	0.63
P3c	30	19.7	18.2	1.50	372	491	0.70
P4	10	4.6	6.0	1.31	363	482	0.57

[a] Expected x_n from [**M1** or **M2**]/[**G3**] ratio, [b] calculated from the [**M1** or **M2**]/[**G3**] ratio, including expected end groups, [c] determined by GPC with RI detection (calibrated against narrow $Đ_m$ polystyrene standards), [d] in chloroform and [e] Ex = 350 nm for polymers **P1a-d**, **P3a-c** and **P4**, and Ex = 370 nm for polymers **P2a-b**, against quinine sulfate standards (in 0.1 M sulfuric acid$_{(aq)}$).

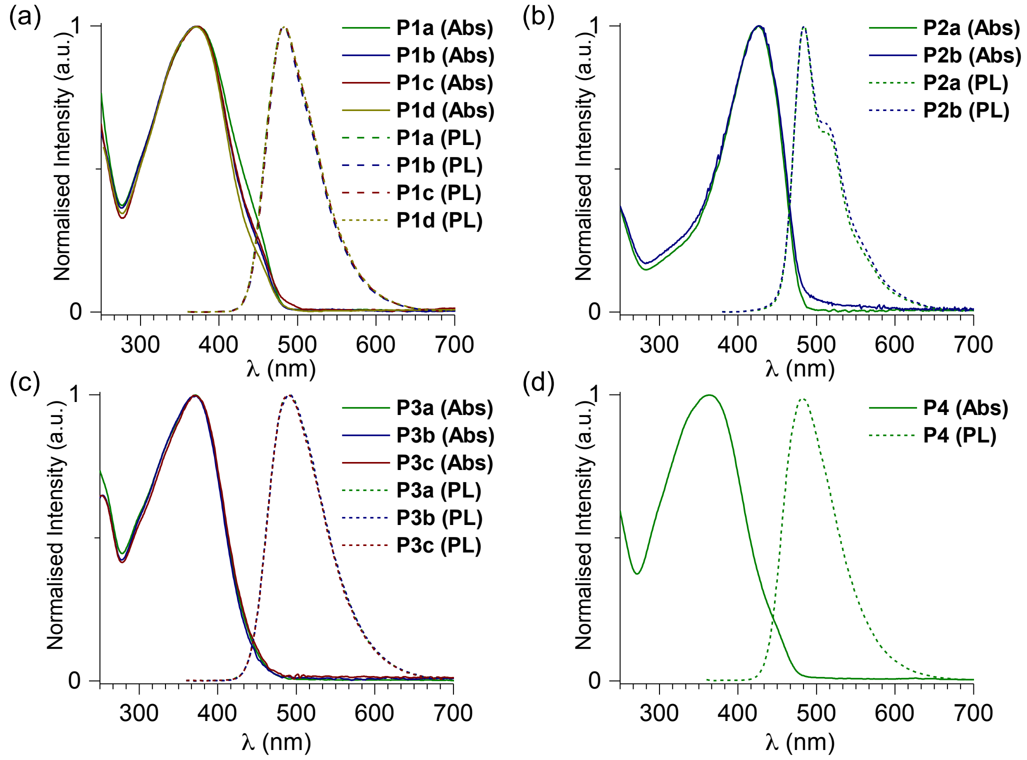


Figure 9. Solution (chloroform) absorption and photoluminescence spectra of polymers; (a) **P1a-d** (Ex = 350 nm), (b) **P2a-b** (Ex = 370 nm), (c) **P3a-c** (Ex = 350 nm) and (d) **P4** (Ex = 350 nm).

A macroinitiator with M_n of 6.0 kg mol^{-1} (expected M_n = 4.6 kg mol^{-1}) and a narrow $Đ_m$ = 1.31 was obtained, indicating minimal secondary metathesis during the extended termination reaction. Incorporation of the α-bromoester end group was confirmed through ^{1}H NMR spectroscopy (**Fig. 10a**) with signals associated with the hydrogens of the methyl groups observed between 2.09 and 2.07 ppm. Integration of these hydrogens against the methylene hydrogens adjacent phenylene ring gave a degree of functionality of 91%. The remainder of the signals are consistent the structure of polymer **P1a**. MALDI-TOF-MS (**Fig. 10b**) showed one major series (■), separated by the mass of the monomer repeat unit, corresponding to polymers with the expected phenyl and α-bromoester end groups. As previously observed degradation of the α-bromoester group to a phenol (□) and vinyl group (○) was also observed in the MALDI-TOF-MS experiment.[27]

The absorption spectra of polymer **P4**, with an α-bromoester end group exhibited a λ_{max} = 363 nm, that was blue shifted by 10 nm, in comparison to the λ_{max} of **P1a**. The fluorescence spectra were identical to that of **P1a**, with a λ_{em} of 482nm. The incorporation of the α-bromoester end group gave a slightly increased PLQY value of 0.57.

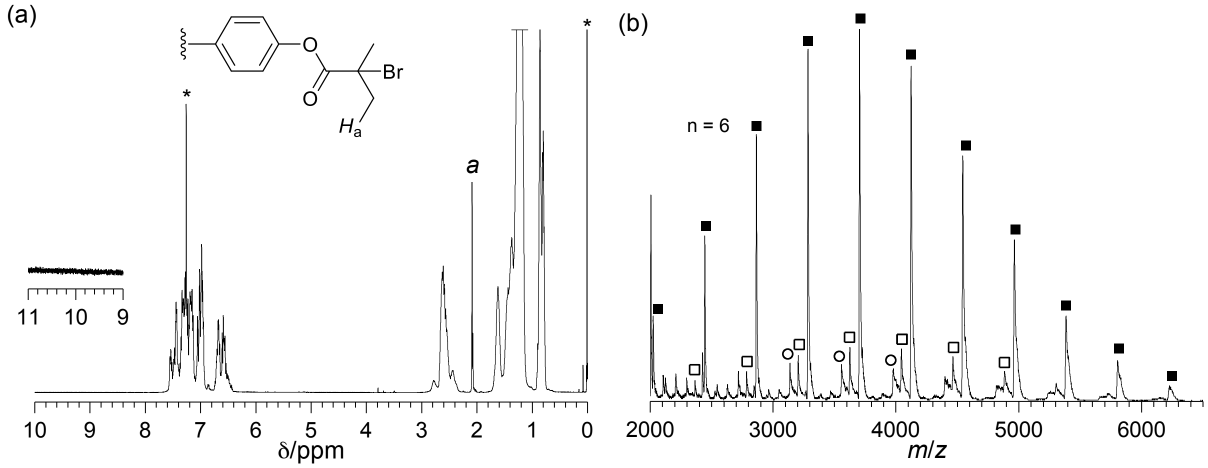


Figure 10. (a) ^{1}H NMR spectrum ($CDCl_3$) of polymer **P4** and (b) MALDI-TOF-mass spectrum of **P4.**

Conclusions

The ROMP of three different *n*-octyl substituted [2.2]paracyclophane-1,9-dienes, initiated with Grubbs ruthenium carbene complexes, has been investigated. Substitution of one phenylene ring of the cyclophanediene with two alkyl chains, **M1**, resulted in a well-controlled chain growth polymerisation. The PPVs were obtained with narrow $Đ_m$ values, predetermined molecular weights, well-defined end groups and an alternating *cis-trans*-vinylene backbone. The controlled nature of the polymerisation of **M1** was demonstrated through the termination of the ROMP with an α-bromoester functionalised vinyl ether to obtain the corresponding functionalised PPV, a suitable macroinitiator for ATRP. Tetra-substitution of the cyclophanediene resulted only in ROMP when the chains were in the pseudo-*geminal* position, for monomer **M2**. The ROMP of tetra-substituted cyclophanediene, with the alkyl chains in pseudo-*ortho* position **M3**, did not proceed, even at elevated temperatures and over extended reaction times.

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