Alkyl Substituted Poly(p-phenylene vinylene)s by Ring Opening Metathesis Polymerisation


The ring opening metathesis polymerisation (ROMP) of three n-octyl substituted [2.2]paracyclopahne-1,9-dienes, initiated by Grubbs ruthenium carbene complexes is reported. The molecular weight of the resulting alkyl-substituted 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 substituted [2.2]paracyclopahne-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 sulfanyl 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-stannylenethane and dialky 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]paracyclopahne-1,9-dienes M1, M2 and M3, and ruthenium carbene initiators G2 and G3, R = n-octyl.
Ring opening metathesis polymerisation (ROMP) of alkox 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 (\(D_n\)), high end-group functionality, a backbone free from non \(\pi\)-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)**

In previous reports on the ROMP of alkox 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 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.](image)

The polymer exhibited a broad \(D_m\) 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 \(D_m\) 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 \(D_m\) 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 \(D_m\) 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

![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.](image)
apparent $M_n$ of polymer $\text{P1a}$ increases from 5.5 to 9.6 kg mol$^{-1}$ after isomerisation.

![Figure 3](image)

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

The $^1$H NMR spectra of polymer $\text{P1a}$ and $\text{P2a}$ are shown in Fig. 3. A complex aromatic/vinylene region is observed for polymer $\text{P1a}$ between 7.63-6.41 ppm, however, the hydrogens of the cis-vinylene bond ($H_b$ and $H_d$) are distinct in the region between 6.80-6.41 ppm. The complex nature of this region is due to $\text{M1}$ containing both an unsubstituted and a substituted phenylene ring. Consequently head-head, tail-tail and tail-head couplings of $\text{M1}$ 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 $\beta$-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 $\beta$-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 $\text{P1a}$ 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 $\text{P2a}$ 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 ($H_b$ 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 $\text{P1a}$ to the all trans-vinylene polymer $\text{P2a}$ (fig. 4). Absorbances associated with the C-H out-of-plane (OOP) bend of the cis and trans vinylene bonds of polymer $\text{P1a}$ are observed at 959 cm$^{-1}$, and at 909 and 838 cm$^{-1}$; respectively. In polymer $\text{P2a}$ 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 $\text{P1a}$ (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](image)

**Figure 4.** FT-IR spectra of cis/trans-vinylene polymer $\text{P1a}$ and trans-vinylene polymer $\text{P2a}$.

![Figure 5](image)

**Figure 5.** MALDI-TOF-mass spectra of polymer $\text{P1a}$. 

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

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

The tetraceyloxy substituted cyclophanedienes were isolated as an inseparable mixture of M2 and M3 (ratio of 17:83).\(^4\) As previously reported for the ROMP of 4,7,12,15-tetraacyloxy-[2.2]paracyclophane-1,9-diene and 5,8,12,15-tetraacyloxy-[2.2]paracyclophane-1,9-diene, only the former isomer, with the long alkoxy chains in the pseudo-geminal positions, could be successfully polymerised.\(^5\) 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.\(^6\) 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 a Celite(acetone column, followed by washing with acetone and extraction with hot chloroform. Polymer P3a exhibited a \(M_n = 7.3 \text{ kg mol}^{-1}\) (expected \(M_n = 6.6 \text{ kg mol}^{-1}\)) and a relatively narrow \(D_m\) 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 \(D_m\) 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](image)

**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.\(^24, 36, 37\)

As both phenylene rings of M2 are substituted with two alkyl groups there are no no-regio 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 \(D_m\) 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.

\[ \text{Figure 8. MALDI-TOF-mass spectrum of polymer P3a.} \]

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 (\(\lambda_{\text{max}}\)) of polymers P1a-d are observed between 370-373 nm, no red-shift was observed on increasing the \(x_a\) indicating that all polymers were above the effective conjugation length of these polymers. \(^{38}\)

The fluorescence emission maxima (\(\lambda_{\text{em}}\)) 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 \(\lambda_{\text{max}}\) 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 \(\lambda_{\text{max}}\) between 462-467 nm. \(^{26}\)

The blue shift of the \(\lambda_{\text{max}}\) of alkyl substituted PPVs is expected due to the reduced electron donation of the alkyl substituents into the \(\pi\)-conjugated backbone. The photoluminescence quantum yield (PLQY) of polymers P1a-d increased with increasing \(x_a\) from 0.53 to 0.64. Isomerisation to the all-trans-vinylene polymers P2a-b resulted in a red shift of the absorption maxima (\(\lambda_{\text{max}}\)) 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 \(\lambda_{\text{max}}\) 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 491 nm, red shifted from the emission of polymers P1a-d by 10 nm.

\(\alpha\)-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 the low molecular weight PPV oligomers have been reported. \(^{39, 40}\)

Consequently, incorporation of an \(\alpha\)-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 \(x_a = 10\)), with an \(\alpha\)-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.**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(x_a) (^{[a]})</th>
<th>(M_r) (kg mol(^{-1})) (^{[b]})</th>
<th>(M_n) (kg mol(^{-1})) (^{[c]})</th>
<th>(D_r) (^{[d]})</th>
<th>(\lambda_{\text{max}}) (nm) (^{[e]})</th>
<th>(\lambda_{\text{em}}) (nm) (^{[f]})</th>
<th>PLQY (^{[g]})</th>
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<td>1.21</td>
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<td>482</td>
<td>0.55</td>
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<tr>
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<td>16.6</td>
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<td>482</td>
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<td>370</td>
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<td>0.57</td>
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\(\text{[a]}\) Expected \(x_a\) from [M1 or M2]/[G3] ratio, \(\text{[b]}\) calculated from the [M1 or M2]/[G3] ratio, including expected end groups, \(\text{[c]}\) determined by GPC with RI detection (calibrated against narrow \(M_n\) polystyrene standards), \(\text{[d]}\) in chloroform and \(\text{[e]}\) 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, \(a_{\text{SO}_4}\)).

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A macroinitiator with $M_n$ of 6.0 kg mol$^{-1}$ (expected $M_n = 4.6$ kg mol$^{-1}$) and a narrow $\bar{D}_n = 1.31$ was obtained, indicating minimal secondary metathesis during the extended termination reaction. Incorporation of the $\alpha$-bromoester end group was confirmed through $^1$H NMR spectroscopy (Fig. 10a) with signals associated with 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 with the structure of polymer P1a. MALDI-TOF-MS (Fig. 10b) showed one major series $(\bullet)$, separated by the mass of the monomer repeat unit, corresponding to polymers with the expected phenyl and $\alpha$-bromoester end groups. As previously observed degradation of the $\alpha$-bromoester group to a phenol $(\square)$ and vinyl group $(\circ)$ was also observed in the MALDI-TOF-MS experiment.$^{27}$ The absorption spectra of polymer P4, with an $\alpha$-bromoester end group exhibited a $\lambda_{\text{max}} = 363$ nm, that was blue shifted by 10 nm, in comparison to the $\lambda_{\text{max}}$ of P1a. The fluorescence spectra were identical to that of P1a, with a $\lambda_{\text{em}}$ of 482 nm. The incorporation of the $\alpha$-bromoester end group gave a slightly increased PLQY value of 0.57.

![Figure 9](image_url) 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).

![Figure 10](image_url) (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 $\bar{M}_n$ 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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References


