Synthesis of tailor-made polyenes via application of living ring opening metathesis polymerisation (ROMP) and the Durham route

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Abstract

The ring opening metathesis polymerisation of 7,8-(bistrifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene using Schrock-type molybdenum alkylidene initiators yields precursor polyacetylene with well defined chain-ends, molecular weights and polydispersities. The precursor polyenes can be thermally converted to the equivalent polyene structures by elimination of hexafluoroxylene. Truly monodisperse soluble oligoene sequences were separated and isolated using reversed-phase HPLC techniques.

Keywords: Polyacetylene; Ring opening metathesis polymerisation; HPLC; Polyene compounds

1. Introduction

Research in the field of conjugated polymers has been in vogue for many years. Many different kinds of conjugated polymers have been made and studied but polyacetylene (PA), the material which first excited the curiosity of theoreticians [1], remains the paradigm for the field. The control of structure at all levels (atomic connectivity, size, stereochemistry, conformation and morphology) is a prerequisite for control of the properties of a polymeric material and is a primary objective of polymer science. Some time ago we introduced a precursor route [2–4] to polyacetylene involving ROMP of monomer (I) to give soluble precursor polymer

(II) which can be thermally converted to polyacetylene (III) as shown in Fig. 1.

The material produced by this route, 'Durham PA', may be obtain in a range of morphologies and densities dependent on the protocol adopted for the conversion step, (II) to (III). This approach makes it possible to produce solid continuous films of PA in a range of orders from almost amorphous isotropic, through to microcrystalline with varying extents of anisotropy. Although PA itself is fairly intractable, it is possible to increase the anisotropy by mechanical drawing before or during the conversion step. The precursor methodology allowed, the convenient fabrication of hybrid polyacetylene–silicon based device structures, such as MISFETs (Metal–Insulator–Semiconductor Field Effect Transistors), which were used to study the fundamental physics of this
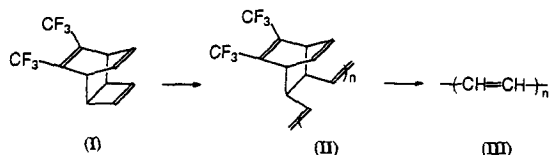
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Fig. 1. The 'Durham route' to polyacetylene.

novel organic semiconductor [5–7]. New possibilities for the observation of the two dimensional organisation of monolayers of this material emanate from the development of the relatively new technique of Scanning Tunnelling Microscopy (STM). The requirement for polyenes for STM experiments is good solubility in hydrocarbon solvents and samples consisting of pure monodisperse compounds. Recent developments in the synthesis and use of well defined ROMP initiators [8–10] allow, in principle, a high level of control in the synthesis of conjugated polymeric polyenes; thus, it is possible to prepare samples in which n, R and R' in the polyene structure (III), shown in Fig. 2, are completely defined. The molecular weight distribution of the as made materials can be very narrow, with values between 1.05 and 1.1.

R is the group originating from the initiating species and can be exchanged in a cross metathesis reaction with a styrene derivative. R' is the group originating from the aldehyde that is used to terminate the polymerisation in a Wittig-like reaction. Since the ROMP of monomer (I) is a living process the degree of polymerisation can be precisely controlled. R, R' and n can, in principle, be varied to control the properties of the resulting polyenes (III).

Here we report the synthesis of new polyenes with defined size and chain-end structures via the Durham route, see Fig. 3.

In this case R' is a solubilising n-alkyl substituent (II and IIIa and IIIc); the short chain polyenes (IIIa and IIIc) can, in principle, be dissolved in common solvents and the individual polyene sequences can be identified and isolated using reversed phase High Pressure Liquid Chromatography, making monodisperse polyenes available for study via spectroscopic methods and STM.

2. Results and discussion

We have synthesised a series of polymers with different molecular weights and/or endgroups. In all cases, we have used the general
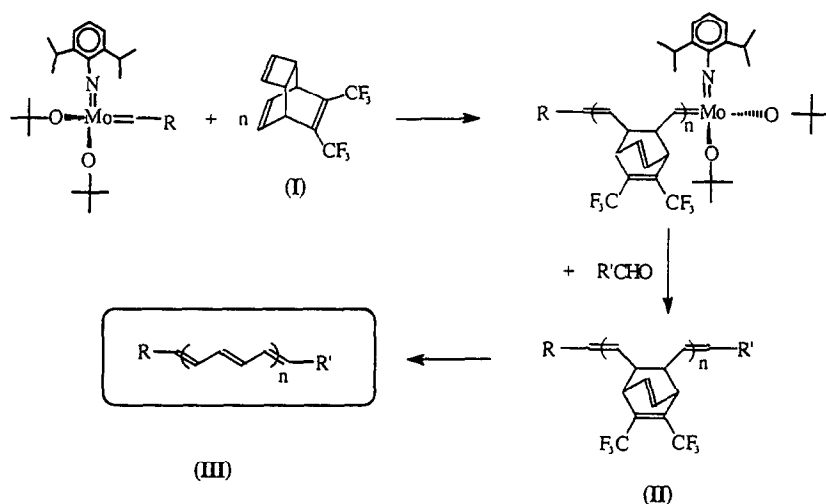

Fig. 2. Living ROMP using well-defined Scrock initiators allows control over the chain end structure, degrees of polymerisation and molecular weight distributions.
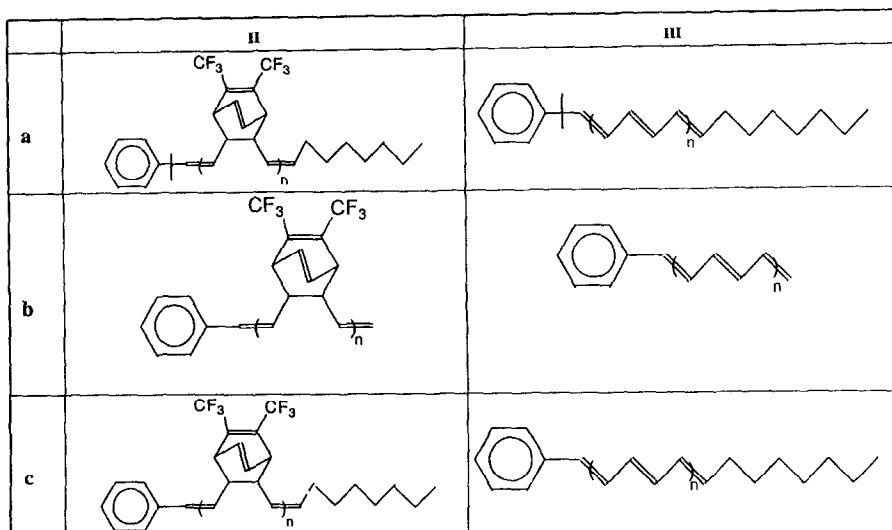
Fig. 3. New polyenes with defined end-groups synthesised via the 'Durham route'.

reaction path shown in Fig. 2. The monomer (**I**) is available in a one step high yield process [11] from commercially obtainable reagents; ring opening metathesis polymerisation operates exclusively on the cyclobutene unit to give the soluble precursor polymer (**II**) after end-capping of the living species with an aldehyde. Using the well defined metathesis initiators of the general formula $Mo(CHR)(NAr)(O-t-Bu)_2$ introduced by Schrock [9], the vinylenes in the backbone of (**II**) have predominately *trans* geometry (> 95%). The different chain-ends (R' and R), summarised in Fig. 4, were obtained through the end-capping reaction of the intermediate species during the synthesis of (**II**), using the required aldehyde and/or through a modifi-

cation of the initiating species via a cross metathesis reaction, see Fig. 5.

Precursor (**II**) is soluble and can therefore be processed into film by standard techniques. Thermal elimination of hexafluoroxylene from a sample of (**II**) is symmetry allowed in the ground state and gives (**III**). All the newly formed double bonds in (**III**) have *cis* geometry and at or above room temperature they isomerize to *trans*.

Preparation of (**IIa**). The presence of an alkyl group at the chain-end not only improves the solubility of oligoenes with up to 15 double bonds dramatically, but also contributes to the efficiency with which they can be separated into their individual components by reverse phase

	R'	R	n
IIa			5, 8, 10, 14, 23, 27
IIb			5
IIc			5

Fig. 4. Summary of the different end-groups and degrees of polymerisation of the polymers made in this study.

HPLC. Monodisperse (**IIIa**) was dissolved in dried and degassed undecane and supplied to the group of Prof. J. Rabe (Humbolt University, Berlin) for STM studies but, although a mono-layer could be detected no well defined two dimensional organisation was observed [12]. A possible cause of this observation was assumed to be the presence of the two relatively bulky $-CH_3$ groups on the chain ends of (**IIIa**) and led us to the preparation of (**IIb**) and (**IIc**) in an attempt to overcome this problem.

A series of precursor polymers (**IIa**) with different degrees of polymerisation ($n = 5$, 8, 10, 14, 23, 27) and an octyl chain-end group have been synthesised by termination of the ROMP of (**I**) with octanal (see Fig. 2, Fig. 3 and Fig. 4). The precursor polymer (**IIa**) ($n = 5$) was converted to the corresponding polyene by heating at 80°C for 3 h and was then dissolved in a suitable mixture of solvents and separated into its individual monodisperse components (see Section 3).

Preparation of (**IIb**). The use of Schrock-type metal alkylidenes for the initiation of ROMP of (**I**), as described above, gives precursor poly-mers with a neopentylidene or a neophylidene
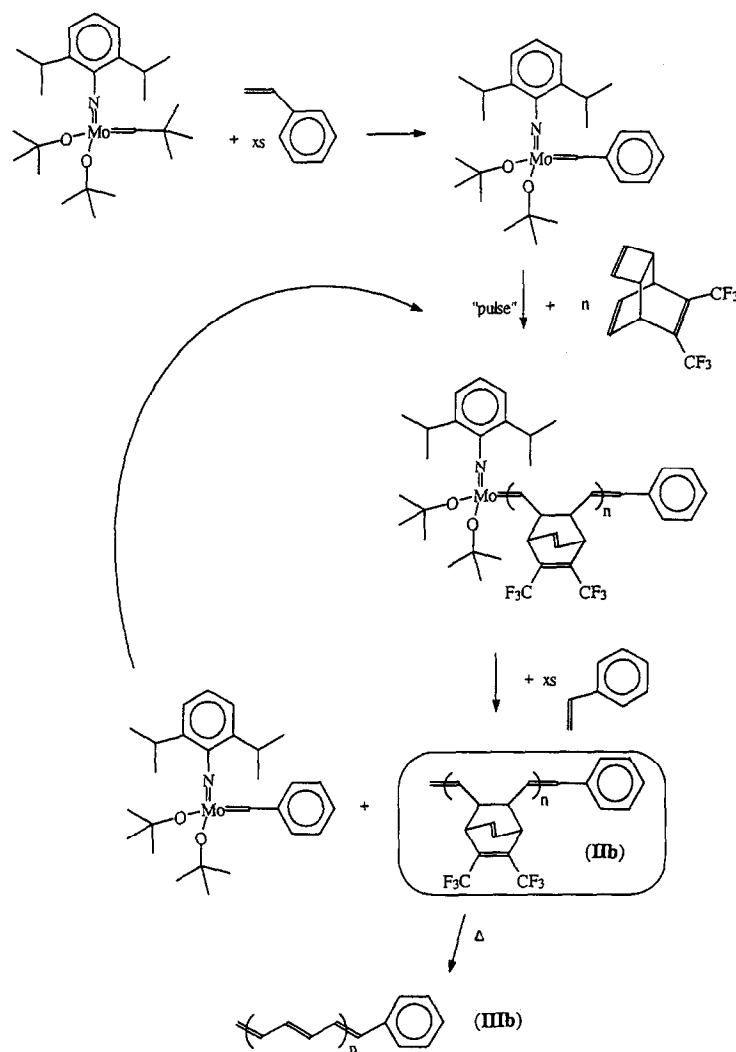

Fig. 5. 'Multiple pulse' ROMP experiment.

chain-end (R). A ROMP method has been developed [13] that not only allows the substitution of R on the initiating species but after each cycle of well-defined polymerisation regenerates the initiator which is then available for a new polymerisation cycle should more monomer be introduced. This method has been described as 'multiple pulse method' and it has been used successfully for the polymerisation of norbornene. In this case we employed the same method to oligomerise (I), as shown in Fig. 5, in order to obtain an oligoene molecule (IIIb) which was free from out of plane $-CH_3$ groups. This in principle would allow better two dimensional packing in a monolayer and subsequent observation by STM. The same reasons lead us to the attempted synthesis of precursor oligomer (IIc), which should have the additional advantage of higher solubility and separability.

3. Experimental

Instrumental. IR spectra were recorded as KBr plates using a Perkin Elmer 1600 FTIR spectrophotometer. Solution ^1H-NMR and ^{13}C-NMR spectra were recorded using a Varian Gemini-200 (199.975 MHz for ^1H, 50.289 MHz for ^{13}C) and a Varian VXR 400 S spectrometer (399.952 MHz for ^1H, 100.577 MHz for ^{13}C), using $CDCl_3$ or acetone-d_6 as the solvent depending on the molecular weight of the samples and internal TMS as reference. Molecular weight distributions were obtained by GPC in THF solution using a Viscotek instrument equipped with a differential refractometer and a viscometer detector using a PL-Gel 10μ mixed column. Measurements were carried out at 0°C, using a flow rate of 1 ml/min. A GPC calibration graph was obtained using a series of polystyrene standards. UV–Vis spectra were recorded on a Perkin Elmer 330 Spectrophotometer.

Synthesis of precursor oligoenes and polyenes (IIa). The living precursor oligomers and polymers (IIa) were prepared via the Durham route, see Fig. 2. Since ROMP using the well defined

molybdenum alkylidene complexes is a living process, the ratio of initiator to monomer was adjusted according to the molecular weight required. The general experimental procedure is described here for a specific example (IIa, $n =$ 10). In an inert atmosphere Glove Box, $Mo(=CHC(CH_3)_2Ph)(NAr)(O^tBu)_2$ (0.0413 g, 0.0751 mmol) solution in dry and degassed toluene (4 ml) was put into the first compartment of a two compartment reaction vessel fitted with greaseless valves (J. Young-Acton). The monomer, 7,8-(bistrifluoromethyl)tricyclo[4.2.2.0$^{2.5}$]deca-3,7,9-triene (0.200 g, 0.751 mmol) was also dissolved in dried and degassed toluene (or toluene:THF mixture (90:10) to enhance the solubility) and placed in the second compartment of the same reaction vessel. The vessel was sealed using Young valves. It was then taken out of the Glove Box, connected onto a nitrogen/vacuum line and immersed into a thermostated cooling bath at -5°C. The two solutions were then allowed to mix with stirring for at least 2 h. A solution of the required dried and degassed octanal (10-fold excess) in toluene (2 ml) was prepared and kept under nitrogen. This solution was then injected into the reaction vessel after one of the Young valves was replaced with a septum seal under a strong counter current of dry nitrogen, and allowed to react for at least 1 h. The polymer was recovered as a white powder (0.216 g, 72%) after repeated precipitation from toluene into cold (-70°C) methanol or hexane, filtration and drying under vacuum at -5°C. The molecular weight of all polymers (IIa) was calculated on the basis of the integration of the peaks due to the chain ends compared to the peaks for the repeat units. This allowed for an absolute and hence more reliable determination of the number average degree of polymerisation as compared to the values obtained by GPC. The GPC analysis was used to determine the molecular weight distributions of these polymers which were very narrow, the polydispersity index being in the region of 1.05–1.10 in all cases. All manipulations including the polymerisation reaction and
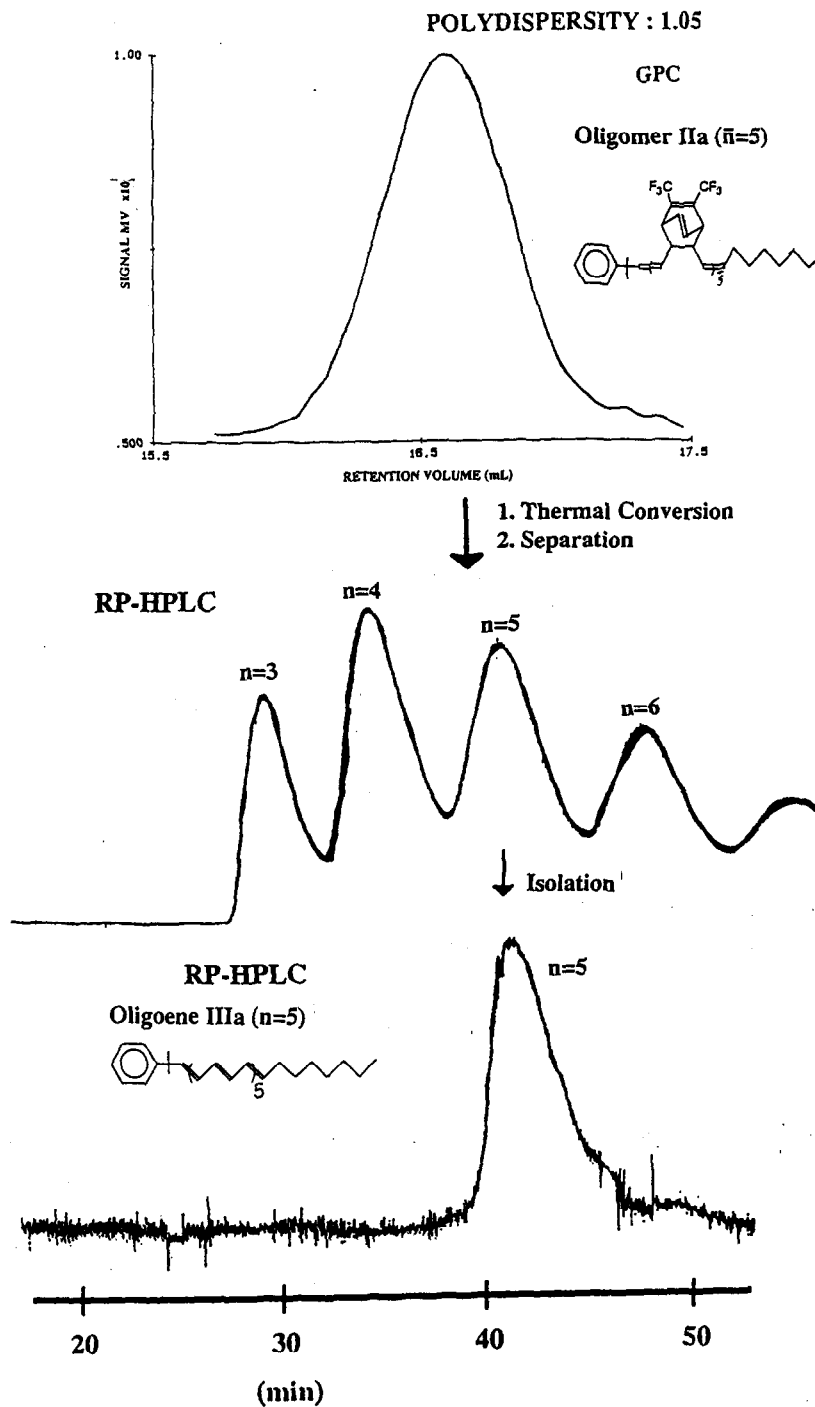
Fig. 6. The separation of oligoene mixtures (**IIIa**) into its individual components. Top trace GPC record (RI detector) of the precursor oligoene (**IIa**) ($\bar{n} = 5$); middle trace RP-HPLC record of the oligoene after conversion (**IIIa**) ($\bar{n} = 5$) (detector set at 400 nm, Econocil C18 Reversed Phase column, mobile phase acetonitrile/chloroform (95:5)); lower trace RP-HPLC record for compound (**IIIa**) ($n = 5$) after separation.

the final storage of the polymer were carried out at temperatures of $-5°C$ or less and under an inert atmosphere in order to avoid partial conversion of the precursor polymer to the polyene.

Synthesis of precursor oligoenes (**IIb**). In an inert atmosphere Glove Box, a $Mo(=CHC(CH_3)_2Ph)(NAr)(O^tBu)_2$ (0.050 g, 0.103 mmol) solution in dry and degassed toluene (5 ml) was prepared. Excess styrene (0.536 g, 5.16 mmol) was added to the mixture which was then sealed in an ampoule with a Young's valve and allowed to react with stirring for 24 h at 35°C. The colour of the mixture turned from yellow to dark red. At this point the sealed ampoule was transferred into the thermostated cooling bath at $-5°C$. Three solutions of 7,8-(bistrifluoromethyl)tricyclo-[4.2.2.0$^{2.5}$]deca-3,7,9-triene (0.1097 g, 0.412 mmol, 4 equivalents) in toluene (1 ml) were prepared in the Glove Box, sealed under nitro-

gen in ampoules and transferred via a double ended needle under dry nitrogen pressure to the mixture at 2.5-h intervals. The mixture was left to stir for an additional 2.5 h after the final addition. The polymer was recovered as a white powder (0.26 g, 79%) after repeated precipitation from toluene into cold ($-70°C$) methanol, filtration and drying under vacuum at 0°C. The isolated product was characterised by ^{1}H-NMR (Acetone-d_6, 399.952 MHz) showing peaks at δ 2.71 (broad, 10H, $>CH-$ allylic), 3.99 (broad, 10H, $>CH-$ allylic), 5.32 (broad, 10H, $=CH-$), 6.65 (broad, 12H, $=CH-$), 7.0 to 7.43 (5H, aromatics).

Synthesis of precursor oligoene (**IIc**). Precursor oligoene (**IIc**) was prepared via a hybrid procedure involving an exchange of the neopentyl substituent for a phenyl after the cross metathesis reaction of the alkylidene with excess styrene as described above, followed by the
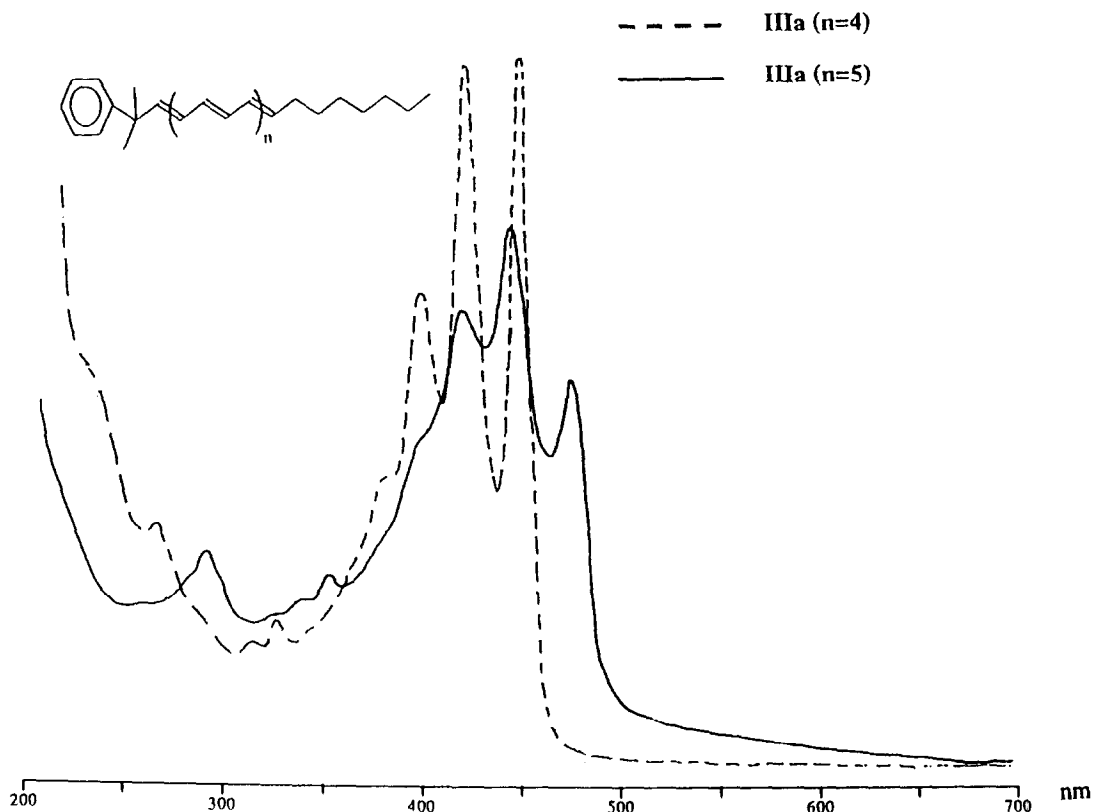

IIIa (n=4)

IIIa (n=5)

Fig. 7. UV–Vis spectra of (**IIIa**) $n = 4$ and (**IIIa**) $n = 5$.

addition of 5 equivalents of monomer and the addition of excess aldehyde after a reaction time of 20 min. This experiment was designed to eliminate the methyl groups on one end of the chain and to introduce a flexible heptyl group on the other end. The product was characterised by ^{1}H-NMR (CDCl$_3$, 399.952 MHz), showing peaks at δ 0.88 (t, 3H, –(CH$_2$) $_6$C$\underline{H}_3$), 1.28 (broad, 12H, –(C$\underline{H}_2$) $_6$–), 2.51 (broad, 10H, > C$\underline{H}$– allylic), 3.78 (broad, 10H, > C$\underline{H}$– allylic), 5.06 (broad, 10H, =C$\underline{H}$–), 6.48 (broad, 12H, = C$\underline{H}$–), 7.3 (5H, aromatics). Peaks assigned to impurities in the aromatic region (~ 7 ppm) and some small broad peaks in the aliphatic area, together with data from GPC

(broad shoulder in the high molecular weight side) and HPLC (two distinctive areas of separation one at 10 to 20 min, attributed to (IIIb) structures and another at 40 to 50 min attributed to (IIIc)) suggest that the impurities present are possibly polystyrene and (IIIb). Although we could observe for (IIIc) a separating pattern similar to (IIIa) under the same conditions, both the low solubility of the material and the presence of these impurities made it impossible to separate it into its individual components on a preparative scale.

Separation of mixed oligoenes (IIIa). The mixture of precursor oligoenes (IIa) with polydispersity index = 1.05 and average degree of
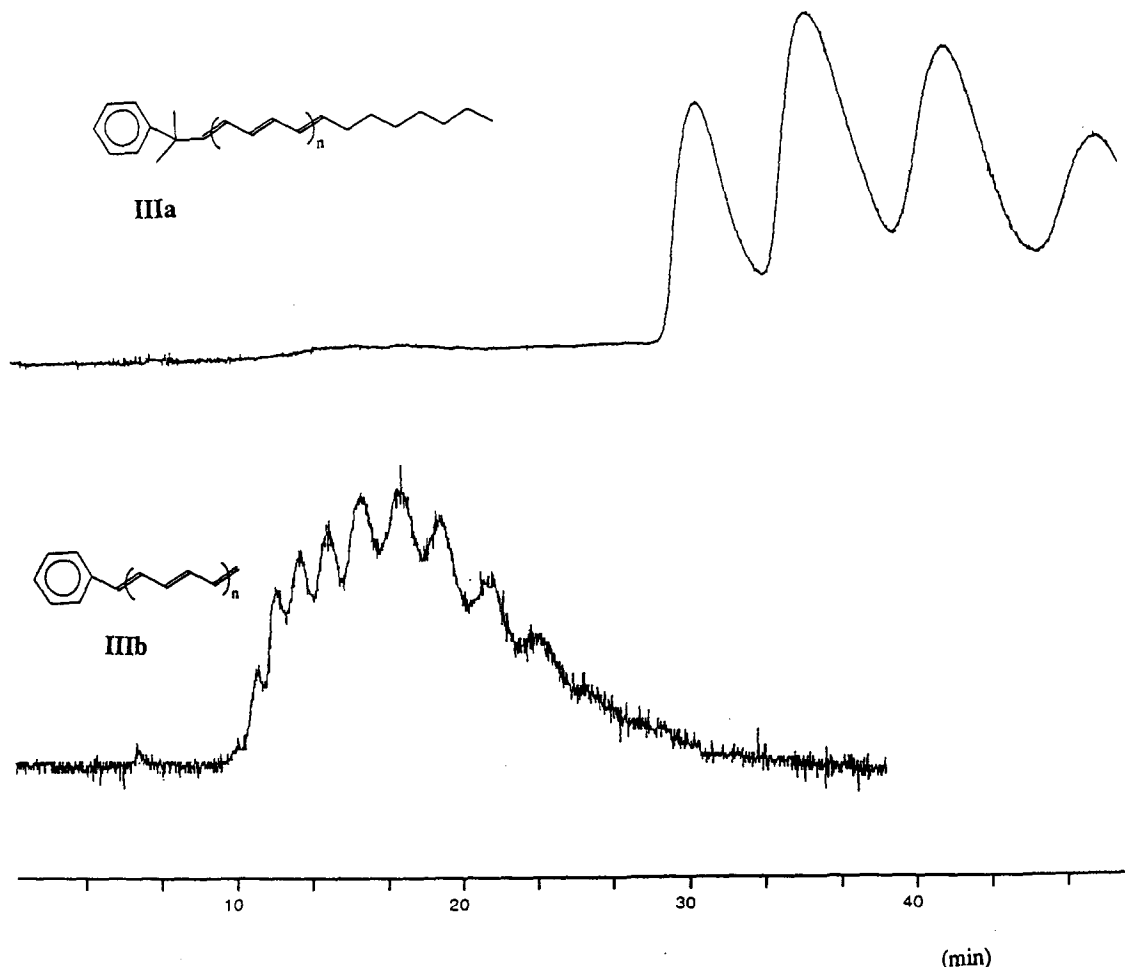

Fig. 8. RP-HPLChromatograms of (IIIa) and (IIIb), Vis detector signals (400 nm), mobile phase acetonitrile/chloroform (95:5).

polymerisation $n = 5$, was produced as discussed above and it was converted to the corresponding oligoenes (**IIIa**) by heating at 80°C under vacuum for 3 h. It was then dissolved in a dried and degassed acetonitrile/chloroform (95:5) mixture and separated to its individual components using a Varian Vista 5500 Liquid Chromatograph, and an Econosil C18 reversed phase column. The apparatus was equipped with a 9090 AutoSampler and an automatic fraction collector; the apparatus was masked and continually purged with dry, oxygen free nitrogen which allowed all the operations to be carried out in the dark and under an inert atmosphere. Two detectors were set at 255 nm and 400 nm. The mobile phase used was acetonitrile/chloroform 95:5 (HPLC grade, degassed).

Fig. 6 summarises and illustrates the separation process employed; the top trace records the GPC results for the mixture of oligomers (**IIa**) ($\tilde{n} = 5$); reverse phase HPLC (the middle trace) shows the converted material resolved into at least five components, two of which $n = 4$ (35 min) and $n = 5$ (42 min) were isolated by semi-prep HPLC, the bottom trace is for the compound (**IIIa**) with $n = 5$. The UV spectra of these two isolated compounds are shown in Fig. 7 and comparison with published results for similar systems [14], showed that the peak at 35 min corresponds to the oligoene with 9 double bonds with that at 42 min corresponding to the oligoene with 11 double bonds; the other components of the distribution are then assigned by analogy.

In Fig. 8 the RP-HPL Chromatograms of oligoenes (**IIa**) and (**IIb**) with average $n = 5$, recorded under the same conditions are compared and show clearly that the solubility and separability of (**IIb**) is much lower than that of (**IIa**) and that it would be extremely difficult to isolate any monodisperse fraction of (**IIb**) in appreciable amounts. The instrument response is automatically adjusted and the S/N ratio is a qualitative indication of the amount of dissolved material giving rise to the observed peaks.

4. Conclusions

The synthesis of oligomers and polymers of polyacetylene with well-defined architectures is possible via application of living ring opening metathesis polymerisation using molybdenum alkylidene (Schrock type) initiators and the 'Durham route'. This method allows control of the chain end structures, molecular weight and molecular weight distribution. The separation and isolation of soluble monodispense oligoene sequences can be achieved via the addition of solubilising alkyl end groups and application of a semi-prep reversed-phase HPLC. The materials whose synthesis and characterisation is described above, were prepared as part of an EU Network and the sequence of polyene precursors and polyenes with narrow polydispersities obtained are the subject of a study of the variation of absorption and photoinduced absorption spectra which will be published elsewhere in due course.

Acknowledgements

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