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A route to low polydispersity linear and star polyethylenes via ring-opening metathesis polymerization

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Living ring-opening metathesis polymerization of cyclopentene, initiated with a well-defined tungsten alkylidene complex, has been used to prepare low polydispersity linear and star poly(1-pentenylene)s. This was achieved by using di- and trifunctional aldehydes in the Wittig-like capping reactions of the living polymers. The resulting materials were hydrogenated to the corresponding polyethylene structures using a diimide derived from *p*-toluenesulfonyl hydrazide. An overview of this process, together with characterization data for the resulting materials, is presented. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Living ring-opening metathesis polymerization (ROMP) is a well-controlled procedure which in favourable circumstances can allow the construction of well-defined macromolecular structures with a high level of precision. Linear homopolymers and block copolymers with narrow molecular weight distributions[1–3], star polymers[4] and comb copolymers[5] have been prepared via ROMP.

In principle, linear, low polydispersity poly(1-pentenylene) can be used as the precursor to linear, narrow molecular weight distribution polyethylene (PE). Polyethylene of low polydispersity has been produced by the hydrogenation of 1,4-polybutadiene prepared by the anionic polymerization of 1,3-butadiene[6]; this approach, almost inevitably, results in polyethylene containing C_2 branches as a consequence of the small amount of 1,2-polymerization which always occurs even in the best-regulated 1,4-polymerizations of butadiene. Structurally perfect 1,4-polybutadiene can be obtained via the ring-opening metathesis polymerization of cyclobutene or cycloocta-1,5-diene, and Grubbs and coworkers have recently shown that well-controlled living polymerization of cyclobutene can be achieved with well-defined tungsten alkylidenes in the presence of trimethylphosphine[7]. Linear, low polydispersity polyethylene is of interest for detailed studies of the physical behaviour of the material, and consequently has always been an important synthetic goal. In this study we have investigated the possibility of using poly(1-pentenylene) as the precursor polymer to achieve this target. Additionally, we have examined the synthesis of well-defined star structures which are expected to resemble linear polymers rather more than networks; thus, for example, they are usually soluble in the same solvents as their linear analogues. However, their architectures have profound effects on their solid state physical and mechanical properties, and on their solution and melt properties[8–10].

Highly branched polymeric structures have been synthesized[4] via ROMP by the addition of a few equivalents of the norbornadiene dimer *exo-trans-exo*-pentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradeca-5,11-diene to living polynorbornene; the resulting structures have been described as 'star polymers'. The living polymer was finally cleaved from the metal in a Wittig-like reaction with benzaldehyde. In that method of synthesis the number of branches is neither fixed nor predictable and it is dependent on various parameters, including reactant ratios, concentrations, temperature and probably stirring and diffusion rates. In this paper we describe an attempt to establish a well-controlled method for the synthesis of star polymers via living ROMP.

RESULTS AND DISCUSSION

Star poly(1-pentenylene)s and polyethylenes via living ROMP

The living ROMP route to star polyethylenes described here is potentially advantageous compared to the method described in the previous paragraph because both the number and length of the branches are defined. The first step is the preparation of living poly(1-pentenylene); it is established that the ring-opening metathesis polymerization of cyclopentene at −45°C can give living polymers of narrow molecular weight distribution[11,12]. The Wittig-like capping reaction of

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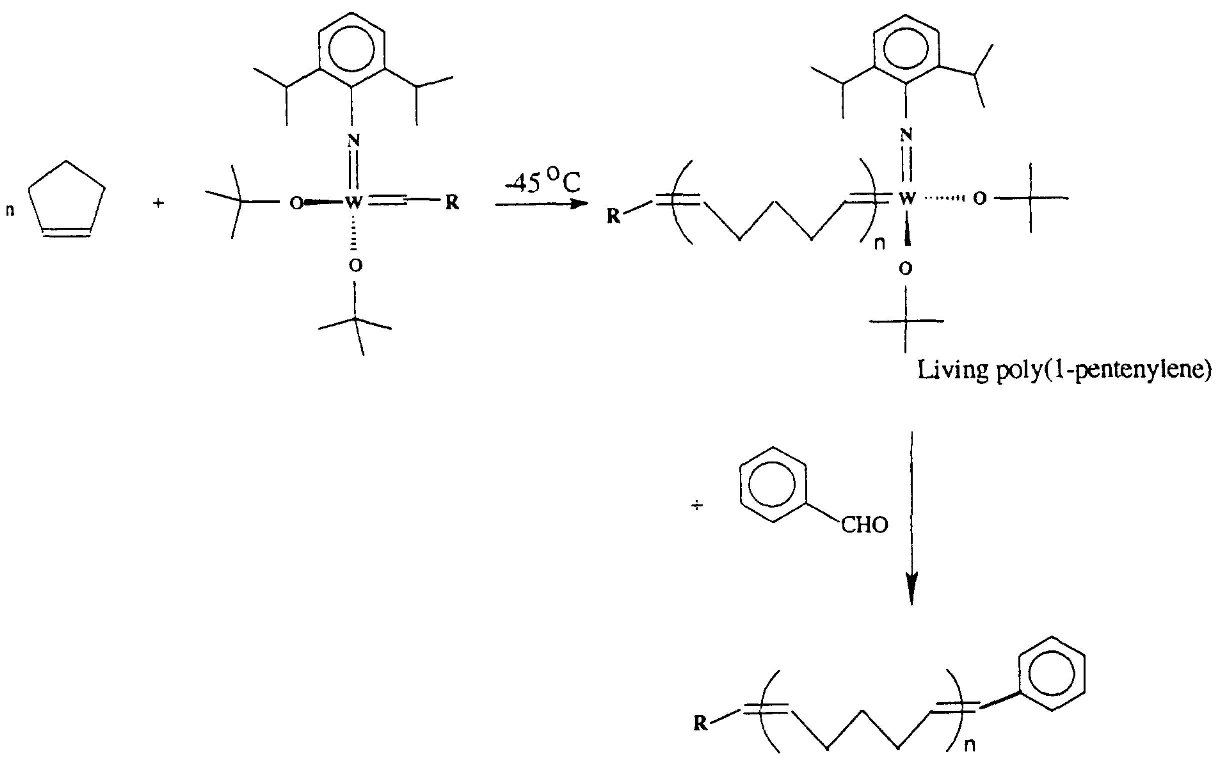

(I)

Figure 1 The living ring-opening metathesis polymerization of cyclopentene

the living polymer chain-end with a monofunctional aldehyde, such as benzaldehyde, produces linear poly(1-pentenylene) (**I**), as shown in *Figure 1*. The product can be obtained in high structural purity and with a narrow molecular weight distribution.

The introduction of difunctional or trifunctional aldehydes for the termination step results, in principle, in polymers which have, respectively, two and three times the molecular weight of the linear polymer produced when the reaction is terminated with benzaldehyde. This is the result of the capping reaction between the active chain-end species of the living polymer and each of the functional groups of these aldehydes. The structures arising from these reactions are in the case of difunctional aldehydes linear polymers with $M_n = 2M_n^L$ (**II**), while in the case of trifunctional aldehydes we obtain structures with a localized core (benzene ring) from which three polymer chains or arms emanate and $M_n = 3M_n^L$ (**III**), where M_n^L is the number average molecular weight of the living polymer before the addition of the aldehyde (see *Figure 2*).

The resulting precursor polymers were soluble and were characterized by conventional gel permeation chromatography (g.p.c.) of solutions in chloroform. The stationary phase was a polystyrene/divinylbenzene gel; a refractive index (r.i.) detector was used and the system was calibrated with polystyrene standards. The experimental g.p.c.-derived M_n values were corrected by a factor[11] of ~ 0.4; this correction factor is in the same range as a previously reported correction factor for a similar polymer (poly(1-butenylene))[7,13,14]. The poly(1-pentenylene) linear and star precursor polymers were hydrogenated using excess *p*-toluenesulfonyl hydrazide to produce linear and star polyethylenes as shown in *Figure 3* and described in detail later.

Preparation and purification of reagents

Cyclopentene was purchased from Aldrich, dried over LiH and vacuum transferred prior to use. Isophthalic dialdehyde (1,3-benzenedicarboxaldehyde) was purchased from Lancaster Synthesis and purified by recrystallization from methanol. It was then sublimed and stored under dry, oxygen-free nitrogen. Glutaric dialdehyde (50% solution in water, electron microscopy grade) was kindly provided by the University of Durham Biology Department. It was extracted from the aqueous solution with diethyl ether and the ether solution was dried over $MgSO_4$. The diethyl ether was removed in a rotary evaporator and the residue was fractionally distilled to give pure glutaric dialdehyde. The ^1H nuclear magnetic resonance (n.m.r.) spectrum showed signals at 9.72 (1H, CHO), 2.49 (2H, CH_2, t, $J_{HH} = 7.0$ Hz) and 1.89 ppm (1H, quintet, $J_{HH} = 7.0$ Hz) with a good signal to noise ratio and no trace of impurities. The product was then stored under dry, oxygen-free nitrogen at −40°C. 1,3,5-Benzenetricarboxaldehyde was prepared as described previously[15–17], and the path followed is shown schematically in *Figure 4* (56% yield, melting point (m.p.) 154°C; literature[16] m.p. 155°C). The ^1H n.m.r. spectral parameters were consistent with the literature data, and for this work we recorded ^1H and ^{13}C n.m.r. spectra for solutions in $CDCl_3$ with high signal to noise ratio in order to estimate the purity attained. The ^1H n.m.r. spectrum (199.975 MHz) displayed peaks at 8.65 (1H, CH aryl, s) and 10.21 ppm (1H,

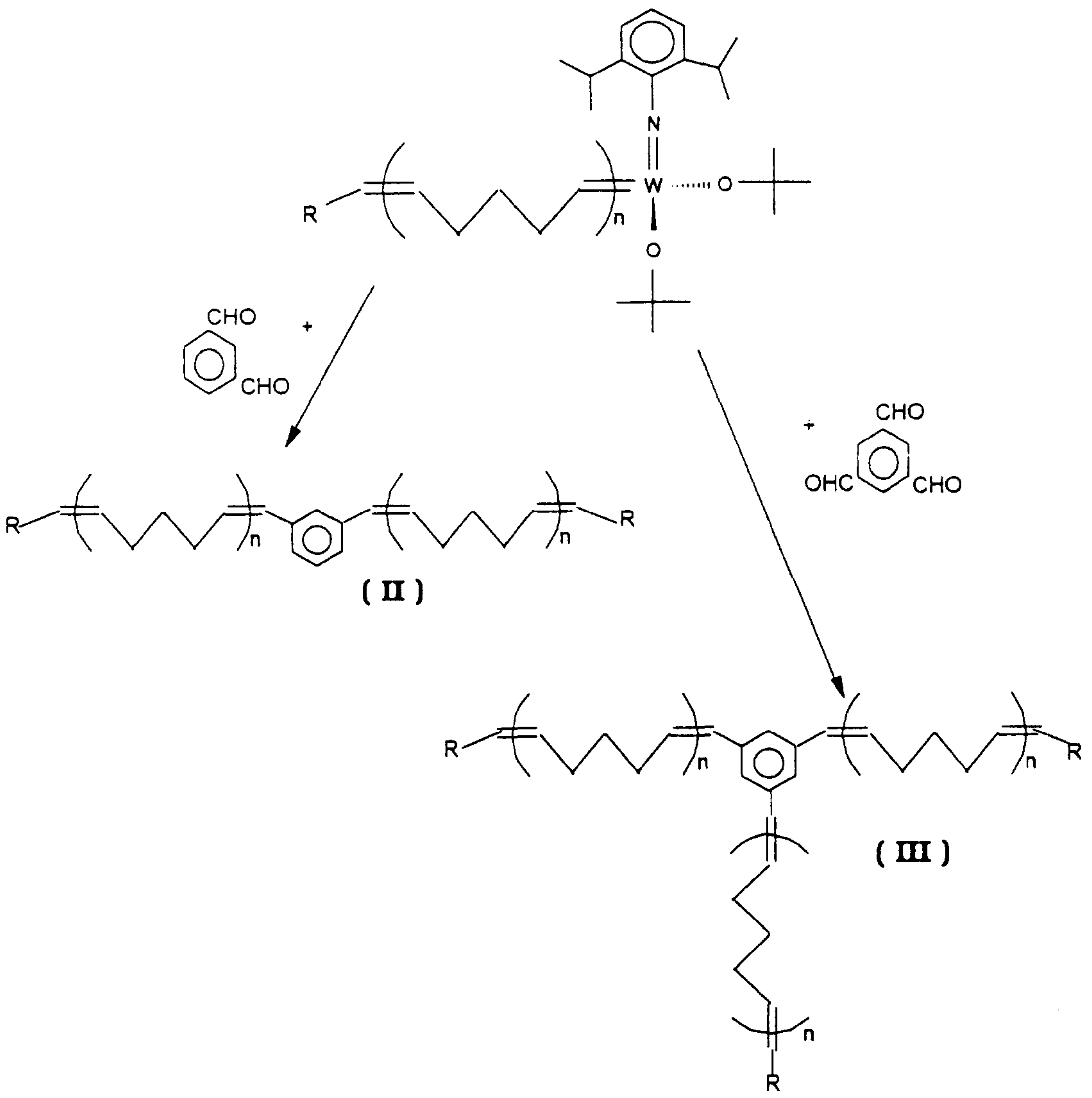

Figure 2 End-capping reaction with multifunctional aldehydes leading to the synthesis of star poly(1-pentenylene)s

CHO, s) and the ^{13}C n.m.r. spectrum (50.3 MHz) peaks at 134.8 (CH aryl), 137.8 (CCHO aryl) and 189.9 ppm (CCHO). However, in the ^{1}H n.m.r. spectrum there were minor peaks present at 10.20 (aryl CHO), 8.85 (aryl H, d) and 8.74 ppm (aryl H, d) which, although they reduced in intensity after repeated recrystallization (from acetone) and sublimation of the sample, could not be entirely eliminated. These signals are consistent with the presence of a partially reduced material in which there are two aldehyde units and one residual carbonyl chloride or carboxylic acid, and in support of this hypothesis a slight shoulder can be seen at the high frequency side of the carbonyl absorption in the infra-red (i.r.) spectrum. Although these data are not good enough to make an unambiguous assignment of the structure of the impurity, it is reasonable to propose as a working hypothesis that there is a difunctional aromatic aldehyde present in this material. Careful expansion and analysis of the ^{1}H n.m.r. spectrum indicates that if this hypothesis is true, the difunctional aromatic aldehyde is present to the extent of ~15 mol%. Although it was disappointing not to get a higher level of purity, it was decided to use this material in subsequent capping experiments. The i.r. spectrum (KBr disc) showed absorptions at 3369 (C=O overtone), 3061 (C–H aromatic), 2871 (O=C–H), 1695 (C=O), 1594 (C=C aromatic), 1454 (skeletal vibrations) and 1377 cm^{-1} (skeletal vibrations) which are consistent with the proposed structure. The electron impact (EI) mass spectrum showed a peak for the molecular ion at m/e 162 (99.78%) with the expected base peak at m/e $M-1$ mass units. Other peaks of high intensity occurred at m/e 133 for $[C_6H_3(CHO)_2]^+$ and 105 for $[C_6H_4(CHO)]^+$. There was no indication of chlorine-bearing species in the mass spectrum. A very small peak at m/e 177 (i.e. $M+15$) may possibly be indicative of a trace of oxidized product.

Preparation of living poly(1-pentenylene)

The polymerization of cyclopentene[11], initiated by $[W(CHBu^t)(NAr)(OBu^t)_2]$ at −45°C, exhibits the characteristics of an ideal living polymerization; thus, it displays well-defined kinetics, a linear increase in molecular weight with percentage monomer conversion, irreversible propagation steps, the absence of chain termination and transfer steps and the rate constant of initiation is greater than that of propagation. The techniques and conditions described in detail elsewhere[11] were used for the first step of the preparation of linear and star polyethylenes.

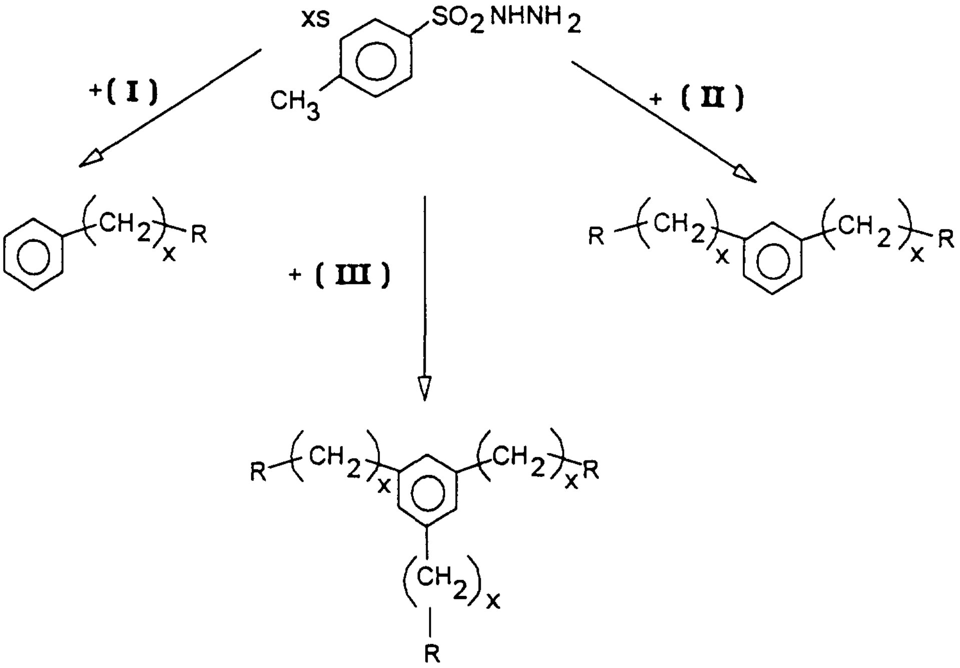

Figure 3 Hydrogenation of (I), (II) and (III) to yield the analogous PE structures

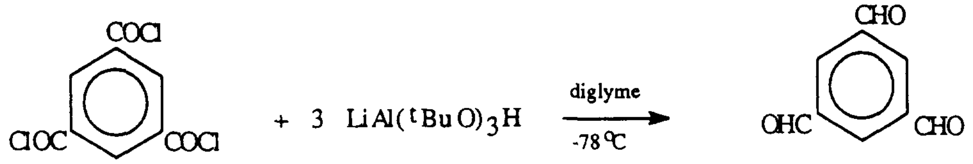

Figure 4 Preparation of 1,3,5-benzenetricarboxaldehyde

Table 1 Raw, i.e. uncorrected, g.p.c. data for polymers (I), (II) and (III) relative to polystyrene standards

Poly(1-pentenylene) capping agent	Product	M_n[a]	M_w[b]	PDI[c]	DP[d]
Benzaldehyde	(I)	23 400	26 800	1.15	340
Isophthalic dialdehyde	(II)	40 200	62 200	1.55	590
1,3,5-Benzenetricarboxaldehyde	(III)	67 900	109 200	1.61	998

[a] Number average molecular weight
[b] Weight average molecular weight
[c] Polydispersity index
[d] Degree of polymerization

End-capping reactions

The following experiment was designed to study the effects of using different aldehydes as the capping agents. In a glove box, three identical, two-compartment reaction vessels were loaded with the same amounts of monomer and initiator solutions. The monomer concentration was 3.8 M in $CHCl_3$. The solutions were allowed to react at −45°C, and after 3 h benzaldehyde, isophthalic dialdehyde and 1,3,5-benzenetricarboxaldehyde solutions in $CHCl_3$ were added to the first, the second and the third reaction vessel, respectively. The solutions were left to react for an additional 45 min. After recovery by precipitation from chloroform into a 10-fold excess of methanol, filtration and drying, the yield of (I) after a 3 h reaction time was found to be 44%, while (II) and (III) under the same conditions were obtained in 56 and 55% yield, respectively. These polymers were soluble in chloroform and were characterized by g.p.c. using PL_{gel} columns (5 μm, 100 Å, 1000 Å and 10^5 Å in series) and an r.i. detector; the results are shown in *Table 1*.

Earlier studies have established that at this time in the reaction we have a living polymer with a narrow polydispersity but incomplete consumption of monomer. If the reaction is allowed to proceed to complete consumption of monomer (~24 h at −45°C), there is some broadening of the molecular weight distribution, so quenching at 3 h was selected as the optimum time. The values quoted in the table are uncorrected, but since we are only concerned with the relative molecular weights and polydispersities of materials obtained by quenching with capping agents of different functionalities, this is not important. The g.p.c. traces reproduced in *Figure 5* show a narrow peak for the monocapped linear poly(1-

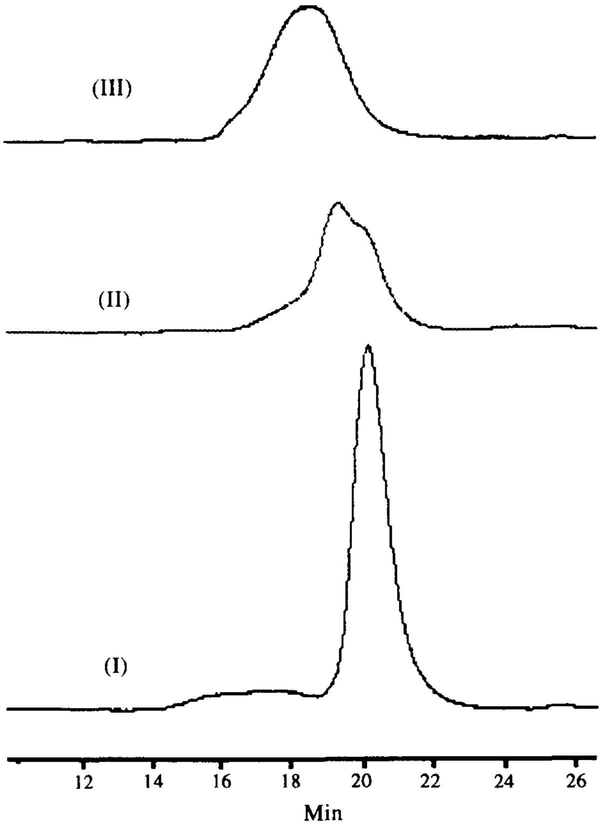

Figure 5 G.p.c. traces of (I), I(II) and (III)

pentenylene) (**I**), while the peak for the dicapped (**II**) is clearly bimodal, apparently corresponding to partially and completely reacted dialdehyde, and the peak for the star poly(1-pentenylene) (**III**) appears to be rather broad but symmetrical. It is clear that capping the living poly(1-pentenylene) with excess benzaldehyde gives the well-defined, narrow polydispersity polymer (**I**) as expected. Preparation of the polymers with double and triple molecular weight ((**II**) and (**III**)) requires exact stoichiometric balance between the aldehyde and the living chain-ends, and it is clear that for the bimodal polymer (**II**) this balance was not fully realized. It is clear from the trace reproduced here that the low molecular weight peak corresponds to the monocapped polymer, and the second peak is the anticipated dimer. There are several possible reasons for this outcome: these experiments were conducted on a small scale, and weighing with precision in a glove box is difficult, which may have led to inaccurate stoichiometric balance; in addition, the capping reagent may not have been completely soluble at the temperature of reaction, and it is also possible that the reaction time and mixing efficiency at the capping stage were inadequate for the purposes of these experiments.

The star polymer (**III**) showed a symmetrical, but broad g.p.c. peak, and it is clear that in this case there is essentially no monocapped polymer present. In theory, the complete linking of arms into stars with constant functionality (f) leads to a narrowing of the molecular weight distribution according to[8]

$$(M_w/M_n)_{star} = 1 + [(M_w/M_n)_{arm} - 1]/f$$

Thus, if ideal behaviour had been attained, we should have had a *PDI* value of 1.05; however, as discussed above, we know that the capping agent was impure and probably contaminated with a difunctional aldehyde to the extent of ~15 mol%. It is clear that the broadening of the molecular weight distribution in this case is greater than can be accounted for by the presence of this impurity, so the effects already discussed for the case of the difunctional aromatic aldehyde must be operating as well.

Nevertheless, if we consider simply the number average molecular weights for (**I**), (**II**) and (**III**) in *Table 1*, it is clear that, although imperfectly accomplished in this case, the process outlined in *Figure 1* has been largely realized. Optimization in order to achieve complete conversion would involve using an excess of living polymer and removing any unreacted material by fractionation after completion of the reaction.

The ^1H n.m.r. spectra of linear and star poly(1-pentenylene) were identical, as were the ^{13}C n.m.r. spectra. The ^1H n.m.r. spectra (400 MHz, $CDCl_3$) showed peaks at 5.38 (H_v), 2.03 (H_α, *t*), 1.98 (H_α, *c*) and 1.39 ppm (H_β). The ^{13}C n.m.r. spectra (100 MHz, $CDCl_3$) showed peaks at 130.35 (C_v, *t*), 129.85 (C_v, *c*), 32.23 (C_α, *tc*), 32.09 (C_α, *tt*), 26.91 (C_α, *cc*), 26.77 (C_α, *ct*), 29.87 (C_β, *cc*), 29.72 (C_β, *ct/tc*) and 29.57 ppm (C_β, *tt*). The symbol v indicates a vinylic proton (or carbon), while a Greek letter indicates the position of this proton (or carbon) relative to the nearest double bond; *t* and *c* indicate an association with *trans* or *cis* double bonds. The chain-ends are not expected to be detected in the n.m.r. spectra since the chains we examined here were too long to permit such an observation. The thermogravimetric analyses of linear and star poly(1-pentenylene) showed the same pattern, with a 2% weight loss at 360°C and maximum weight loss (97%) at 480°C.

As a further test of the procedure, polymer (**IV**) was formed after the capping reaction between the living polymer chains and half an equivalent of the aliphatic capping reagent glutaraldehyde. The resulting polymer was a linear poly(1-pentenylene) with $2n + 1$ repeat units in the chain and identical (R) chain-ends, as shown schematically in *Figure 6*.

Cyclopentene (600 equivalents, 1 g, 0.0147 mol) was polymerized at −45°C using $[W(CHBu^t)(NAr)(OBu^t)_2]$ (14 mg, 0.0245 mmol) as the initiator, and a small sample was taken out of the reaction vessel after 5 h. The g.p.c. analysis of this aliquot showed $M_n = 33\,800$, $M_w = 37\,200$ and $PDI = 1.1$. A solution of half an equivalent of glutaraldehyde (1.2 mg, 0.0122 mmol) in 1 ml $CHCl_3$ was prepared in the glove box and sealed under N_2. It was then taken out of the box, transferred via cannula under N_2 into the living polymer solution at −45°C, immediately after the sample for analysis was taken out, and allowed to react for 1.5 h. G.p.c. analysis of the final product (**IV**) showed $M_n = 61\,500$, $M_w = 94\,500$ and $PDI = 1.5$. It is clear that the M_n value is double that of the living polymer before quenching. However, the overlaid g.p.c. traces, shown in *Figure 7*, suggest the presence of unreacted polymer chains, this result being consistent with glutaraldehyde being in slight excess at the capping stage. The presence of these monocapped polymer chains in the solution leads to broadening of the molecular weight distribution. There is also evidence of a small broad peak at high molecular weight in the uncapped sample, probably a result of slight contamination with oxygen during sampling[18].

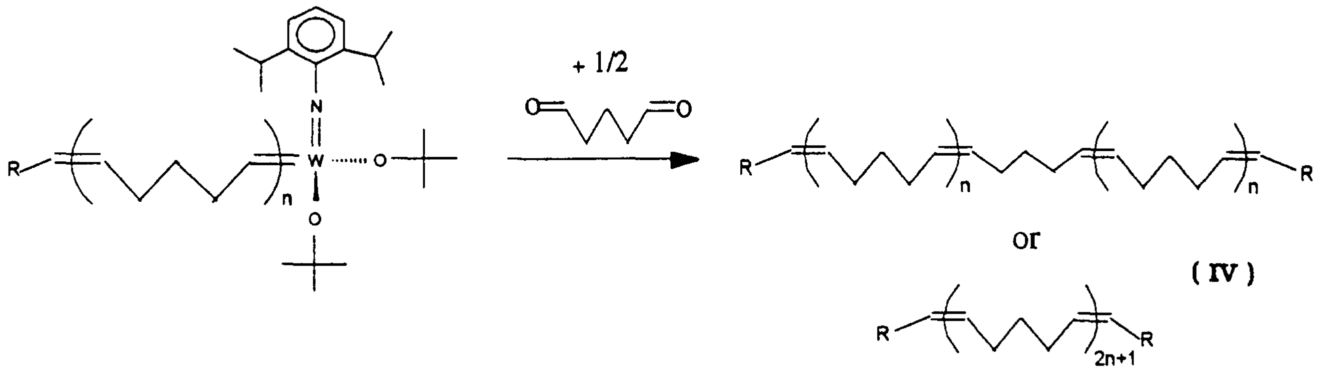

Figure 6 End-capping reaction with glutaraldehyde leading to the synthesis of a linear poly(1-pentenylene) with double molecular weight (IV)

Table 2 Raw, i.e. uncorrected, g.p.c. data for polymers (V) and (VI) relative to polystyrene standards

Polymer	Ratio of monomer to initiator	Polymerization reaction time (h)	Aldehyde	M_n	M_w	*PDI*
(V)	600:1	4	1,3,5-Benzenetricarboxaldehyde	53 000	78 000	1.5
(VI)	600:1	20	1,3,5-Benzenetricarboxaldehyde	95 300	147 000	1.5

Samples of three-branched star structures (V) and (VI) were also synthesized. The reaction conditions and the g.p.c. results of some of these experiments are summarized in *Table 2* in order to demonstrate that control over the molecular weight can be achieved by variation of the polymerization reaction time and the monomer to initiator ratio.

Hydrogenation of poly(1-pentenylene)-derived structures to give linear, narrow molecular weight distribution polyethylenes and star polyethylenes

The hydrogenation of linear, low polydispersity poly(1-pentenylene) using a diimide derived from the thermal decomposition of *p*-toluenesulfonyl hydrazide[19,20] yields linear polyethylene with the same molecular weight distribution. The same considerations apply to poly(1-pentenylene)s with different topologies – they will presumably maintain their architectures, chain lengths and molecular weight distributions after the hydrogenation. The resulting polyethylenes were not soluble in $CHCl_3$ or THF, and g.p.c. analysis of these samples was not possible with the systems available to us.

In a typical experiment, poly(1-pentenylene) (1 g, 0.015 mol repeat units) was dissolved in 150 ml *p*-xylene in a 250 ml, two-necked, round-bottomed flask. The flask was immersed in an oil bath and the solution was stirred and heated at 120°C. *p*-Toluenesulfonyl hydrazide (22.3 g, 0.12 mol, eight-fold excess) was added, and the solution was left to stir for 2 h. The hot solution was added slowly to excess methanol and polyethylene precipitated as a white powder. Methanol was removed via a filter cannula and the PE powder was dried under vacuum for several hours. The amount of recovered polymer was 0.98 g (98% yield).

I.r. spectroscopy provided information concerning the presence or not of residual double bonds in the polymer after hydrogenation. Solvent-cast (from hot *p*-xylene) films of the polyethylenes produced were used for these experiments. The overlaid spectra of the precursor poly(1-pentenylene) and the resulting polyethylene show complete conversion (*Figure 8*). The peaks at 1654 (C=C stretch), 966 (=C–H *trans* out of plane bend) and 3004 cm^{-1} (=CH stretch) visible in the poly(1-pentenylene) spectrum do not appear in the spectrum of the hydrogenated polymer. The spectrum of the resulting polyethylene consists only of the peaks at 2922 and 2852 (antisymmetric and symmetric CH_2 stretch), 1455 and 1437 (CH_2 bend), 721 (CH_2 rock) and ~1000–1300 cm^{-1} (weak absorptions).

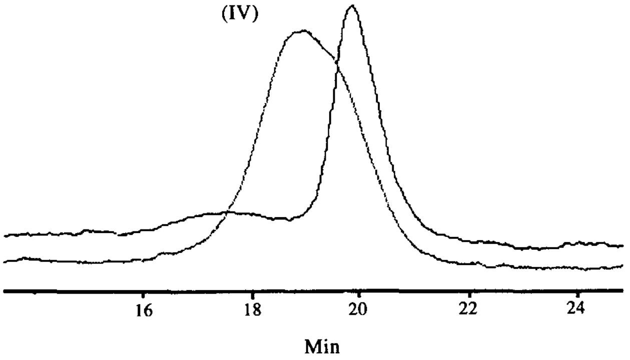

Figure 7 G.p.c. traces of poly(1-pentenylene) before and after end capping with glutaraldehyde

The differential scanning calorimetry (d.s.c.) traces used to determine the melting points and the degrees of crystallinity for the linear and star polyethylenes were recorded using a Perkin–Elmer DSC 7 instrument. The degree of crystallinity was calculated on the basis of a heat of fusion ΔH^0 of 293 J g^{-1} for 100% crystalline PE[21,22]. All the melting temperatures of the linear and star PEs studied were in the same range (*Table 3*). The melting range of these polymers is within the range expected for linear PE produced by classical Ziegler chemistry. For this small sample set it appears that the broader the molecular weight distribution, the broader

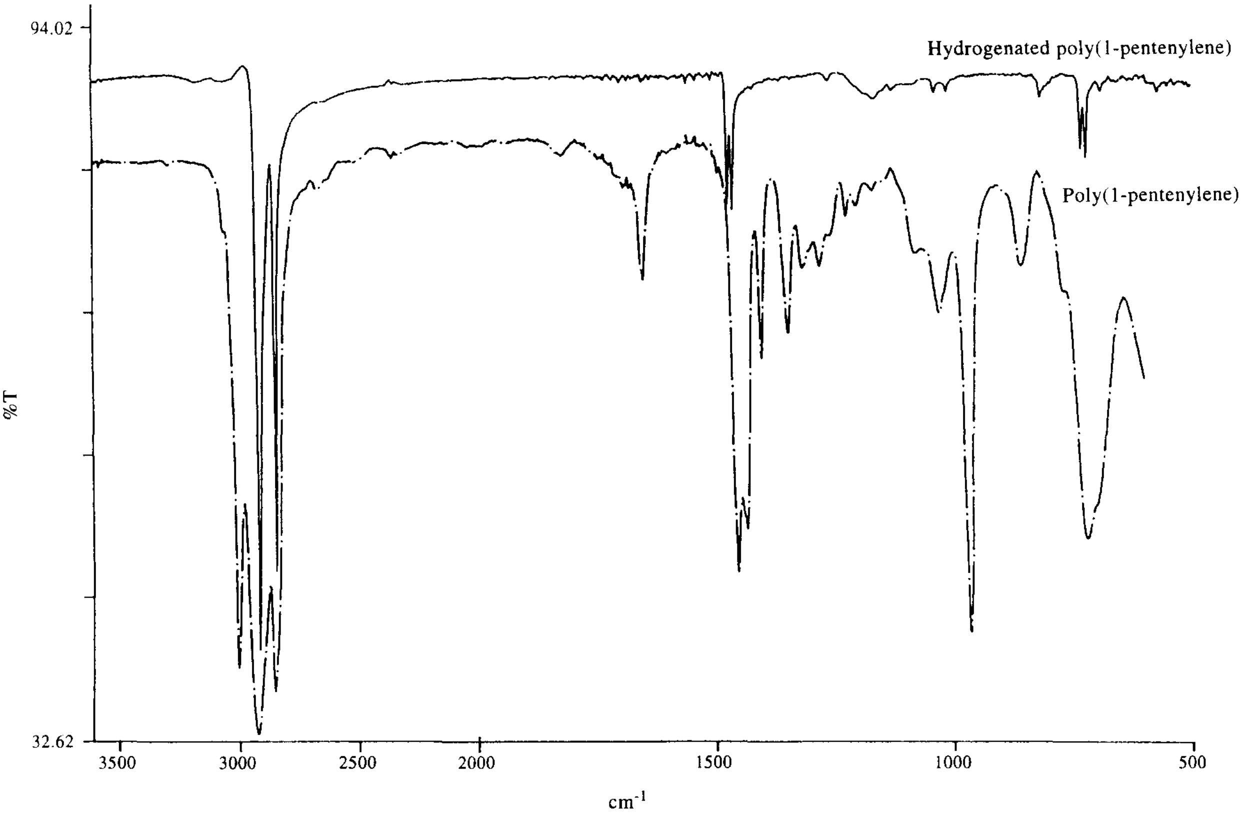

Figure 8 Typical i.r. spectra of poly(1-pentenylene) structures before (dashed line) and after (solid line) hydrogenation

Table 3 Melting temperatures (T_m) and degrees of crystallinity for some linear and star polyethylenes produced in this study

M_n[a]	M_w[a]	*PDI*[a]	Maximum T_m (°C)	Onset T_m (°C)	Degree of crystallinity (%)	PE
21 640	23 020	1.06	129.7	126.2	58	Linear
49 800	97 000	1.42	129.2	124.3	46	Three-branched star
62 800	97 000	1.54	131.1	123.1	59	Three-branched star
95 300	147 000	1.54	131.1	124.4	56	Three-branched star

[a] G.p.c. values obtained for the equivalent poly(1-pentenylene)s before hydrogenation; molecular weight averages relative to polystyrene standards

the melting range. The percentage crystallinity for the three-armed star with the lowest molecular weight was significantly lower than that for all the other samples. We are uncertain why this is the case, but it may be a consequence of the disordering effects of the junction points which would be greatest in the lowest molecular weight sample.

CONCLUSIONS

The polymerization of cyclopentene using $[W(CHBu^t)(NAr)(OBu^t)_2]$ as the initiator can produce narrow molecular weight distribution, linear, living poly(1-pentenylene) which, after quenching with the appropriate aldehyde, yields poly(1-pentenylene)s with the expected structures and appropriate multiples of the initial molecular weight. If exact stoichiometry can be achieved, this should lead to structures with narrower molecular weight distributions relative to the linear starting polymer. Although the general principle was demonstrated, molecular weight distribution narrowing was not observed in this work, probably as a result of not obtaining precise stoichiometry control in these small scale reactions and of not obtaining 100% pure capping agents; nevertheless, sufficient experimental evidence was acquired to demonstrate the viability of the approach. Hydrogenation of these polymers produces the corresponding polyethylenes; linear polyethylenes with *PDI* $\approx$ 1.04 and star polyethylenes were prepared.

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