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Synthesis of three- and six-arms polystyrene via living/controlled free radical polymerisation

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Abstract

Three new polyfunctional TEMPO-based initiators have been synthesised by reaction of some mesitylene cores and 2,2,6,6-tetramethyl-1-(2-hydroxy-1-phenylethoxy)-piperidine. They have been employed in the living/controlled radical polymerisation of styrene to provide three- and six-arm star macromolecules. These polymers have molecular weight ranging from 6000 to 11000 g/mol and narrow molecular weight distributions (PD < 1.3). Cleavage of the link between the core and the arms was achieved, using a two-step sequence implying the preliminary removal of the TEMPO chain ends followed by catalytic hydrogenolysis. The dimensions of the individual arms so obtained closely match the values expected from the styrene/initiator molar ratio in the polymerisation feed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polymers; Macromolecules; Initiators

1. Introduction

The continuous intense interest on highly branched macromolecules such as dendrimers [1], hyperbranched [2], dendrigraft [3] and star macromolecules [4] is aimed at achieving well-defined structure/properties relationships. Dendrimers offer in the most perfect structure, however they suffer from tedious syntheses involving iterative steps. In contrast, hyperbranched, dendrigraft or star macromolecules are less perfect, but their preparation is less laborious and time-consuming. For example, hyperbranched macromolecules are generally prepared by a single step polycondensation process starting from AB_x monomers [3]. Unfortunately, the resulting materials possess irregular branching and broad molecular weight distributions.

On the other hand, satisfactory control of both the molecular architecture and molecular weights can be achieved in the synthesis of combburst and star polymers employing 'living' polymerisation procedures. In the past the most used approach to the synthesis of star macromolecules has been ionic polymerisation [5,6]. More recently various living radical techniques such as ATRP [7], RAFT [8], SFRP [9] have been developed and successfully applied to star synthesis. Notably, the molecular weight of the arms can be accurately controlled and the polydispersities have values close to those obtained in living ionic polymerisations. The TEMPO-based unimolecular initiator approach developed by Hawker is particularly versatile since it can be applied to the synthesis of star molecules and other even more complex molecular architectures [9]. Moreover it appears simple and provides considerable control in the polymerisation of styrene and other variously functionalised monomers.

Owing to our interest in the synthesis of polymeric materials having branched architectures [10–12] we have investigated the applicability of this polymerisation technique to our systems. We wish to report herein the synthesis of the initiators **1**, **2** containing three styrene-TEMPO groups and **4** which have six TEMPO groups. The polymerisation of styrene initiated from these TEMPO derivatives and the characterisation of the resulting star polymers is also reported.

2. Experimental

2.1. Analytical methods

^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 NMR spectrometer operating at 200.13 and 50.00 MHz, respectively. Elemental analyses were carried out at the

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Department of Organic Chemistry of the University of Firenze. The gel permeation chromatography (GPC) measurements were carried out at r.t. on 100 μl samples (5 g/l polymer solutions in chloroform), using a system composed by a JASCO PU-1580 pump with Rheodyne injector, two in series Polymer Lab Mixed C columns (30 cm × 7.5 mm), and a Perkin Elmer LC-25 RI detector. Chloroform was employed as the mobile phase at a flow of 1.0 ml/min. Fourteen polystyrene standards, with nominal molecular weight ranging from 0.4 to 1460 kD, were used for the calibration curve, which was a third order polynomial.

2.2. Materials

Styrene (Aldrich) was distilled from CaH_2 under reduced pressure. Phenylacetylene, butyllithium, NaH 60% dispersion in mineral oil, D_2O (99.9% D), Lindlar catalyst and 10% Pd/C were obtained by Aldrich. Deuterium (99.9% D) was obtained by SIAD. 1,3,5-Tris(bromomethyl)benzene [13], 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene [14], 2,2,6,6-tetramethyl-1-(2-hydroxy-1-phenylethoxy)-piperidine [15] and the hexachloride 3 (6-cascade:benzene[3-1,3,5]:(4-methoxypyridin-2,6-yl)^2:chloromethyl) [11] were synthesised as described in the literature.

2.3. Synthesis of trideuteriovinylbenzene (styrene-d_3)

To a chilled (−10°C) solution of phenylacetylene (11 ml, 100 mmol) in *n*-hexane (50 ml) were added dropwise 50 ml (125 mmol) of a 2.5 M solution of butyllithium in *n*-hexane. The resulting suspension was stirred at r.t. for 1 h, then it was cautiously treated with 3 ml of D_2O. The organic phase was separated and distilled under reduced pressure to give 10 ml of phenylacetylene-d_1 (yield: 90%, deuteration degree: 98% by NMR). Phenylacetylene-d_1 was diluted with 15 ml of *n*-hexane and 1 ml of quinoline and charged into a hydrogenation apparatus with 100 mg of Lindlar catalyst. The deuteration was carried out at room conditions by monitoring the formation of styrene-d_3 by GLC. After attainment of complete conversion of phenylacetylene (ca. 2.5 h), the catalyst was removed by filtration and the organic phase washed with HCl 1 M (2 × 15 ml), and brine, and finally dried on $MgSO_4$. Distillation at reduced pressure afforded 7.6 g (74% overall yield) of styrene-d_3 (deuteration degree 98% ca. by NMR).

2.4. Synthesis of TEMPO-based initiators

1: To a solution of 2,2,6,6-tetramethyl-1-(2-hydroxy-1-phenylethoxy)-piperidine (480 mg, 1.72 mmol) in dry THF (20 ml) was added NaH (60% dispersion in mineral oil, 126 mg, 3.15 mmol). The suspension was stirred under argon for 0.5 h at r.t., then 1,3,5-tris(bromomethyl)benzene (180 mg, 0.5 mmol) was added. The resulting yellow mixture was stirred at 60°C for 12 h; then it was treated with CH_3OH and taken to dryness. The oily residue was partitioned between dichloromethane and water. The organic phase was washed with water, dried over $MgSO_4$ and evaporated to give **1**. The crude product was purified by column chromatography (silica gel) eluting with 95:5 (v/v) dichloromethane-ethyl acetate. The trifunctional initiator was obtained as pale yellow oil. Yield 78%. Anal. calcd for $C_{56}H_{79}N_3O_6$: C = 76.15%, H = 9.27%, found C = 76.03%, H = 9.38%.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 0.66$ (br s, 9 H, CH_3), 0.98 (br s, 9 H, CH_3), 1.04 (br s, 9 H, CH_3), 1.31 (br s, 9 H, CH_3), 1.3–1.6 (br m, 18 H, CH_2), 3.63 (dd, 3 H, CHH), 3.94 (dd, 3 H, CHH), 4.29 (s, 6 H, $ArCH_2$), 4.84 (dd, 3 H, CH), 6.75 (s, 3 H, ArH), 7.28–7.34 (m, 15 H, ArH). ^{13}C-NMR ($CDCl_3$, ppm): $\delta = 16.48$, 20.20, 33.65, 40.32, 59.47, 72.52, 72.60, 85.27, 125.35, 127.10, 127.62, 127.81, 138.32, 141.84.

2: This compound was obtained in 67% yield following the same procedure detailed for **1**. Anal. calcd for $C_{63}H_{93}N_3O_6$: C = 76.45%, H = 9.48%, found C = 76.67%, H = 9.20%.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 0.64$ (br s, 9 H, CH_3), 1.03 (br s, 9 H, CH_3), 1.14 (br s, 9 H, CH_3), 1.48 (br s, 9 H, CH_3), 1.3–1.7 (br m, 18 H, CH_2), 1.9 (s, 9 H, $ArCH_3$), 3.64 (dd, 3 H, CHH), 3.98 (dd, 3 H, CHH), 4.31–4.38 (AB q, 6 H, $ArCH_2$), 4.76 (dd, 3 H, CH), 7.20–7.35 (m, 15 H, ArH).

4: This compound was obtained in 58% yield following the same procedure detailed for **1**.

Anal. calcd for $C_{132}H_{183}N_9O_{15}$: C = 74.23%, H = 8.64%, found C = 74.13%, H = 8.82%.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 0.68$ (br s, 18 H, CH_3), 1.05 (br s, 18 H, CH_3), 1.21 (br s, 18 H, CH_3), 1.29 (br s, 18 H, CH_3), 1.3–1.6 (br m, 36 H, CH_2), 3.81 (dd, 6 H, CHH), 4.08 (dd, 6 H, CHH), 4.54 (s, 12H, $pyCH_2$), 4.92 (dd, 12 H, $ArCH_2$ and CH), 6.69 (s, 6 H, pyH), 7.21–7.41 (m, 30 H, ArH), 7.47 (s, 3H, ArH). ^{13}C-NMR ($CDCl_3$, ppm): $\delta = 17.06$, 20.17, 33.86, 40.36, 59.83, 69.14, 73.44, 85.15, 105.62, 126.54, 127.21, 127.77, 136.87, 141.77, 160.06, 166.01.

2.5. Preparation of polystyrene star polymers

P1: A solution of the trifunctional initiator **1** (175 mg, 0.19 mmol) in styrene (1.30 g, 12.5 mmol) under argon was reacted with stirring at 125°C for 72 h. The crude polymer was dissolved in dichloromethane (5 ml) and precipitated in *n*-hexane (100 ml). The resulting rubbery material was redissolved in dichloromethane and reprecipitated in methanol (100 ml). P1 was obtained as a white powder in 66% yield. $M_n = 6700$ and PD = 1.09.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 0.2$–0.5 (br d), 0.8–2.8 (br m), 3.1 (br s), 3.2–3.4 (br m), 4.04.5 (br m), 6.0–6.2 (br m), 6.3–7.4 (br m). The partially deuterated analogue of P1 displays signals at $\delta = 0.2$–0.5 (br d), 0.8–1.6 (br m), 2.4–2.8 (br m), 3.2–3.4 (br m), 4.1–4.2 (br m), 6.3–7.4 (br m).

P2: This polymer was obtained in 68% yield following the same procedure detailed for P1. $M_n = 8400$ and PD = 1.26.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 0.2–0.5$ (br d), 0.8–2.8 (br m), 3.1 (br s), 3.2–3.4 (br m), 4.0–4.5 (br m), 6.0–6.2 (br m), 6.3–7.4 (br m). The partially deuterated analogue of P2 displays signals at $\delta = 0.2–0.5$ (br d), 0.8–1.6 (br m), 1.95 (br s), 2.4–2.8 (br m), 3.2–3.4 (br m), 4.1–4.2 (br m), 6.3–7.4 (br m).

P3: This polymer was obtained in 65% yield following the same procedure detailed for P1. $M_n = 9900$ and PD = 1.11.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 0.2–0.5$ (br d), 0.8–2.8 (br m), 3.1 (br s), 3.2–3.4 (br m), 4.0–4.5 (br m), 4.6–4.8 (br m), 6.0–6.2 (br m), 6.3–7.4 (br m). The partially deuterated analogue of P3 displays signals at $\delta = 0.2–0.5$ (br d), 0.8–1.6 (br m), 2.4–2.8 (br m), 3.2–3.4 (br m), 4.1–4.2 (br m), 4.6–4.8 (br m), 6.3–7.4 (br m).

2.6. Cleavage of the TEMPO units

In a typical experiment, to a toluene solution of P1 (0.62 g in 10 ml) were added 10 ml of acetic acid and 0.30 g of Zinc dust. The resulting suspension was stirred under argon at 90°C for 8 h, then the solid phase was filtered off and the resulting solution taken to dryness under reduced pressure. The residue was dissolved in dichloromethane and precipitated in methanol to afford 0.48 g of P1a. (82% yield).

^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.2–2.8$ (br m), 3.2–3.4 (br m), 4.1–4.3 (br m), 6.3–7.4 (br m). The partially deuterated analogue of P1a displays signals at $\delta = 2.4–2.8$ (br m), 3.2–3.4 (br m), 4.1–4.3 (br m), 6.3–7.4 (br m).

Analogously, P2a was obtained in 65% yield.

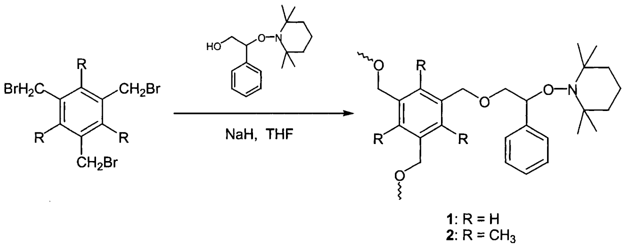
^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.2–2.8$ (br m), 3.2–3.4 (br m), 4.1–4.3 (br m), 6.3–7.4 (br m). The partially deuterated analogue of P2a displays signals at $\delta = 1.95$ (br s), 2.4–2.8 (br m), 3.2–3.4 (br m), 4.1–4.3 (br m), 6.3–7.4 (br m).

The same procedure afforded P3a in 67% yield.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.2–2.8$ (br m), 3.2–3.4 (br m), 4.6–4.8 (br m), 6.3–7.4 (br m). The partially deuterated analogue of P3a displays signals at $\delta = 2.4–2.8$ (br m), 3.2–3.4 (br m), 4.6–4.8 (br m), 6.3–7.4 (br m).

2.7. Catalytic hydrogenolysis

P1b: Into a stainless steel autoclave (total volume ca. 100 ml) were charged a dichloromethane solution of P1a (480 mg in 10 ml), 3 ml of methanol and 50 mg of 10% Pd/C. The reactor was purged with argon, pressurised at 30 bar with H_2 and heated under stirring at 90°C. After 24 h the autoclave was cooled at r.t., the residual gas vented off and the reaction mixture was filtered to remove the catalyst. The resulting solution was evaporated under reduced pressure, and the residue dissolved in chloroform (3 ml) and precipitated by methanol addition (15 ml) to give a white powder (270 mg, 57% yield). GPC analysis showed that only partial cleavage of the benzylic ethereal linkages has occurred at this stage, therefore, a 200 mg sample of the recovered polymer was treated with H_2 under the above conditions for additional 48 h. The usual workup procedure afforded 120 mg of P1b (overall yield: 35%).



Scheme 1.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.2–2.5$ (br m), 6.3–7.4 (br m).

Analogous sequence of treatments afforded P2b in 37% overall yield.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.2–2.5$ (br m), 6.3–7.4 (br m).

Under the same conditions, the hydrogenolysis of P3a went to completion in 24 h affording P3b in 68% yield.

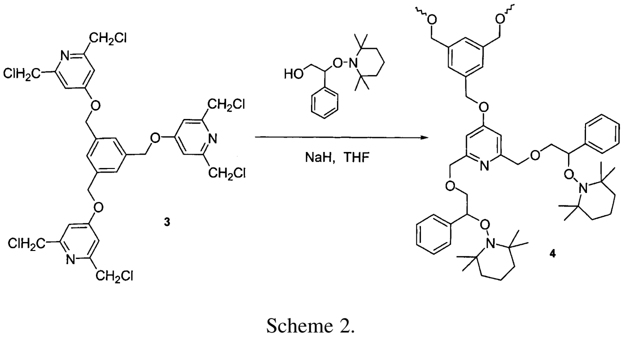
^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.2–2.5$ (br m), 6.3–7.4 (br m). The partially deuterated analogue of P3b displays signals at $\delta = 2.5$ (br s, OH), 6.3–7.4 (br m).

3. Results and discussion

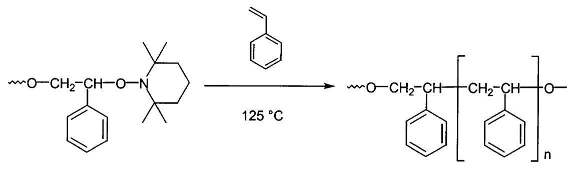
3.1. Synthesis of the initiators

The trifunctional initiator cores **1** and **2** were synthesised by reaction of 2,2,6,6-tetramethyl-1-(2-hydroxy-1-phenylethoxy)-piperidine with 1,3,5-tris(bromomethyl)benzene and 1,3,5-tris-(bromomethyl)-2,4,6-trimethylbenzene in the presence of NaH in dry THF, respectively (Scheme 1). Chromatographic purification of the reaction crudes afforded **1** and **2** in 78 and 67% yield, respectively.

Analogously, the hexafunctional core **4** was obtained from the reaction of 2,2,6,6-tetramethyl-1-(2-hydroxy-1-phenylethoxy)-piperidine with the hexachloride **3** in 58% yield after chromatographic purification (Scheme 2). The initiator cores **1**, **2**, **4** were characterised by ^{1}H- and ^{13}C NMR spectroscopy and elemental analysis (see Section 2).



Scheme 2.



1, 2, 4

P1, P2, P3

Scheme 3.

3.2. Polymerisation of styrene

The polymerisation of styrene in the presence of TEMPO based initiators has been extensively investigated [15,16]. Such studies have shown that high polystyrene yields are achieved in 24–48 h operating at 120–130°C. Thus, our polymerisation experiments were carried out at 125°C for 72 h (Scheme 3).

The styrene/initiator molar ratio was kept low (ca. 60–90) to make easier the detection of the NMR resonances. For the same purpose, some experiments were performed using trideuteriovinyl-benzene ($CD_2{=}CD{-}C_6H_5$, styrene-d_3).

The polymers were obtained as highly viscous oils or glassy solids, which were first dissolved in a small amount of dichloromethane and then precipitated into *n*-hexane. The rubbery materials so obtained were redissolved in dichloromethane and precipitated in methanol to give white powdery solids.

Thus, star polymers with molecular weight ranging from 6000 to 11000 g/mol (M_n by GPC) with polydispersity < 1.3 were prepared in 65–70% yield (Table 1). These yields are certainly lower than the actual figures for the monomer conversions, owing to the low molecular weight of the polystyrene produced, which led to unavoidable losses during the purification steps.

3.3. Polymer characterisation

The ^{1}H NMR spectra of the isolated materials agree with the formation of polystyrene-like materials. As a matter of fact, the ^{1}H NMR spectrum of P1 (Fig. 1a) shows the intense and broad resonances attributable to the CH_2 and CH groups of polymer backbone at 1.6–2.5 ppm and those of the aromatic protons at 6.3–7.4 ppm. The resonances relevant to the TEMPO moieties (0.2–1.6 ppm) [17,18], which are partially masked by the broad signals of CH and CH_2 protons, are promptly recognised in the spectrum of the polymer prepared using styrene-d_3 (Fig. 1b). In this spectrum the broad resonances at 4.2–4.1, 3.4–3.2 and 2.8–2.4 ppm of relative intensity 2:2:1 are attributed to the benzylic, ethereal methylene and methine protons of the $Ar{-}CH_2{-}O{-}CH_2{-}CH\sim$ core moiety, respectively.

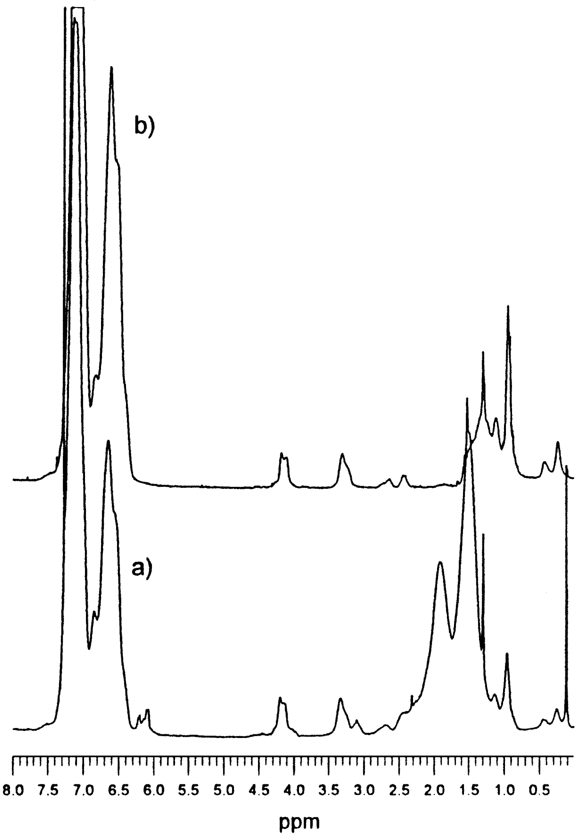


Fig. 1. (a) ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of P1; (b) ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of partially deuterated P1.

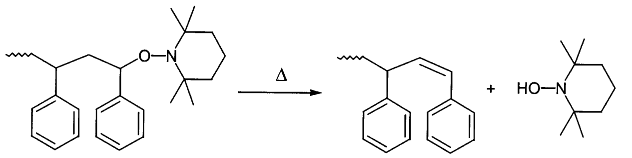
Literature data for TEMPO-terminated polystyrene point out that the resonance of the benzylic proton of the styrene unit bonded to the piperidinyloxy group ($\sim$CH(Ph) –ON) appears to be split in two sets of signals at 4.5–4.3 and 4.0 ppm [17,18]. Accordingly, the ^{1}H NMR spectrum of P1 (Fig. 1a) shows two broad resonances at 4.5–4.3 and 4.1–4.0 ppm, which are partially superimposed to the signal of the benzylic protons of the core.

Inspection of the spectrum in Fig. 1a reveals additional resonances at 6.0–6.2 and 3.1 ppm, which on the basis of literature data [19] are consistent with the presence of

Table 1
Molecular weight data for star polymers P1–P3

Init.	Styr./init (mol/mol)	Time (h)	Polymer (yield%)	M_n (GPC)	M_w (GPC)	M_w/M_n	M_n[a] (calcd)
1	66	72	P1 (68)	6700	7300	1.09	7857
2	90	72	P2 (66)	8400	10600	1.26	10389
4	120	72	P3 (65)	9900	11000	1.11	14698

[a] M_n calculated from the styrene/initiator feed ratio.



Scheme 4.

olefin-terminated polystyrene. Accordingly, these latter signals are not present in the spectrum of deuterated P1. Integration of these resonances indicates that ca. 30% of the star arms have olefin end groups. The formation of such end groups can be rationalised by invoking a thermal decomposition process (Scheme 4) analogous to the spontaneous thermal decomposition observed by Priddy and co-workers on heating 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidine at 120°C in the absence of styrene [20].

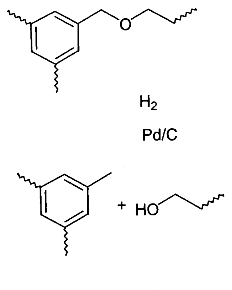
Since P1 has a narrow molecular weight distribution (see below), the formation of the observed olefin-terminal groups likely occurs on standing at high temperature after complete consumption of the monomer.

The ^{1}H NMR spectrum of P2 is almost identical to that of P1. In fact, the two polymers differ only for the methyl substituents on the central core, the presence of which is confirmed by a singlet at 1.95 ppm in the ^{1}H NMR spectrum of P2 obtained using styrene-d$_3$. Also in this case, signals at 3.1 and 6.0–6.2 ppm indicating the formation of ca. 25% of olefin end groups were observed.

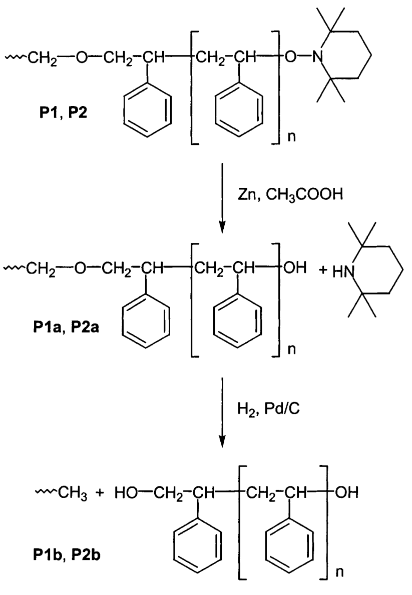
The ^{1}H NMR spectrum of P3 is also quite similar to those of P1 and P2; the main difference consists in a broad resonance at 4.6–4.8 ppm attributable to the methylene groups linked to the pyridine nuclei (the signals of the aromatic pyridine protons are masked by the other aromatics).

As expected for a 'living' free radical polymerisation, GPC analysis shows that the polymeric materials P1–P3 have narrow polydispersities (see Table 1) similar to those attainable by anionic polymerisation. The experimental molecular weights M_n obtained from the GPC data appear to be lower than those expected on the basis of the monomer to initiator ratio in the feed. However, this discrepancy is not surprising and is consistent with the formation of star shaped polymers, which have hydrodynamic volumes lower than those of linear polymers of comparable molecular weight [21].

Therefore, to get a more accurate characterisation of P1–P3 we have undertaken an investigation to determine the molecular weight of the single arms.



Scheme 5.



Scheme 6.

Initially, the removal of the core molecule was attempted by treating P1 with trimethylsilyliodide, a well-known reagent for the cleavage of ethers [22]. However, both at 25 and at 65°C the reaction failed providing the unchanged starting product.

Following a different approach P1 was treated with molecular hydrogen under pressure (20 atm) in the presence of 10% Pd/C (Scheme 5). Once again, the cleavage of the benzylic ether linkages was unsuccessful, and the unchanged star polymer was recovered in almost quantitative yield.

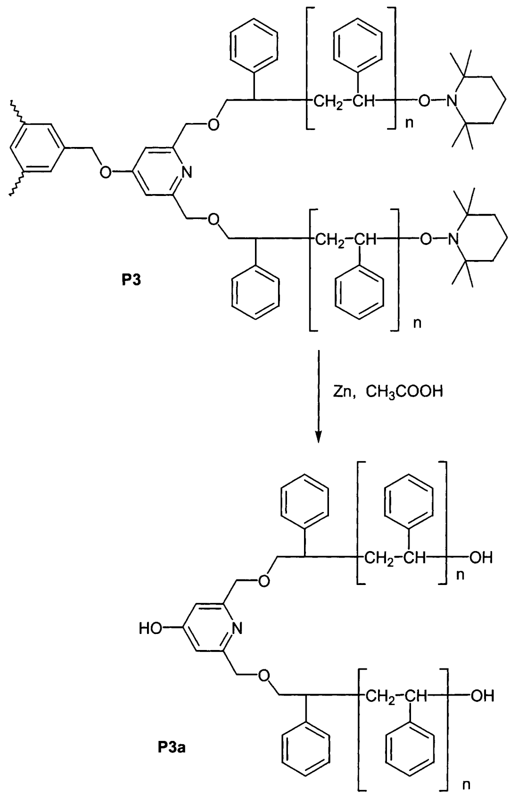
GC-MS analysis of the mother reaction liquor showed the presence of small amounts of 2,2,6,6-tetramethylpyperidine, the presence of which account for the failure of the catalytic cleavage, since it is known that aliphatic amines inhibit the palladium-catalysed hydrogenolysis of benzylic ethers [23]. Therefore, a different two-steps cleavage strategy, implying first the removal of the TEMPO moiety by reaction with Zn dust in acetic acid [24,25] followed by the hydrogenation of the benzylic moieties in the presence of Pd/C, was devised (Scheme 6).

In Table 2 are reported the GPC data of the polymeric species recovered after treatment with Zinc in acetic acid,

Table 2
Molecular weight data for the polymers isolated from the reaction with Zn/CH$_3$COOH

Polymer	Yield (%)	M_n (GPC)	M_w(GPC)	M_w/M_n	M_n[a](calcd)
P1a	82	6400	7100	1.11	6327
P2a	65	8600	10700	1.24	8154
P3a	67	3800	4500	1.18	9075

[a] Calculated by subtracting the contribution of the TEMPO moieties from the M_n (GPC) data of Table 1.



Scheme 7.

along with the values calculated subtracting the contribution of the TEMPO moieties from the respective M_n values in Table 1.

The GPC data indicate no substantial variation in the molecular weights of P1a and P2a with respect to the starting species. This result is consistent with the small molecular weight of the split off species, which is further underestimated as the consequence of the star-like structure of the macromolecules, and is therefore compatible with the experimental error typical of the GPC technique. In particular, the calculated M_n for P2a is even slightly larger than that of its precursor P2, while their GPC maxima match exactly. Such apparently inconsistent result arises from the lower weighed contribution of end tail of the elution curve of P2a, possibly due to further fractionation during the repeated purification procedures following the hydrogenolysis, eventually leading to preferential loss of lower molecular weight material. Indeed, the removal of the TEMPO moieties are substantiated by the ^{1}H NMR spectra of the partially deuterated analogues of P1a and P2a in which the resonances of these groups are no longer recognisable.

In contrast, a significant decrease of M_n was observed for P3a, the polymer recovered after having treated P3 with Zinc under the same conditions used for P1 and P2. Inspection of the ^{1}H NMR spectrum of P3a reveals that also the central core has been removed along with the TEMPO groups. Thus it appears that the treatment with Zn/CH$_3$COOH cleaves both Tempo-polystyrene and central core-polystyrene linkages, as shown in Scheme 7.

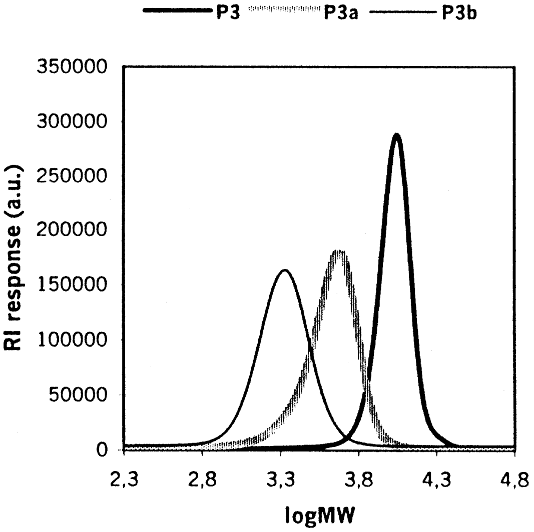


Fig. 2. Gel permeation chromatograms of polymer P3 and its derivatives P3a and P3b.

The proposed structure for P3a was confirmed by treatment with molecular hydrogen in the presence of 10% Pd/C which afforded the free polystyrene arms. The recovered material P3b was found to have $M_n = 1940$ (GPC, see Table 3 and Fig. 2) which is in good agreement with the value expected ($M_n = 2252$) on the basis of monomer to initiator ratio in the feed.

In keeping with the good results achieved, P1a and P2a were treated with molecular hydrogen in the presence of Pd/C for 24 h at 90°C.

In both cases, the GPC chromatograms of the recovered materials showed two partially overlapping elution curves indicating a bimodal distribution of the molecular masses. Since the first eluted peak has the same retention time of the star precursor, while the second one has a higher retention time indicating the presence of macromolecules of much lower molecular weight, we assumed that only a partial cleavage of the benzylic linkage had occurred upon hydrogenation. Thus, the recovered products were most likely composed in both cases of mixtures of cleaved single polystyrene arms, partially cleaved two-arm stars, and unreacted three-arm precursor.[1]

To substantiate this hypothesis the recovered samples were treated with hydrogen in the presence of Pd/C for additional 48 hours. After this additional treatment, the recovered materials P1b and P2b show monomodal GPC elution curves with $M_n = 2280$ and 2800 (GPC), respectively. These values are in good agreement with those

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[1] Deconvolution of the GPC curves indicated that the main components of the mixtures were the three-arms star and the single cleaved arm. The two-arm star was present to a minor extent (ca. 10%). This finding suggests that the core of the partially cleaved two-arm star is more easily hydrogenated than the starting three-arm star.

Table 3
Molecular weight data for the polymers recovered after hydrogenolysis

Polymer	Yield (%)	M_n (GPC)	M_w (GPC)	M_w/M_n	M_n[a] (calcd)
P1b	35	2280	2600	1.14	2460
P2b	37	2800	3530	1.26	3292
P3b	68	1940	2230	1.15	2252

[a] M_n calculated from the styrene/initiator feed ratio including two OH terminal groups.

expected on the basis of monomer to initiator ratio in the feed (see Table 3). In both cases the polydispersity index is close to the unity.

4. Conclusive remarks

Tempo-functionalised central cores were used to build polymeric stars having three or six arms via living/controlled radical polymerisation. The resulting polymers have low polydispersities and M_n in the 7000–12000 D range.

The ethereal linkage at the core of P1 and P2 appears to be chemically robust, being able to withstand chemical attack by trimethylsilyliodide or catalytic hydrogenolysis catalysed by Pd/C. Cleavage of the ethereal bridges has been achieved only after the TEMPO moieties were removed by reaction with Zn/CH_3COOH. The star macromolecule P3 appears to be less chemically inert since upon treatment with Zn/CH_3COOH the core is partially cleaved leading to a linear polymer in which a pyridine nucleus bridges two polystyrene arms.

The chemical inertness of the cores, together with the possibility to form OH terminated star branches, makes these products of interest for potential application as new functional materials for diverse applications.

References

[1] Newkome GR, Moorefield CN, Vögtle F. Dendritic molecules: concepts, synthesis, perspectives. Weinheim: VCH, 1996.
[2] Hult A, Johansson M, Malmström E. Adv Polym Sci, vol. 143. Berlin: Springer, 1999. p. 1.
[3] Schlüter AD, Rabe JP. Angew Chem Int Ed 2000;39:864.
[4] Hadjichristidis N. J Polym Sci Part A: Polym Chem 1999;37:857.
[5] Grest GS, Fetters LJ, Huang JS, Richter D. In: Prigogine I, Rice SA, editors. Advances in chemical physics, vol. 84. New York: Wiley, 1996. p. 67.
[6] Kennedy JP, Jacob S. Acc Chem Res 1998;31:835.
[7] Zhang X, Xia J, Matyjaszewski K. Macromolecules 2000;33:2340 and references therein.
[8] Chong YK, Le TPT, Moad G, Rizzardo E, Tang SH. Macromolecules 1999;32:2071.
[9] Hawker CJ. Acc Chem Res 1997;30:373 and references therein.
[10] Chessa G, Scrivanti A. J Chem Soc Perkin Trans 1996;1:307.
[11] Chessa G, Scrivanti A. J Heterocycl Chem 1997;34:1851.
[12] Scrivanti A, Fasan S, Matteoli U, Seraglia R, Chessa G. Macromol Chem Phys 2000;201:326.
[13] Vögtle F, Zuber M, Lichtenthaler RG. Chem Ber 1973;106:717.
[14] Van der Made AW, Van der Made RH. J Org Chem 1993;58:1262.
[15] Hawker CJ. J Am Chem Soc 1994;116:11185.
[16] Georges MK, Veregin RPN, Kazmaier PM, Hamer GK. Macromolecules 1993;26:2987.
[17] Georges MK, Veregin RPN, Kazmaier PN, Hamer GK. Trends Polym Sci 1994;2:66.
[18] Georges MK, Hamer GK, Listigovers NA. Macromolecules 1998;31:9087.
[19] Hamaya T, Yamada S. Makromol Chem 1979;180:2981.
[20] Li I, Howell BA, Matyjaszewski K, Shigemoto T, Smith PB, Priddy DB. Macromolecules 1995;28:6692.
[21] Burchard W. Adv Polym Sci, vol. 143. Berlin: Springer, 1999. p. 113.
[22] Jung ME, Lyster MA. J Org Chem 1977;42:3761.
[23] Czech BP, Bartsch RA. J Org Chem 1984;49:4076.
[24] Rayburn CH, Harlan WR, Hanmer HR. J Am Chem Soc 1950;72:1721.
[25] Fieser LF, Fieser M. Reagents for organic chemistry, vol. 1. New York: Wiley, 1967. p. 1276.