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Synthesis of hybrid dendrimer-star polymers by the RAFT process

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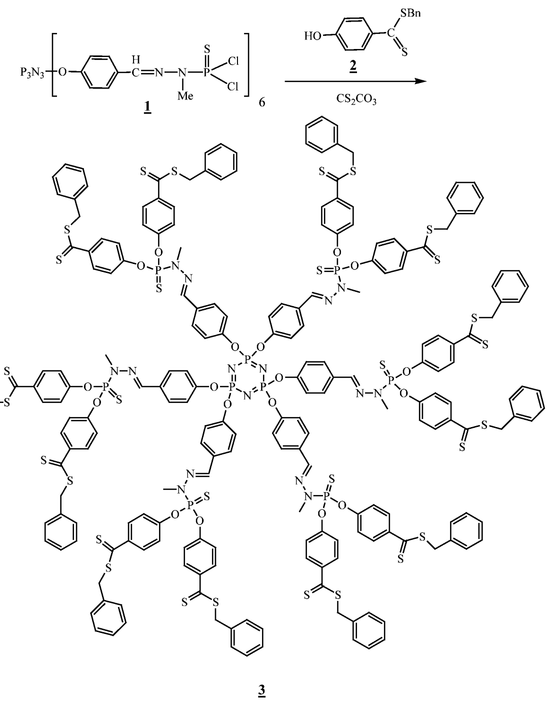
A first generation phosphorus-containing dendrimer with twelve terminal benzyl dithiobenzoate functions was designed and subsequently used as a multifunctional agent to derive hybrid star copolymers consisting of a dendritic core surrounded by twelve polystyrene branches by reversible addition-fragmentation chain transfer (RAFT).

Dendrimers are highly branched and perfectly defined molecules known to adopt a globular shape and possess a precise number of functional end groups.[1] Surprisingly, only a few examples of dendrimers have been used as multifunctional cores in "controlled/living" chain polymerisations in the literature.[2] In the past five years, a significant development in controlled/living radical polymerisation came about with the use of thiocarbonylthio compounds, Z–C(S)SR, as chain transfer agents (CTAs) in the so-called reversible addition-fragmentation chain transfer (the RAFT process).[3] The RAFT mechanism is based on the succession of sequences of radical reactions involving, first, the addition of propagating radicals to the CS double bond of the CTA leading to a transient radical. The latter species then undergoes a β-scission reaction where the R° group that is released can re-initiate the polymerisation by generating a new thiocarbonylthio compound. A rapid chain-to-chain transfer of ω-thiocarbonylthio groups between dormant chains and radical active species ensures a controlled/living growth of the chains. Among the various types of RAFT agents prepared[3–5] only a few of them have been used for star polymer synthesis.[4–5] Two types of multifunctional CTAs can be contemplated for use in a RAFT process: those implying an outward growth of arms from the core and those involving the reaction of linear chains with the functional core, following "core-first" and "arm-first" approaches, respectively. These two approaches are complementary with their respective merits and drawbacks.[4–5] A recent report by the Davis group has described the use of hyperbranched polyesters with trithiocarbonate end groups as scaffolds for the RAFT polymerisation of styrene and n-butylacrylate.[5] Here we show the first example of a perfectly defined dendrimer that was used as a multifunctional RAFT agent to prepare hybrid dendrimer–polystyrene stars, by the "arm-first" approach.

A dodecafunctional phosphorus-containing dendritic RAFT agent was synthesized according to Scheme 1, following a procedure similar to that described previously[6] except that *S*-benzyl-4-hydroxydithiobenzoate was used to functionalise the surface of the dendritic precursor carrying $SPCl_2$ end groups. The chemical purity of compound **3** was checked using different analytical techniques†.

The experimental results for the self-thermal polymerisation of styrene carried out in bulk at 110 °C in the presence of this dendritic dodecafunctional RAFT agent are summarized in Table 1. A theoretical molar mass of 416 000 g mol^{-1} for 100% conversion of the monomer was targeted, *i.e.* [**3**] = 2.4×10^{-3} mol L^{-1}. The evolution of molar masses of the polystyrene (PS) samples recovered was monitored by size exclusion chromatography (SEC) equipped with a photodiode array (PDA) detector, which allowed us to visualize the populations in the whole range of wavelengths of the UV spectrum. A typical SEC is shown in Fig. 1. After 20 h and 69% conversion of styrene (entry 7, Table 1), a bimodal distribution of molar masses was observed at 254 nm, that is where the phenyl rings of styrene units are revealed, whereas only one population was detected at 310 nm, a wavelength that is characteristic of the reddish thiocarbonyl thio (SC–S) groups. The monomodal population A of high molar mass (M_n = 147 500 g mol^{-1})



Scheme 1 Synthesis of the dendritic RAFT agent **3**.

Table 1 Thermal RAFT polymerisation of styrene in bulk at 110 °C in the presence of **3** ([**3**] = 2.4×10^{-3} mol L^{-1})[a]

Entry	Time/ h	Conv.[b] (%)	$M_{n,\mathrm{th}}$[c] star/g mol^{-1}	$M_{n,\ \mathrm{exp}}$[d] star/g mol^{-1}	M_w/M_n[d] star
1	1	3	14 000	11 000	1.09
2	2	10	60 000	32 500	1.06
3	3.5	15	61 000	45 500	1.05
4	5	24	93 000	50 000	1.06
5	8	32	126 000	83 000	1.06
6	14.5	54	208 000	124 000	1.07
7	20	69	264 000	147 500	1.10
8	30	82	310 000	181 500	1.18

[a] Only the M_n of the dendrimer-star PS were considered. [b] Conversion determined by gravimetry. [c] Theoretical M_n = [Styrene]/[**3**] × conv. [d] Determined by SEC using a RI detector.

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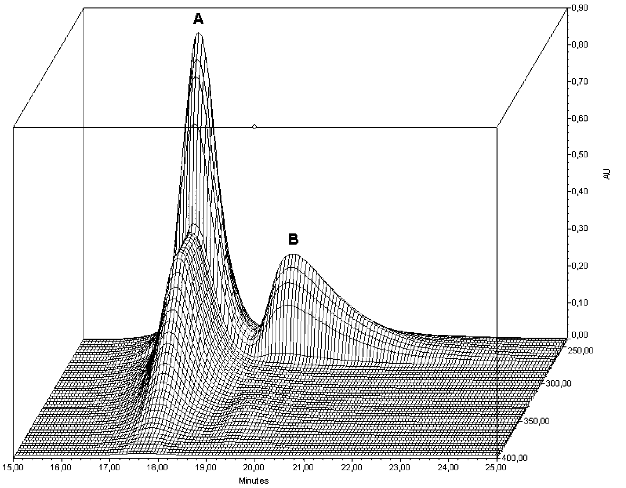
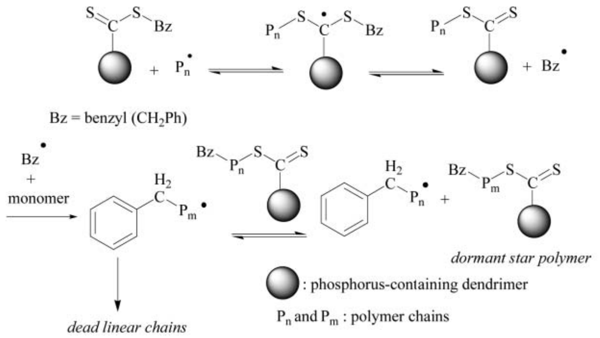


Fig. 1 SEC in THF using a PDA detector for styrene polymerisation in the presence of **3** (see entry 7 in Table 1).



Scheme 2 RAFT mechanism with a simplified structure of **3**.

was attributed to the dendrimer-star polystyrene while a population B of lower molar mass (M_n = 21 000 g mol^{-1}, PDI = 1.27) indicated the presence of dead linear chains formed by irreversible terminations.

Indeed, looking closely at the RAFT mechanism employing **3** as a multifunctional CTA shows that it involves the formation of linear propagating chains exclusively (arm-first growth).[4–5] After the addition-fragmentation transfer reactions to the dendritic core, these chains become the dormant arms of the star (Scheme 2). However, as the dendrimer is progressively shielded by polymeric arms, the accessbilty to the –S(CS)– by growing chains is limited ("shielding effect").[4–5] Consequently, growing linear chains are likely to experience a higher probability of irreversible termination occuring by couplings of polystyryl radicals and forming dead linear polymers free of any thiocarbonylthio groups.

Pure dendrimer-star PS could be isolated from linear contaminants by selective extraction with cyclohexane, as follows. The crude product formed a homogeneous solution in hot cyclohexane and, upon cooling to room temperature overnight, two phases were obtained. This is illustrated in Fig. 2: the bottom phase was viscous and reddish indicative of a high molar mass population containing the –S(CS)– chromophores, whereas the colourless top layer enclosed the dead chains free of any –S(CS)– groups, consistently with the mechanism discussed above. After decantation, characterisation by SEC showed a pure hybrid dendrimer-star PS (see Fig. 2). It was found that the molar mass ratio of the two species detected by MALLS/SEC revolved around a value of 6, which means that these dead polymers were mainly the results of couplings between linear chains, the latter species representing twice the size of the arms of dendrimer-star polymers. Subsequent treatment of a pure dendrimer-star PS with diethylamine yielded linear PS chains whose SEC trace showed a unimodal distribution of molar masses (PDI < 1.2) supporting a uniform growth of the chains from all the dithioester groups.

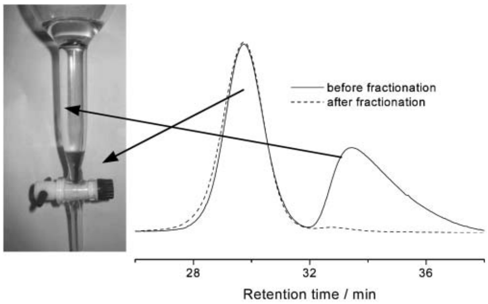


Fig. 2 SEC traces using RI detector of star polystyrene (M_n = 147 500 g mol^{-1}, M_w/M_n = 1.1) before (solid line) and after (dash line) extraction with cyclohexane.

In summary, well-defined hybrid dendrimer-star polystyrenes were prepared *via* the RAFT process, following an arm-first approach whose main advantage is to avoid complications generally encountered in core-first star synthesis, such as star–star and/or linear chain–star couplings. However, due to the contamination of the dendrimer–star polymer by dead linear chains, a final extraction step is required to isolate the pure hybrid compounds. The same methodology can well be applied to generate star polymers with larger number of arms using dendrimers of higher generations.

Notes and references

† *Spectral data for* **3**: **^{1}H NMR** ($CDCl_3$, 200 MHz, δ ppm): 3.19 (d, $^3J_{HP}$ = 10.4 Hz, 18H, NCH_3), 4.49 (s, 24H, SCH_2), 6.95 (m, 12H, Har), 7.12 (d, J = 8.6 Hz, 22H, Har), 7.28 (m, 66H, Har), 7.51 (m, 16 H, Har and CHN), 7.90 (d, J = 8.6 Hz, 22H, Har). **^{31}P NMR** ($CDCl_3$, 81.02 MHz, δ ppm): 11.8 (s, P_0), 64.2 (s, P_1). **^{13}C NMR** ($CDCl_3$, 75.5 MHz, δ ppm): 33.4 (d, $^2J_{CP}$ = 12.5 Hz, NCH_3), 42.8 (s, SCH_2), 121.5 (d, $^2J_{CP}$ = 4.7 Hz, C_1^2), 121.9 (bs, C_0^2), 128.3 (s, C_1^3), 129.0 (brs, C_0^3, C_6H_5), 129.1 (s, C_6H_5), 129.7 (s, C_6H_5), 132.3 (s, C_0^4), 135.2 (s, C_6H_5), 139.5 (d, $^3J_{CP}$ = 15.0 Hz, CHN), 142.1 (s, C_1^4), 151.8 (bs, C_0^1), 154.2 (d, $^2J_{CP}$ = 7.0 Hz, C_1^1), 225.6 (s, CS). Anal. Calcd for $C_{216}H_{180}N_{15}O_{18}P_9S_{30}$: C, 57.47; H, 4.02; N, 4.65. Found: C, 57.55; H, 4.07; N, 4.69.

1 J. P. Majoral and A. M. Caminade, *Chem. Rev.*, 1999, **99**, 845.
2 (*a*) A. Heise, S. Diamanti, J. L. Hedrick, C. W. Frank and R. D. Miller, *Macromolecules*, 2001, **34**, 3798; (*b*) B. Comanita, B. Noren and J. Roovers, *Macromolecules*, 1999, **32**, 1069.
3 G. Moad, J. Chiefari, B. Y. K. Chong, J. Krstina, R. T. A. Mayadune, A. Postma, E. Rizzardo and S. H. Thang, *Polym. Int.*, 2000, **49**, 993.
4 (*a*) Y. K. Chong, J. Krstina, T. P. T. Le, G. Moad, A. Postma, E. Rizzardo and S. H. Thang, *Macromolecules*, 2003, **36**, 2256; (*b*) J. Chiefari, R. T. A. Mayadunne, C. L. Moad, G. Moad, E. Rizzardo, A. Postma, M. A. Skidmore and S. H. Thang, *Macromolecules*, 2003, **36**, 2273; (*c*) M. H. Stenzel and T. P. Davis, *J. Polym. Sci. Part A: Chem.*, 2002, **40**, 4498; (*d*) A. Duréault, D. Taton, M. Destarac, F. Leising and Y. Gnanou, *Macromolecules*, 2004, **37**, 5513.
5 M. Jesberger, L. Barner, M. H. Stenzel, E. Malmström, T. P. Davis and C. Barner-Kowollik, *J. Polym. Sci. Part A: Chem.*, 2003, **41**, 3847.
6 P. Marchand, L. Griffe, A.-M. Caminade, J.-P. Majoral, M. Destarac and F. Leising, *Org. Lett.*, 2004, **6**, 1309.