Stars and Dendrimer-Like Architectures by the Divergent Method Using Controlled Radical Polymerization

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SUMMARY: Using novel multihalide compounds based on 4-*tert*-butylcalix[4,6,8]arenes as initiators, molecularly well-defined polystyrenes (PS) and poly[alkyl-(meth)acrylates] could be obtained by atom transfer radical polymerization (ATRP). This core-first approach and therefore the very same initiators also served to derive star block copolymers. Dendrimer-like architectures based on poly(ethylene oxide) (PEO) and PS were prepared upon combination of anionic polymerization for the inner PEO part and ATRP for the outer PS shell.

Introduction

The current interest in branched polymers that are molecularly well-defined is fuelled by the growing demand for structures exhibiting shape persistence, the role played by the branching points being to lower the conformational entropy of such objects [1].

There are essentially two strategies to engineer branched polymers: one can either resort to the "arm-first" method [2] or turn to the "core-first" route [3], the two approaches being complementary with their respective merits and drawbacks. Although straightforward, the arm-first method is limited to stars based on polystyrene or polydienes derived from anionic polymerization, the corresponding stars being obtained by deactivation of the « living » carbanions by chlorosilane functions [2]. It is only recently that the core-first approach came to maturity after it was shown in the 90's that stars of precise functionality could be obtained from multiionic initiators [3]. Our group contributed to the breakthrough in this domain. For instance, we derived hexaarm stars from an initiator containing six phenyl ethyl chloride groups that were used to trigger the living cationic polymerization of styrene as well as that of isobutylene [4].
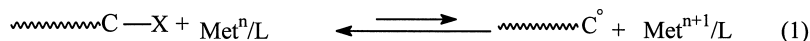
In addition to its versatility, the core-first approach also offers the possibility to chemically transform the arm tips. For instance, we could fulleranate the above hexaarm polystyrene (PS) stars through functionalization of their arm ends [5]. The same was done with triarmed PEO stars obtained, in this case, by living anionic polymerization of ethylene oxide [6].

On the other hand, the cationically-derived PS stars precursors were used to engineer branched copolymers constituted of PS and poly(ethylene oxide) (PEO) by switching from a

cationic mechanism to an anionic one. Amphiphilic star block copolymers (PS$_6$-b-PEO$_6$) as well as arborescent-like homologues (PS$_6$-b-PEO$_{12}$) could be obtained by this way [7].

This paper will focus on the use of controlled radical polymerization (CRP) as a means to assemble branched architectures by the core-first methodology. The recent development of CRP techniques [8] has indeed opened up a potentially broad route to macromolecular engineering [9]; polymeric materials with specific topologies - including star and dendrimer-like polymers - can be now derived by CRP.

Among CRP techniques, atom transfer radical polymerization (ATRP) is generally preferred to prepare star-like polymers [10]. ATRP provides excellent control over chain length and functionality, proceeding through successive transfers of halide from dormant polymer chain ends to transition metal compounds (MetX with X=Br or Cl) activated by appropriate ligands (L) and *vice versa* [8,9] (see equation (1) below).

$$\text{\textasciitilde\textasciitilde\textasciitilde C} - X + Met^n/L \quad \rightleftharpoons \quad \text{\textasciitilde\textasciitilde C}^\circ + Met^{n+1}/L \qquad (1)$$

The following sections describe our recent contributions in the field of macromolecular engineering *via* ATRP: stars of high functionality [11-12], star block copolymers [13] as well as dendrimer-like copolymers [14] were derived following the "core-first" methodology.

Stars of precise and high functionality by ATRP [ref 11-13]

Prior to the synthesis of star molecules, perfectly defined initiators were designed, from *tert*butylcalix[*n*]arenes (Scheme 1) in order to trigger the polymerization of the following monomers, i.e. styrene and alkyl (meth)acrylates.

4-*tert*-butylcalix[n]arene

n = 4,6,8

multifunctional initiators

Z = CH$_3$ or H
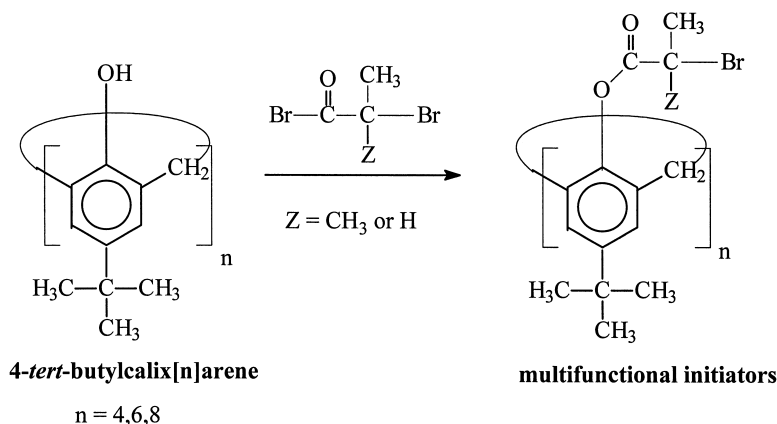
Scheme 1: Synthesis of multifunctional initiators for ATRP

PS stars with predictable molar masses and polydispersity index close to unity, constituted of precisely four, six and eight arms (see Figure 1) could be synthesized by ATRP, starting from initiator with Z = H and n = 8 (Scheme 1). For instance, octafunctional PS stars exhibiting molar masses as high as 600000 g.mol^{-1} could be prepared by polymerizing styrene, in bulk, using CuBr/bipyridyl as catalytic system at 100°C. However, the polymerization had to be restricted to low conversion, typically below 15-20%, to prevent stars from mutually coupling and avoid their contamination with species of higher functionality. In the case of hexa- and tetrafunctional PS stars, well-defined samples could be obtained within a large range of conversion because of the lower probability of such hexa- and tetraarmed species to get coupled, as compared to the case of the above octafunctional system.

Octaarm poly(methyl methacrylate) (PMMA) stars (Figure 1) were also derived, using the octafunctional initiator with Z = CH$_3$ and n =8 (Scheme 1), in the presence of CuCl/bipyridyl at 90°C in 50% diphenylether solution. In this case also, the polymerization had to be discontinued at relatively low conversion (< 25-30%) in order to isolate samples with the expected functionality of 8. Even though the ATRP of MMA is associated with a larger K_{eq} value than styrene, the probability for two stars to couple was lower than for PS stars, just because k_p/k_t is higher for the former monomer. Therefore, for similar [M]/[I] ratios, the polymerization could be carried out to higher conversion before the star-star coupling phenomenon occurred. PMMA stars of high molar mass were thus obtained using large [M]/[I] ratios and restricting the polymerization to low conversion.

In contrast, no intermolecular couplings were detected while synthesizing poly(*tert*-butyl acrylate) (PtBuA) stars (Figure 1) because the ATRP of t-BuA is associated with a much lower equilibrium constant (K_{eq}) between dormant and active species. In this case, either CuBr/2,2'-bipyridyl [12] or CuBr/pentamethyl diethylene triamine (PMDETA) [13] was used as catalyst in the presence of 10% in volume of ethylene carbonate. As expected, the use of PMDETA as ligand instead of bipyridyl led to a faster polymerization rate and narrower molar masses distribution, due to faster exchanges between active radicals and dormant halide species [15].

These conditions were also employed [13] to grow octafunctional poly(n-butyl acrylate) stars of controlled molar masses (see Table 2 below).

In all cases, the functionality of the stars obtained was checked by comparing their molar mass with that of their individual arms, the latter being isolated after hydrolysis of the ester functions of the central core. The ratio $M_{n\ star}/M_{n\ linear\ chains}$ was found to revolve around the expected functionality f (f = 4, 6 or 8).
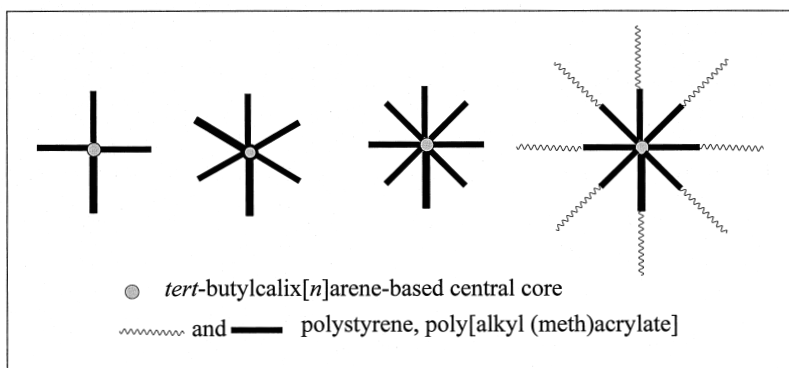
Figure 1. Stars & Star Block copolymers synthesized by ATRP

Octafunctional star block copolymers by ATRP [ref 13]

Due to the presence of the terminal halide function on each of their arm, some of the stars described above served as multifunctional macroinitiators for the formation of star block copolymers. For instance, stars constituted of eight PtBuA-b-PMMA blocks of tunable composition were successfully synthesized through sequential addition of the corresponding monomers, using the octafunctional initiator with Z = H, n= 8 (Scheme 1), CuBr and PMDETA (Table 1). The molar mass of these star block copolymers calculated by ^{1}H NMR and that measured by light scattering fell in close agreement with the expected values. The polydispersity index were relatively low (< 1.4) and the MALLS/SEC eluograms of the block Copolymers were all unimodal and symmetrical (Figure 2). These results indicated that the
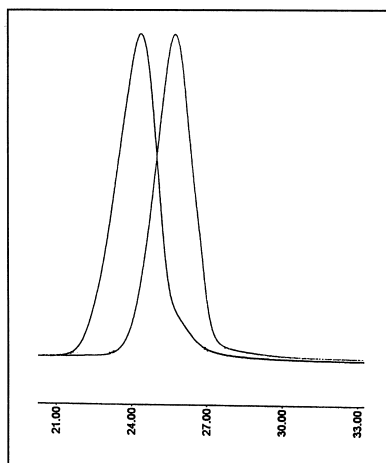

Figure 2. SEC traces of PtBuA$_8$ star (right) and PtBuA$_8$-b-PMMA$_8$ star block copolymer (left)

cross over reaction between PtBuA and PMMA blocks occurred as expected, with a blocking efficiency close to 1.

The *tert*-butyl groups of PtBuA blocks could be selectively hydrolyzed by treating the star-block copolymers with trifluoroacetic acid in methylene chloride, affording amphiphilic octaarm star-block poly(acrylic acid)-b-PMMA copolymers, similar to those described by Hedrick and coll. [16]. Investigations by ^{1}H NMR of these star-shaped copolymers showed that they responded to changes of the polarity of the solvent in which they were placed, meaning that these systems were capable to form stable "unimolecular micelles".

Table 1: Synthesis of star-block PtBuA$_8$-b-PMMA$_8$

Run	[M]/[I]	Time (min)	Conv. (%)	$M_{n\ theo}$ (g.mol^{-1})	$M_{n\ SEC}$ [a] (g.mol^{-1})	$M_{n\ LLS}$ [b] (g.mol^{-1})	PDI [b]
1	16000	150	24	536000	303000	560000 [c]	1.36
2	16000	60	11	270000	122000	304000 [d]	1.28

a) determined by size exclusion chromatography (SEC) in THF; calibration with linear PS standards. b) determined by a multiangle laser light scattering detector connected to a SEC line (MALLS/SEC). c) M_n determined by ^{1}H NMR = 525000 g.mol^{-1}. d) M_n determined by ^{1}H NMR = 249000 g.mol^{-1}.

Well-defined octaarm star block copolymers made of poly(n-butyl acrylate) and PMMA segments were also synthesized from the same initiator, by sequential ATRP of nBuA and MMA (Table 2). Such branched copolymers composed of an inner soft part (low T$_g$) and one outer hard layer (high T$_g$) are expected to find applications as thermoplastic elastomers.

Table 2: Synthesis of star-block PnBuA$_8$-b-PMMA$_8$

| Run	[M]/[I]	Time (min)	Conv. (%)	$M_{n\ theo}$ (g.mol^{-1})	$M_{n\ SEC}$ [a] (g.mol^{-1})	$M_{n\ LLS}$ [b] (g.mol^{-1})	PDI [b]
3	16000	25	3	173500	51300	142200	1.27
4	25000	15	2.5	191000	101600	184000	1.30

a) determined by SEC in THF; calibration with linear PS standards.
b) determined by MALLS/SEC.

Stars and Dendrimer-Like Architectures Based on PEO and PS [ref 14]

As mentioned above, the possibility to generate reactive stars and derivatize their arm tips is another reason for the attractiveness of the core-first method. Taking advantage of this feature, we could associate PS and PEO in unprecedented topology, combining anionic polymerization of ethylene oxide with ATRP of styrene.

Star block copolymers with an inner PEO core surrounded by a polystyrene corona (PEO$_f$-b-PS$_f$ with n= 3 or 4) were for instance engineered. For this purpose, tri- and tetraarm PEO stars of expected molar masses were first synthesized by the core first method using, respectively, 2-ethyl-2-hydroxymethyl-1,3-propanediol and pentaerhytritol as precursor, diphenylmethyl potassium (DPMK) as deprotonating agent of the hydroxyl groups and ethylene oxide. In the second step, the chemical modification of the OH end-groups of the PEO stars into 2-bromoproprionate functions was accomplished (see Scheme 2).
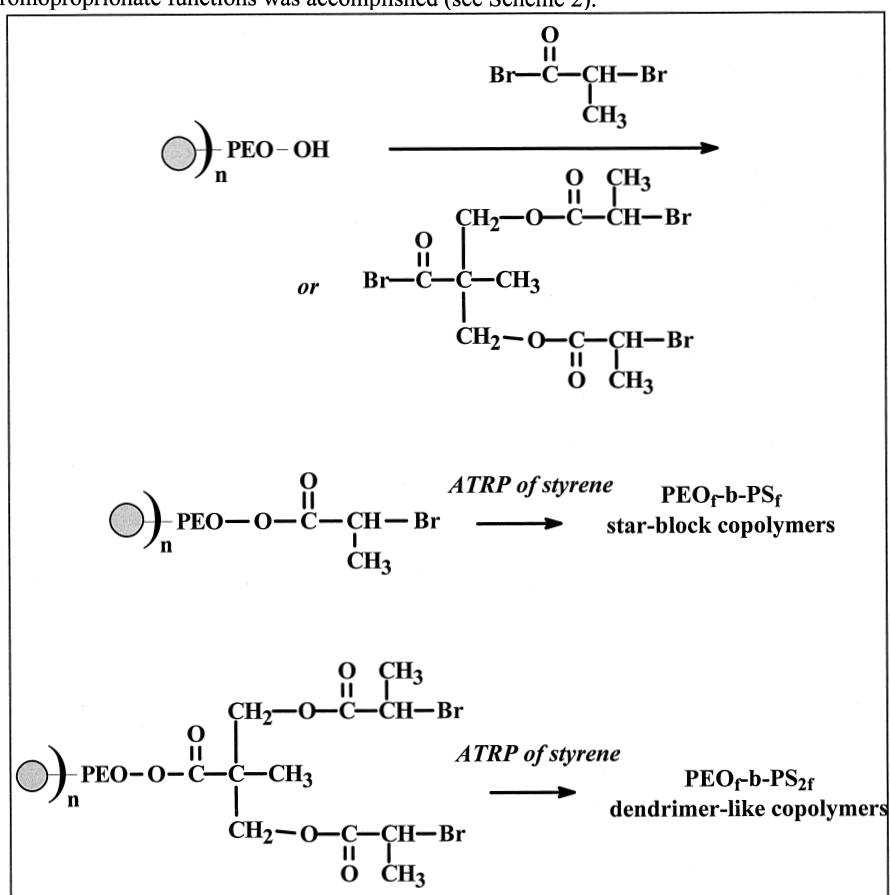
Scheme 2: End-functionalization of multiarm PEO's

The growth of PS blocks was carried out from these 2-bromopropionate functions upon polymerizing styrene in bulk by ATRP, at 100°C, in the presence of CuBr/2,2'bipyridine as catalyst system and discontinuing the chain growth at rather low monomer conversion.

The expected branched structure of the corresponding block copolymers was confirmed after hydrolysis of the ester functions linking the PS blocks to the PEO ones. The monomodal SEC traces of the PS recovered after cleavage (polydispersity index close to 1.2) appeared at lower retention volumes than those of the PEO_f-b-PS_f precursors, confirming the controlled character of the bulk ATRP of styrene that was triggered by the tri- and tetrafunctional macroinitiators.

The term "dendrimer-like" [17] designates architectures that exhibit similar features as those of regular dendrimers (i.e. precise number of branching points and outer functions in all molecules, presence of a central core) but, in this case, their successive generations are constituted of polymeric size. To generate PEO_f-b-PS_{2f} (n = 3 or 4) block copolymers, the hydroxyl groups of our tri- and tetraarm PEO precursors described above were first transformed into twice as many 2-bromoproprionate groups through the condensation of a branching agent –the latter was synthesized in two steps from 2,2-bis(hydroxymethyl) propionic acid and 2-bromopropionyl bromide- onto the PEO termini and were subsequently used to initiate the ATRP of styrene (Scheme 2).

Two PS arms of well-controlled size were grown from each of the branching points using the same conditions described above, thus affording amphiphilic dendrimer-like copolymers PEO_f-b-PS_{2f} with n = 3 or 4 (Figure 3). The hydrophilic/hydrophobic balance was adjusted by the initial feed ratio of styrene to the PEO-based macroinitiators.

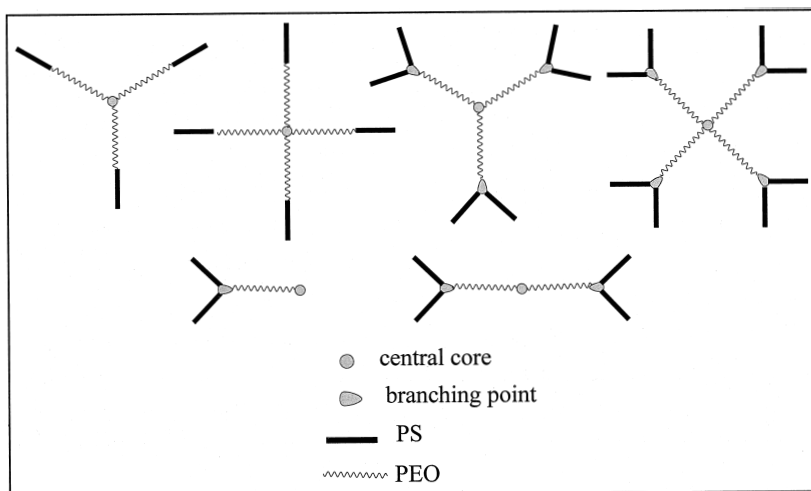central core

branching point

PS

PEO

Figure 3. Amphiphilic star-like & dendrimer-like copolymers based on PEO & PS

The number of PS branches present in the dendritic block copolymers was determined after cleavage of the ester functions linking the PEO part to the PS one, by checking that the $\overline{M_n}$ values of the hydrolyzed linear PS chains and those of the PS part in the dendritic precursor are in good agreement, confirming that these structures had the expected number of PS arms. Additional investigations by ^{1}H NMR showed that these amphiphilic branched copolymers exhibited self-associating properties. Indeed, in a mixture of $CD_3OD/CDCl_3$ (70/30 v/v), the protons due to the PS chains were no longer detected, suggesting that PEO arms were able to wrap the hydrophobic parts, the latter preferring to stay within the core of the micellar structure. In THF, the PEO arms stayed in the inner part in a slightly more compact form than in chlorinated solvent, the dendritic and hydrophobic parts extending outward.

PEO_1-b-PS_2 miktoarm stars and PS_2-b-PEO-b-PS_2 H-type copolymers were also produced as follows. Starting respectively, from DPMK in THF and a DMSO solution of partially deprotonated 2,2-dimethyl-1,3 propanediol, α-OH and α,ω di-OH PEO were first synthesized and the same sequence described above of branched reaction followed by ATRP of styrene could be achieved. Thus, depending upon the structure of the precursor, either miktoarm stars and H-type copolymers were obtained (Figure 3).

Conclusion

This paper discusses the conditions that are best suited to the preparation of stars of precise functionality (f = 4, 6 or 8) by ATRP. Stars of PS, PtBuA, PnBuA and PMMA as well as the corresponding star block copolymers could indeed be obtained using multihalide initiators. Dendrimer-like PEO_f-b-PS_{2f} (f = 3 or 4) copolymers were also derived in three steps that involved the preparation of PEO stars by anionic polymerization, then the derivatization of the star arm ends and finally the growth of the outer PS blocks by ATRP.

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