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Core-First Synthesis of Star Polymers with Potentially Ionogenic Branches

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ABSTRACT: Star-shaped macromolecules have been synthesized anionically by initiating the polymerization of a suitable monomer from "living" multifunctional cores. These cores result from the anionic polymerization of a small amount of divinylbenzene under very specific conditions in dilute tetrahydrofuran (THF) solution. The main advantage of this method is to allow functionalization at the outer end of the branches. Star block copolymers can also be synthesized by this method, provided the polymerization of the second monomer can be initiated by the carbanions of the first one. An alternate method has been attempted. Initiating cores comprising short polystyrene arms resulted from an arm-first synthesis. These cores were used to initiate the polymerization of *tert*-butyl acrylate, the branches being grown from the cores. This latter method has the advantage of allowing a better control of the functionality of the cores and yielding rather well-defined polymers. The monomer used in this work was *tert*-butyl acrylate, a monomer which can be polymerized anionically to living polymers if lithium chloride is present in the reaction medium as indicated by Teyssié. Star-shaped poly(*tert*-butyl acrylate) samples were obtained as well as star block copolymers, the branches of which are polystyrene–poly(*tert*-butyl acrylate) block copolymers. These species were characterized adequately.

Introduction

The synthesis of star-shaped polymers by sequential anionic "living" copolymerization can be performed in two different ways.

Some *arm-first methods* are based upon deactivation of the living sites of a linear precursor polymer by the electrophilic functions of a plurifunctional reagent.[1,2] The functionality f of the star molecules is then determined by that of the reagent, provided the reaction conditions are appropriate.

The anionic living precursor polymer, fitted at one chain end with a carbanionic site, can also be used to initiate the polymerization of a small amount of a suitable bis-unsaturated monomer.[3-5] A tiny cross-linked core is thus generated, which is linked to the f precursor chains that have contributed to its initiation. The branches can be characterized independently, and the average number of branches f per star molecule arises from molecular weight measurements on the star polymer and on the precursor. Account has to be taken, if necessary, of the weight of the core.[6] The method is quite suitable for the synthesis of star polymers with f ranging from 5 to 15, although higher values of f have been obtained under proper conditions. The value of f cannot be chosen at will, but the distribution of molecular weights in such star polymer samples is rather narrow.[7] An interesting feature of this method is that no gelation of the reaction medium was ever observed, even when the bis-unsaturated monomer amounts to over 40% of the total weight of monomers used. Obviously, the protection exerted by the arms on the core prevents formation of linkages between individual molecules.

All arm-first methods have a common drawback: the branches cannot be functionalized at their outer end.[5] This is why repeated attempts have been made to synthesize star molecules in which the branches were grown from preexisting plurifunctional cores.

In *core-first methods* the bis-unsaturated monomer is polymerized first under conditions chosen such as to avoid (or to restrict) aggregation of the cores to small gel particles. Burchard[8,9] was a pioneer: Upon polymerizing pure p-divinylbenzene (DVB) with butyllithium in a hydrocarbon solvent at high dilution, he obtained a stable microgel suspension. Each of these particles was coated with metal organic functions, which subsequently served as initiating sites for the polymerization of styrene. The polymer samples obtained exhibited extremely high molecular weights ($>10^7$) and high polydispersity indices as well.

A similar approach was chosen by Funke:[10,11] The polymerization of divinylbenzene in a hydrocarbon solvent was initiated by means of short "living" chains of poly-

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(*tert*-butylstyrene). This precursor polymer was selected because of its solubility in the reaction solvent, allowing Funke to take advantage of the protecting effect exerted by the branches in arm-first star polymer synthesis. The plurifunctional cores subsequently served to grow further branches from the cores.

Our approach was somewhat different:[12-14] The cores were made in a polar solvent (tetrahydrofuran (THF)) at very high dilution, and the DVB polymerization was initiated by electron transfer instead of by addition. The critical parameter in the synthesis of the cores is the mole ratio of DVB to initiating sites. Low values are to be chosen to avoid formation of microgel. The best values were between 1.5 and 2.5 mol of DVB per anionic site (i.e., per Li^+). It should be remembered that initiation by electron transfer involves a radical dimerization step. The isomer composition of the DVB also plays a role in the core formation process.[12]

The living poly(DVB) cores were used subsequently to initiate the polymerization of suitable monomers. The branches that were grown from the cores were fitted with anionic sites at their outer ends, thus giving opportunities for block copolymerization and/or for functionalization of the branches at their outer ends.

This method was applied first to the synthesis of polystyrene and of poly(ethylene oxide) star polymers carrying terminal OH functions.[12,13] The number of branches per core, f, was usually large, depending upon the conditions chosen for the preparation of the cores. Star block copolymers such as polystyrene–poly(ethylene oxide)[12] or polystyrene–poly(2-vinylpyridine)[14] were also made by this method.

The present paper is devoted to further developments concerning the synthesis of star-shaped macromolecules, using core-first methods, and to their extension to other monomers, such as *tert*-butyl acrylate.

It is well-known that side reactions occur when acrylic esters are polymerized anionically, whereby the active sites are deactivated. However, Teyssié et al.[16,17] have recently shown that *tert*-butyl acrylate can be polymerized anionically to living polymers using a lithium organic initiator, provided lithium chloride is present. This method can be extended to the core-first synthesis of poly(*tert*-butyl acrylate) star polymers. Since *tert*-butyl ester functions are easily hydrolyzable, access could be gained to star-shaped polyelectrolytes.

Experimental Section

Monomers and Solvents. Styrene, 1,1-diphenylethylene, and divinylbenzene (commercial mixture of meta and para isomers containing 35% of the corresponding ethylstyrenes) were vacuum distilled over sodium metal into Schlenk vessels. *tert*-Butyl acrylate was distilled over calcium hydride into a tight buret.

Tetrahydrofuran and benzene were made pure and moisture free according to classical procedures.

Initiators. Lithium naphthalenide was made by reacting small pieces of lithium metal with naphthalene in THF under an inert atmosphere. A fresh initiator solution had to be made for each experiment, as it slowly decomposes. The initiator concentration was determined by titration with acetanilide.

sec-Butyllithium was made in benzene solution by reaction of 2-chlorobutane with lithium at room temperature under an inert atmosphere.

Procedure. Core-First Star Macromolecules. An airtight reactor was fitted with an argon inlet, a magnetic stirrer, a temperature controller, and devices meant to introduce solvent and monomers under an inert atmosphere. Dry lithium chloride (0.4 g) was introduced first. The reactor was heated to 120 °C and submitted to several vacuum–argon cycles. After cooling, 300 mL of THF was introduced. A few drops of lithium naphthalenide were necessary to neutralize the remaining protonic impurities. Then the chosen amount of initiator solution was added ($(1-5) \times 10^{-3}$ mol), and the mixture was cooled to about −40 °C.

The selected amount of a 30% divinylbenzene solution in benzene was added dropwise into the dilute lithium naphthalenide solution. Stirring was continued for an additional 30 min at the same temperature to ensure complete formation of the cores. Next a few drops of 1,1-diphenylethylene were added to the reaction mixture to decrease the nucleophilicity of the active sites located in the cores.

The temperature of the reaction medium was then lowered to approximately −55 °C, and *tert*-butyl acrylate (10–30 g) was introduced slowly under efficient stirring. The color of the reaction mixture changed at once from dark red to faint yellow, and polymerization proceeded, whereby the branches were grown. The mixture was kept at the same temperature for another 30 min, and the sites were then deactivated by addition of methanol.

The solution was filtered to eliminate any microgel particles that may have been formed, and it was precipitated into a large volume of methanol/water mixture (85/15 by volume) at −10 °C. The polymer was recovered as a fine powder. It was filtered, dried under vacuum, and, if necessary, redissolved and reprecipitated.

Star Block Copolymers by Core-First Methods. To make star block copolymers the procedure used was quite similar: Once the "living" poly(DVB) cores had been made, styrene was added slowly at −40 °C under efficient stirring to build the branches. After the addition of a few drops of 1,1-diphenylethylene, the temperature was lowered to −55 °C. *tert*-Butyl acrylate was then introduced slowly into the reaction medium under efficient stirring. The *tert*-butyl acrylate polymerization was allowed to proceed for 30 min. Methanol was then added to deactivate the sites. The polymer was recovered, filtered, and dried as described above.

Heteroarm Star Copolymers. An alternate three-step method has been investigated: First short linear living polystyrene chains were made in THF (containing lithium chloride), using butyllithium as the initiator. A small part of this precursor solution was sampled out for purposes of characterization. To the remainder, the selected amount of DVB (3–6 DVB's per living site) was added at once at −40 °C under efficient stirring. The cores are built, each of them being fitted with active sites. Another part of the solution was sampled out to determine the average number of arms of this star polystyrene, f, which is equal to the average number of active sites per core.

After addition of a few drops of 1,1-diphenylethylene, *tert*-butyl acrylate was added dropwise at −55 °C under stirring, and the reaction was allowed to proceed for 30 min. The polymer was recovered and purified as described above.

Characterization of the Polymers Formed. Three techniques have been used to characterize the polymers obtained:

Differential refractometry was used to determine the chemical composition of the samples, especially that of the star block copolymers and of the heteroarm star copolymers. Alternately, access to the composition was provided by NMR and by elemental analysis.

Light scattering measurements were performed to determine the molecular weights of the whole samples and, whenever possible, to determine the mean-square radius of gyration.

Size exclusion chromatography (*GPC*) *measurements* were meant merely to evaluate the breadth of the molecular weight distribution of the star molecules obtained. The apparent molecular weights arising from GPC are largely underestimated because of the compact shape of the star molecules.

Results and Discussion

As mentioned above, *tert*-butyl acrylate can be polymerized anionically to "living" polymers using lithium organic initiators, provided an appropriate amount of lithium chloride is present in the reaction medium.[16-19] The molecular weight of the polymer can be chosen at will, and its polydispersity index is of the order of 1.1. Functionalizations at chain ends and block copolymer-

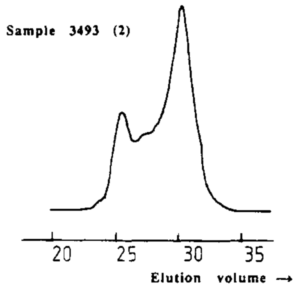


Figure 1. GPC diagram of a star polymer made by the core-first method. The apparent size distribution of the molecules is broad, which implies that the MWD is even broader.

izations have been performed. It has been noticed[19] that the polymerization rates of monomers such as styrene, vinylpyridine, and methacrylic esters are slowed down by the presence of LiCl.

The core-first methods have been applied to the synthesis of star-shaped poly(*tert*-butyl acrylate) and of star block copolymers in which each branch is a block copolymer of styrene and *tert*-butyl acrylate (tBuA). A three-step method involving core-first growth of the tBuA branches will also be discussed.

I. Poly(*tert*-butyl acrylate) Star Molecules by the Core-First Method. The synthesis of small "living" poly(DVB) cores in the presence of LiCl is a prerequisite to the extension of the core-first method to that system. The reaction was carried out under the same experimental conditions as previously:[12] slow addition of DVB (diluted with twice its volume of dry benzene) into a dilute lithium naphthalenide solution in THF at −30 °C. Efficient stirring was necessary. As mentioned previously, the $[DVB]/[Li^+]$ mole ratio is the critical factor in the core synthesis: If it is too low, unconsumed lithium naphthalenide is likely to remain; if it is too high, the cores tend to aggregate, yielding a suspension of microgel particles fitted with metal organic sites. The $[DVB]/[Li^+]$ mole ratio was best chosen between 1.5 and 2.5.

The presence of LiCl does not introduce any major change in the process of core formation. It may even be favorable, since the propagation rate is decreased, thus reducing the probability of microgel formation upon coupling between cores.

It has not been established whether the intermediate addition of 1,1-diphenylethylene to the solution of living cores is really necessary. However, we did so to prevent loss of active sites as the result of side reactions involving the ester carbonyl of the monomer.

The immediate color change upon addition of *tert*-butyl acrylate to the solution of "living" cores indicates that the active sites are easily accessible to the monomer. The living character of the branches is demonstrated by the fact that polymerization resumes after a second addition of the monomer, 30 min later.

The characterization data are gathered in Table I. They call for a few comments:

(i) In a core-first synthesis of star polymers the average length of the individual arm is not accessible experimentally. The values of M_{br} listed in Table I are calculated from the mole ratio of tBuA polymerized to active sites, which is a reasonable assumption, as shown above. Yields are always quantitative.

(ii) The weight-average molecular weights of the star molecules, M_{w^*}, have been determined by light scattering after removal of the aggregates, if any, by filtration or centrifugation. The weight-average number of branches per star was calculated from the ratio of M_{w^*} to M_{br}. The weight of the core can be neglected in this case.

(iii) Though the "grafted aggregates" present have been removed (they never amount to more than 5% under the experimental conditions selected), the GPC chromatograms witness the broad (and sometimes bimodal) molecular weight distribution of the samples. This polydispersity is a consequence of the width of the core size distribution within a sample. A fractional precipitation was performed on one of our samples, the result of which is shown in Table II.

(iv) It is noteworthy that the apparent molecular weights arising from GPC (using a calibration curve set up with linear polystyrene) are always far below those obtained by light scattering. This testifies to the highly branched structure of the polymer molecules. A similar conclusion can be drawn from the values of the radius of gyration arising from light scattering. Although the values of $\langle r^2\rangle^{1/2}$ are z averages (i.e., they refer to the M_z values, which are higher than the M_w values shown), they are small compared to those expected from linear homologues of the same molecular weight dissolved in the same solvent.

(v) Upon adding fresh monomer, polymerization resumes and the molecular weight increases correspondingly. This result demonstrates that most of the branches have remained living.

(vi) It should be emphasized that the molecular weight distributions of samples originating from a given core solution are affine to each other, as shown by the GPC diagrams (Figure 2).

(vii) As the average length of its branches increases, the radius of gyration of a star polymer (with many branches) is expected to be roughly proportional to the cubic root of the amount of monomer polymerized. Table III shows that this is indeed the case, at least in the range of molecular weights covered (star block copolymer 3495(3) is an exception). It should be emphasized that no proportionality between radius of gyration and cubic root of the molecular weight can be expected upon studying the fractions originating from one given sample (Table II), because the number of the branches changes from fraction to fraction.

(viii) No conclusions can be drawn concerning the factors influencing the functionality of the cores. Sample 3469 contains some aggregates, whose presence is due to the higher value of the $[DVB]/[Li^+]$ mole ratio. Even when the floating gel particles have been entirely removed, the star polymers exhibit very broad molecular weight distributions, covering thus a large spectrum of f values. Still, the measured weight-average number of branches, f_w, reaches values of several hundreds in some cases. Incidentally, this may indicate that the cores are not as compact as it could have been thought: The bulkiness of so many arms around the core implies that sufficient space be available.

II. Polystyrene–Poly(*tert*-butyl acrylate) Star Block Copolymers. Of special interest is the characterization of the star block copolymers, in which each arm is a styrene–*tert*-butyl acrylate block copolymer. Styrene is polymerized first, followed by the acrylate monomer. The intermediate addition of 1,1-diphenylethylene is meant to prevent side reactions. The data shown in Table I indicate that the polymerization proceeds as expected: the number of branches remains roughly the same in samples 3495(1) and 3495(2). The radius of gyration of the star block molecules increases as predicted by the cubic root law mentioned above. The highly branched structure of these macromolecules and the heterocontact interactions between the two polymeric constituents (PS and PtBuA) tend to impart to these polymers a core–shell structure,

Table I
Core-First Synthesis of Star-Shaped Polymers

sample	[DVB]/[Li+][a]	M_{br}(calc)	M_{w*}[b]	f_w[c]	$(r^2)^{1/2}$ [b]	% PS
			Homopolymers			
3469(1)	2.5	5 000	6.5×10^6	1300	350	
3469(2)		11 000	11×10^6	1000	416	
3493(1)	1.5	10 000	1.04×10^6	104	194	
3493(2)		23 000	2.4×10^6	101	257	
3494	1.8	40 000	0.85×10^6	22	192	
			Star Block Copolymers			
3495(1)[d]	1.7	10 000	1.9×10^6	190	255	100
3495(2)		20 000	3.5×10^6	180	296	51
3495(3)		40 000	12.7×10^6	320	800	30

[a] [DVB]/[Li+] mole ratio in the core synthesis. [b] By light scattering (*z*-average radii of gyrations in angstrom units). [c] f_w is the weight-average number of branches per core. [d] In sample 3495, 1 refers to the core-first PS star molecules; 2 and 3 are obtained upon addition of *tert*-butyl acrylate to the living sites.

Table II
Fractionation Data on Star Polymer 3493(2) (Core-First)[a]

fraction	weight, g	M_w(LS)	radius of gyration	M_w(GPC)
1	1.0	16.4×10^6	746	1.2×10^6
2	1.5	2.88×10^6	308	
3	0.9	1.84×10^6	385	0.42×10^6
4	5.3	0.27×10^6		

[a] M_w(exp) = 2 400 000, M_w(calc) = 2 740 000, M_n(calc) = 420 000 (assuming the fractions to be monodisperse).

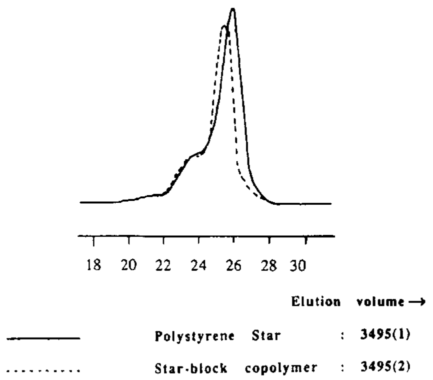


Figure 2. GPC diagrams of a star block copolymer and its star precursor: (1) core-first star polystyrene, precursor of star-block copolymer; (2) star-block copolymer in which each branch contains an outer poly(*tert*-butyl acrylate) block. The shift in elution volumes is rather small.

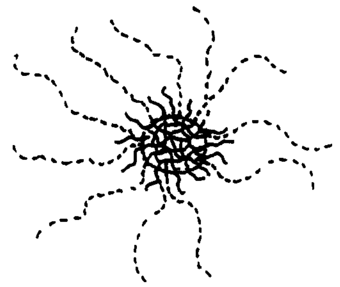
Table III
Proportionality between Radius of Gyration and Cubic Root of Molecular Weight

sample	$10^{-6}M_{w*}$	$(r^2)^{1/2}$	$(r^2)^{1/2}/M^{1/3}$
3495	1.9	255	2.06
	3.5	296	1.95
	(12.7	800	3.43)
3469	6.5	350	1.87
	11	416	1.88
3493	1.04	194	1.92
	2.4	257	1.92

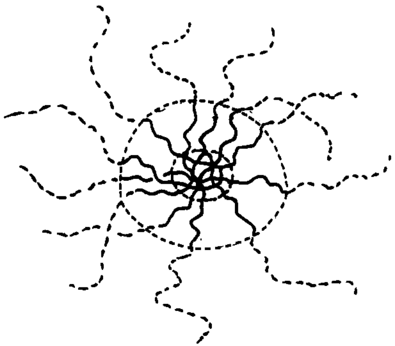
as shown in Scheme I. The discrepancy already mentioned in the case of sample 3495(3) is not easy to account for. In that case both molecular weight and radius of gyration are probably overestimated, the latter more than the former because the radius of gyration is a *z* average. Characterization of samples of extremely high molecular weight always involves difficulties.

Scheme I

Representation of a Star-Shaped Molecule Obtained by the Three-Step Method Showing the Long Poly(*tert*-butyl acrylate) Branches and the Short Polystyrene Branches of the Precursor



Representation of the Core–Shell Structure Expected from Star Block Copolymers (PtBuA Blocks Are the Outer Blocks)



III. Poly(*tert*-butyl acrylate) Star Polymers by the Three-Step Method. An alternate way to make poly(*tert*-butyl acrylate) star molecules is to have the branches grow from a polyfunctional initiating core that had been obtained precedingly by the arm-first procedure. The synthesis of heteroarm star copolymers, disclosed recently,[20] takes advantage of the efficient protection against gelation that is exerted on the core by the surrounding branches.[6] In a similar fashion, Funke's microgel particles are stabilized by the soluble branches attached.[11] The method we have designed to synthesize poly(*tert*-butyl acrylate) star molecules involves three steps:

(i) A linear, low molecular weight, monocarbanionic polystyrene precursor was made first upon initiation of the styrene polymerization with *sec*-butyllithium in THF in the presence of LiCl.

(ii) This living precursor was used to initiate the polymerization of an adequate amount of DVB to build the living cross-linked cores. No aggregate formation was observed.

(iii) In the third step, the anionic sites located in the cores were used to initiate the polymerization of *tert*-butyl acrylate, under appropriate conditions. Poly(*tert*-butyl acrylate) branches were thus grown from cores already fitted with short polystyrene arms. The overall styrene content of the star polymers was kept low. An intermediate addition of diphenylethylene was meant to prevent side reactions.

Table IV
Star-Shaped Poly(*tert*-butyl acrylate) Obtained by the Three-Step Method

sample	prec PS M_n(GPC)	[DVB]/[LE][a]	star PS M_w[b]	heteroarm star copolymer wt % tBuA	M_{w*}[b]	M_{br}[c]	f
3499	1500	2.6	21 000	91.5	275 000	21 000	12
3502	1700	3.0	30 000	95	330 000	21 000	15
3507	3000	4.0	35 000	96	400 000	38 000	10

[a] [DVB]/[PS-Li] mole ratio chosen to form the cores of the PS stars. [b] Measured by light scattering. [c] Calculated from the molecular weight of the star copolymer and the number of arms, taking into account the weight percent of tBuA in the stars. $M_{br} = M_{w*} \times (\text{wt \% tBuA})/f$, where f is the average functionality of the cores of the PS star molecules. $f = M_{w,PS*}/[M_{pr} + m_{DVB}([DVB]/[LE])]$, where m_{DVB} is the molar weight of DVB monomer.

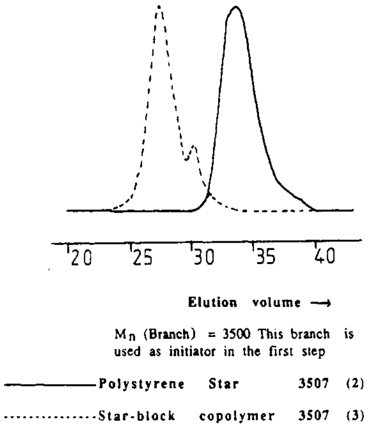


Figure 3. GPC diagrams of a star polymer sample made by the three-step method: (1) star polystyrene precursor with very short branches; (2) star block copolymer obtained upon growing poly(*tert*-butyl acrylate) branches from that precursor. The shift in elution volumes between samples 1 and 2 is very large, but the apparent size distribution in the star polymer sample is not as broad as in the case of stars made by the core-first method.

The results obtained are gathered on Table IV and they call for a few comments:

(i) The aim being the synthesis of poly(*tert*-butyl acrylate) star polymers, the polystyrene precursor chains were kept short. Their molecular weights ranged from 1500 to 3000. The precursor polystyrene was made in the presence of LiCl, using *sec*-butyllithium as the initiator.

(ii) Since f precursor chains have contributed to the initiation of a given core, the latter is fitted with f carbanionic sites: If all of them do initiate the polymerization of the acrylic monomer, the number of branches growing from the core should be equal to the number of short polystyrene arms already attached to it.

(iii) These polystyrene branches efficiently protect the poly(DVB) cores that are formed in the second reaction step. With mole ratios of DVB to living ends ranging from 2.5 to 4, the cores formed exhibit functionalities above 10. The polydispersity of the star molecules obtained by arm-first methods is far lower than that of samples made by core-first methods (Figure 3).

(iv) The first drops of *tert*-butyl acrylate added induced a drastic color change, demonstrating that free access of the monomer to the sites is provided. The cores may not be as tight as it had been thought initially, but the short length of the branches attached may also contribute to this easy access.

(v) Although it yields samples far less polydisperse, the three-step method does not allow a precise control of the functionality f of the cores, which results from the first step of the process. Several factors may influence f, especially the mole ratio of DVB to living ends and the length of the precursor chains.

Conclusion

Two methods have been described for the synthesis of poly(*tert*-butyl acrylate) star polymers. One of them is a core-first method, poly(DVB) cores fitted with carbanionic sites being used to initiate the polymerization of the acrylic monomer. The other is a three-step method, in which the cores of a living polystyrene star polymer are used to initiate the polymerization of the acrylic monomer and thus to grow further branches.

The two methods are similar in several respects, and both have been used successfully. If rather well-defined samples are wanted, the three-step method should be preferred, even though each star molecule then carries an equal number of short PS and of long PtBuA branches. The specific advantage of this method is that experimental access is granted to the number of branches of either kind, from the ratio of the molecular weights of the PS star molecules and of its linear precursor.

If high molecular weights and high numbers of branches are wanted, the first method is obviously more appropriate, although the molecular weight distributions of the samples obtained are very broad. It should also be remembered that the core-first methods can give access to star molecules fitted with functions at the outer ends of their branches.

Core-first methods are also appropriate for the synthesis of star block copolymers, in which each branch is a block copolymer. This is of special interest in the case investigated here, because poly(*tert*-butyl acrylate) blocks can be easily hydrolyzed: Access is thus provided to potentially amphilic star block copolymers. A previous example of such species was polystyrene–poly(ethylene oxide) star block copolymers[12] in which the hydrophilic blocks were nonionic.

Once hydrolyzed, the PS–PtBuA star block copolymers comprise a polyelectrolytic block in each of their branches, and it should exhibit a strongly pH-dependent behavior. The acid hydrolysis and the properties of the resulting amphiphilic star block copolymers will be discussed in a forthcoming paper.

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