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Synthesis and Characterization of Star and Comb Polystyrenes Using Isometric Poly(chloroethyl vinyl ether) Oligomers as Reactive Backbone

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ABSTRACT: In the course of studies dealing with the synthesis and the characterization of the properties of highly branched polymers with controlled chain parameters, the selectivity of the grafting reaction of polystyryllithium chains onto poly(chloroethyl vinyl ether) has been investigated. To that purpose, a series of isometric poly(chloroethyl vinyl ether) oligomers with precise degree of polymerization, ranging from 3 to 9, were prepared by selective fractionation of a poly(CEVE) of narrow polydispersity into its different *n*-mers. The latter were used as reactive backbone for grafting PSLi chains. Characterization of the graft copolymers shows that the substitution of chloride of CEVE units is quantitative and yields comblike copolymers with a number of branches corresponding to the number of monomer units in the isometric poly(CEVE) backbone. The poly(CEVE)-*g*-polystyrenes show the typical solution behavior of star polystyrenes.

Introduction

It is now well established that the solution and bulk properties of macromolecules are strongly influenced by their chain architecture. Specific characteristics resulting from the chain topology have already led to a number of interesting applications, and recently an increasing research activity has been devoted to the preparation of polymers with highly branched architecture such as stars or comb polymers,[1−3] etc. The development of new synthetic procedures still constitutes an important challenge.

In the course of studies dealing with the preparation and the characterization of the properties of highly branched polymers, a new route to the preparation of graft copolymers with a star or comblike chain topology has been recently developed in our group.[4,5] It involves the selective deactivation of polystyryllithium onto poly(chloroethyl vinyl ether), poly(CEVE), backbone. One advantage of this approach is that both the cationically and the anionically prepared constitutive polymers, i.e, the PS graft and the poly(CEVE) backbone, can be obtained by living type polymerization, thus allowing the precise control of their dimensions. A second advantage of the method deals with the high efficiency of the coupling reaction between the carbanionic polystyrene end and the chloroethyl ether function of the poly(CEVE). To confirm the selectivity and the quantitativity of the grafting reaction, this process was applied to the synthesis of star and comb polystyrenes with a precise number of branches, using isometric poly(CEVE) oligomers (i.e., of same molar mass and degree of polymerization) as reactive backbone. The preparation of the latter oligomers by selective fractionation of a poly(CEVE) into its different *n*-mers is first reported. The synthesis, the characterization, and the solution behavior of the corresponding poly(CEVE)-*g*-polystyrene copolymers will then be described.

Experimental Section

Materials. Benzene and toluene (Prolabo, France) were purified by distillation over sodium benzophenone. Chloroethyl vinyl ether (CEVE) (Sigma-Aldrich France) was washed with an aqueous NaOH solution (1 N) and distilled over calcium hydride. Styrene (99%, Sigma-Aldrich France) was purified by distillation over calcium hydride at reduced pressure. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA) (Sigma-Aldrich France) was dried and purified by distillation over sodium. *sec*-Butyllithium (1.3 M in cyclohexane) (Sigma-Aldrich France) was used as received.

HCl gas (Setic Labo France) was used as received. Zinc chloride (Sigma-Aldrich France) was dissolved in dry diethyl ether (7×10^{-3} mol L^{-1}).

All the reactants were stored under dry nitrogen in glass apparatus fitted with PTFE stopcocks.

Polymerization Procedures. *Preparation of the Poly(CEVE). (a) Polymerization.* α-Chloro(2-chloroethyl) ethyl ether, the HCl−CEVE adduct, was used as chain precursor. It was prepared by bubbling HCl gas through a solution of CEVE, in dry diethyl ether, at −10 °C.[4] The CEVE polymerization was carried out in toluene, at −30 °C under nitrogen, by sequential addition of the precursor, the monomer, and $ZnCl_2$ in diethyl ether. The polymerization was terminated by addition of a 10% solution of lutidine in dry methanol, thus yielding a poly(CEVE) oligomer with an acetal end group. The polymer solution was then washed several times with neutral water, and the poly(CEVE) was recovered by solvent evaporation under vacuum and characterized.

The potentially reactive chloroethoxymethoxy acetal end of the poly(CEVE) oligomer was converted into a dimethoxy acetal terminus by polymer treatment, in methylene dichloride at 20 °C, with acidic methanol for 24 h. The end-modified polymer was then purified and recovered as previously indicated.

(b) Fractionation of poly(CEVE) into isometric oligomers. The crude poly(CEVE) oligomers ($\overline{DP}_n = 6$) was fractionated into a series of isometric oligomer fractions by semipreparative high-performance liquid chromatography using a silica column (Spherisorb S5W, 5 μm, 60 Å) and a THF/hexane mixture (15/85 v/v) as eluent. The number of CEVE units in each oligomer series was determined by proton NMR and SEC (see below).

(c) Poly(CEVE) Characterization. The molar mass and the $\overline{DP}_n$ of the crude poly(CEVE) and of the different isometric fractions were determined by ^{1}H NMR from the integration ratio of the acetal end and the CEVE units and by size exclusion chromatography (SEC) on the basis of a polystyrene calibration.[4,6]

Synthesis of the PS Grafts. The anionic polymerization of styrene was performed under nitrogen in a flamed glass

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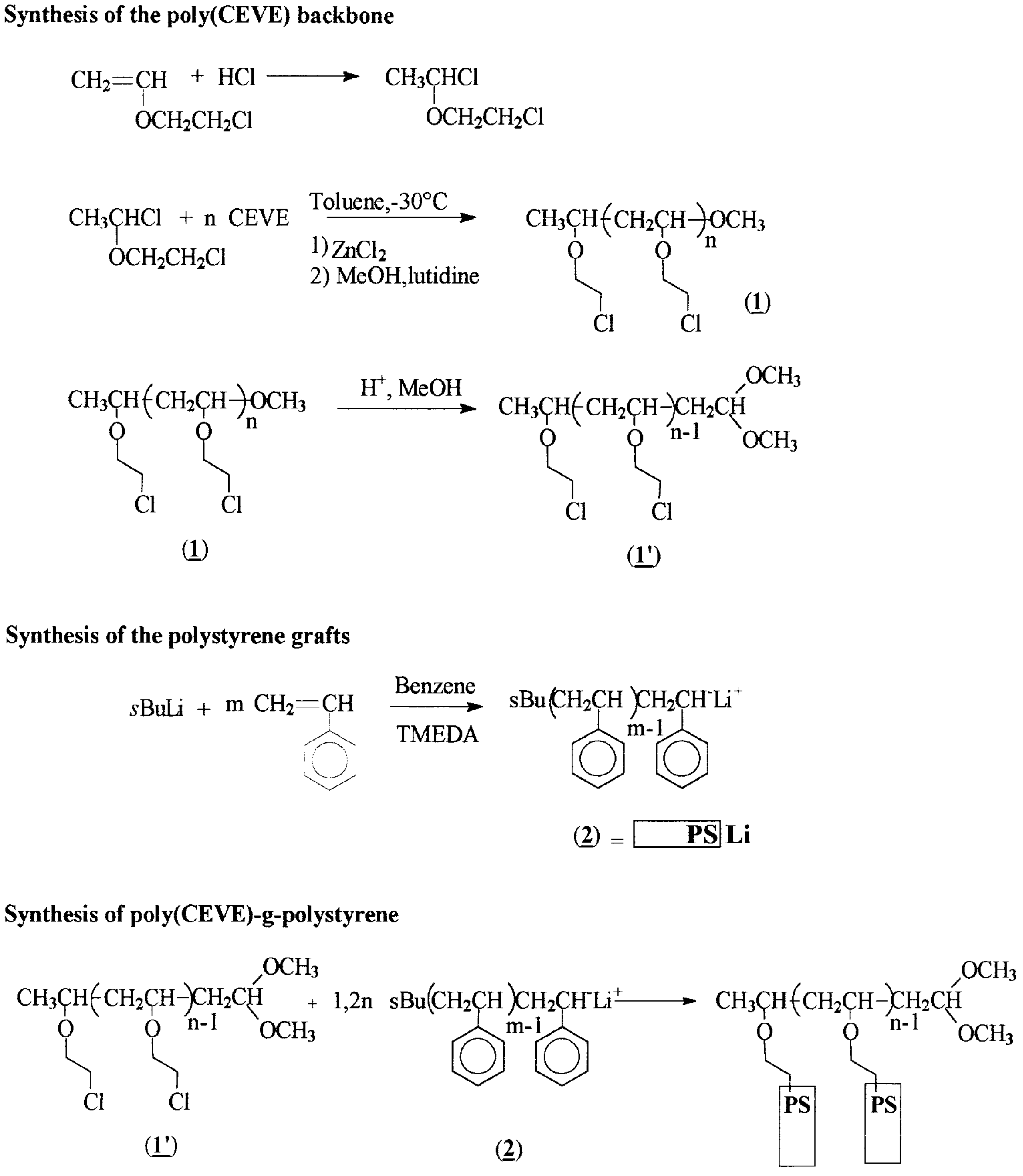
Scheme 1



reactor. Benzene, styrene, and TMEDA (1 equiv with respect to initiator) were first introduced, and the reactor was thermostated at 5 °C. Then, a calculated amount of *sec*-butyllithium initiator was added. After 10 min, the temperature was increased to 25 °C for 2 h. The living polystyryl solution was finally transferred into a graduated tube fitted with a PTFE stopcock and stored until use. A small aliquot of the PSLi solution, deactivated by degassed methanol, was used for characterization.

Preparation of Poly(CEVE)-g-polystyrene Copolymers. (a) Grafting Reaction. The polystyryllithium solution was incrementally added to a weighted amount of poly(chloroethyl vinyl ether), previously degassed under vacuum and dissolved in dry benzene. The rate of PSLi addition was determined by the disappearance of the coloration of the poly(CEVE) solution. Addition of PSLi was performed until a fading pink color of the reacting media remained over about a 24 h period. Residual PSLi was finally deactivated by addition of degassed methanol.

(b) Fractionation of the Graft Copolymers. Separation between the graft copolymers and unreacted or dimerized PS was achieved using selective adsorption onto silica gel of the high molar mass fraction corresponding to the graft copolymer.[4]

Apparatus. ^{1}H NMR spectra were recorded on a BRUKER AC 200 MHz in $CDCl_3$.

HPLC fractionation was achieved on a JASCO apparatus PU987 equipped with an RI detector and fitted with a semipreparative silica column (spherisorb S5W, 280 × 20 mm).

SEC measurements were performed in THF on a Varian apparatus equipped with refractive index (Varian) and laser light scattering (Wyatt Technology) dual detection and fitted with three TSK columns (G4000HXL, G3000HXL, G2000HXL). Calibration in the case of refractive index detection was performed using linear polystyrene standards. For light scattering detection, the d*n*/d*c* of the graft copolymers was determined separately for each sample, in THF, with a laser source operating at 633 nm.

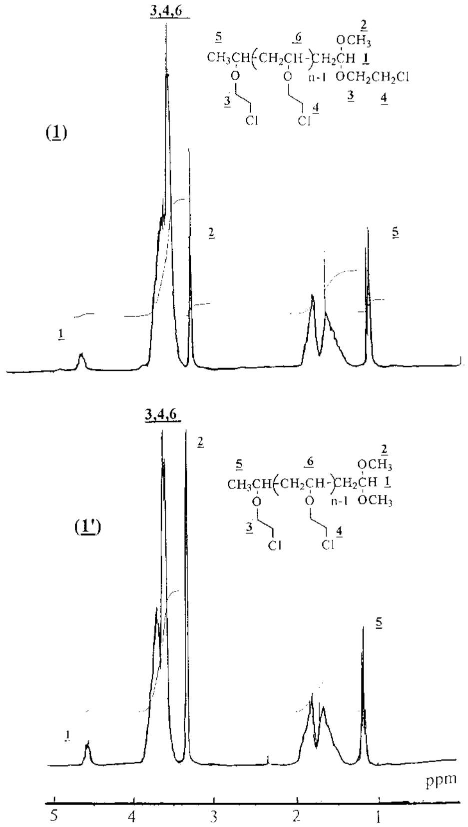


Figure 1. ^{1}H NMR of poly(CEVE) with chloroethoxy, methoxy acetal (**1**), and dimethoxyacetal (**1′**) end groups.

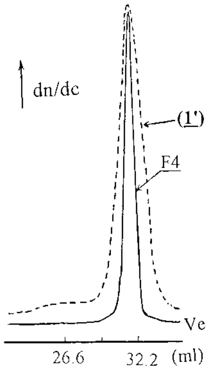


Figure 2. SEC chromatograms of poly(CEVE) (**1′**) ($\overline{DP}_n = 6$) and of one of its isometric fractions (DP = 4).

Results and Discussion

The general strategy developed for the synthesis of poly(CEVE)-*g*-polystyrene graft copolymers is described in Scheme 1. It involves first the preparation of the poly(CEVE) as reactive backbone (**1**) by conventional living type cationic polymerization. To avoid the grafting of one PS branch on the unstable chloroethoxy group of the chloroethoxymethoxy acetal oligomer terminus, the latter was converted into a dimethoxyacetal end group by treatment of the poly(CEVE) into acidic methanol, thus yielding quantitatively poly(CEVE) (**1′**). The ^{1}H NMR spectra of **1** and **1′** are presented in Figure 1. The SEC chromatogram of the dimethoxyacetetal-terminated poly(CEVE) is shown in Figure 2. The main characteristics of the poly(CEVE) oligomer (**1′**) synthesized for the present study are summarized in Table 1.

Polystyryllithium (**2**) was synthesized by addition of *sec*-butyllithium on a benzenic solution of styrene and *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TMEDA), in equimolar amount with respect to the lithiated initiator. A polystyryllithium with $\bar{M}_n = 10\,400$ and $\bar{M}_w/\bar{M}_n = 1{,}02$ was prepared and used for the whole study.

Table 1. Conditions of Synthesis and Characteristics of the Poly(CEVE) Oligomer

precursor (10^{-3} M)	CEVE (M)	**1** $\overline{DP}_n^{\,th\,a}$	**1′** $\overline{DP}_n^{\,th\,a}$	$\bar{M}_n^{\,th}$	$\bar{M}_n^{\,exp\,b}$	$\overline{DP}_n^{\,exp\,c}$	$\bar{M}_w/\bar{M}_n$
71	0.50	7	6	743	650	6	1.18

[a] Polymerizations performed up to complete monomer conversion. [b] Determined by SEC on the basis of PS calibration. [c] Determined by proton NMR from the ratio CEVE units/terminal acetal.

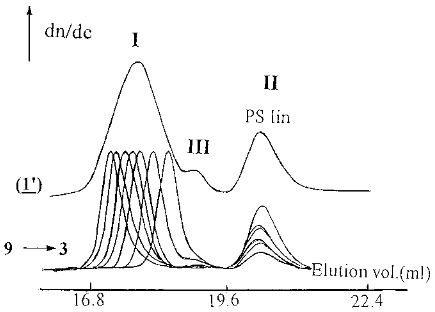


Figure 3. SEC chromatograms of poly(CEVE)-*g*-polystyrenes prepared from poly(CEVE) (**1′**) ($\overline{DP}_n = 6$) and from its various isometric fractions (DP = 3−9).

The grafting reaction was then achieved by adding dropwise the PSLi solution[4] onto a known amount of poly(CEVE), previously dried under vacuum and dissolved in dry benzene. A rapid discoloration of the carbanionic solution was observed at the very beginning. Then, on further addition of PSLi, the discoloration rate of the reaction mixture slowed, and complete discoloration of the last PSLi aliquots required several hours. To achieve complete PS grafting, i.e., one PS graft per CEVE unit, the PSLi was added in slight excess with respect to poly(CEVE) units (about 1,1−1,2:1), until persistent light-red coloration of the medium. Degassed methanol was finally introduced to deactivate the living polystyrene in excess.

The SEC chromatogram of the crude graft copolymer obtained from the poly(CEVE) oligomer ($\bar{M}_n = 650$ and $\bar{M}_w/\bar{M}_n = 1.18$) and PSLi ($\bar{M}_n = 10\,400$ and $\bar{M}_w/\bar{M}_n = 1.02$) is presented in Figure 3. The main signal (I) corresponds to the poly(CEVE)-*g*-polystyrene graft copolymer. As it may be seen, the peak is unimodal and quite narrow ($\bar{M}_w/\bar{M}_n < 1.21$), in agreement with a clean grafting process. The second polymer population (II) (about 20% in weight), correspond to deactivated PSLi, whereas the third one (III), in minute amount (<5% of the grafted polystyrene), can be attributed to dimerized polystyrene chains.[7] A similar behavior was observed using a poly(CEVE) of $\overline{DP}_n = 26$ as reactive backbone.

To investigate more precisely the selectivity and the quantitativity of the grafting reaction and to prepare comblike copolymers constituted of macromolecules with an identical number of branches, the poly(CEVE) oligomer (**1′**) ($\overline{DP}_n = 6$) was fractionated into a series of isometric (of same molar mass and degree of polymerization) poly(CEVE) oligomers, having an identical number of reactive chloroethyl grafting sites. These isometric oligomer fractions were obtained by high-

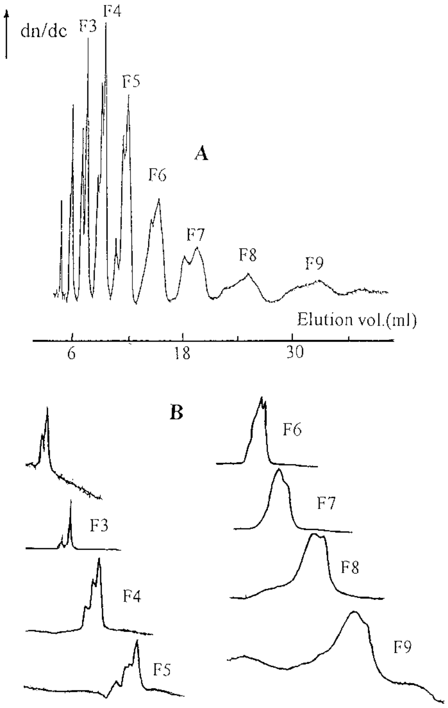


Figure 4. HPLC chromatograms of isometric poly(CEVE)s (DP = 3−9) obtained by HPLC fractionation of poly(CEVE) (**1′**), ($\overline{DP}_n$ = 6): A, crude product; B, isolated isometric fractions.

performance liquid chromatographic fractionation of the crude poly(CEVE) on a silica column using an hexane/THF solvent mixture. As may be seen in Figure 4, each oligomer fraction is characterized by a complex eluogram that may be interpreted by the presence of several configurational isomers possessing different elution time. The formation of such configurational isomers is supported by the multiple ^{13}C resonances of the main-chain methylene carbon observed for the poly(CEVE) chain ($\overline{DP}_n$ = 120, prepared in the same conditions) and the isometric fractions; see Figure 5. The number of CEVE units per chain for each oligomer fraction was determined by ^{1}H NMR from the ratio between the $-CH_2-CH_2-Cl$ methylene protons and the H− and CH_3O- acetal ones of the chain ω-end. A series of isometric oligomer with DP ranging from 3 to 9 was isolated in the present case. The SEC chromatogram of an isometric oligomer fraction (DP = 4) is compared with the initial poly(CEVE) one in Figure 2. The experimental $\bar{M}_w/\bar{M}_n$, determined by SEC for the different fractions, ranges from 1.01 to 1.03, in good agreement with their expected isometric structure.

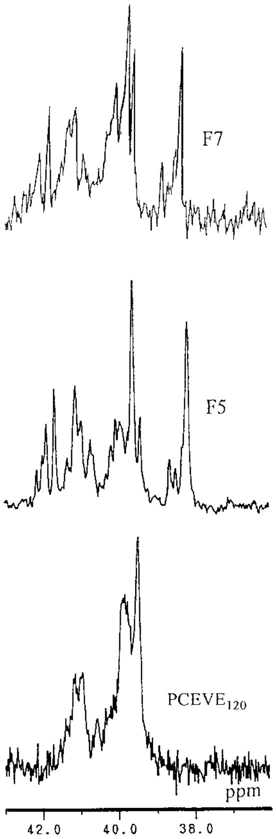


Figure 5. Expanded methylene ^{13}C signal of CEVE units for two isometric poly(CEVE) fractions (DP = 5 and 7); tacticity and chain end effects.

Table 2. Poly(CEVE-*g*-styrene) Graft Copolymers Obtained from Isometric Poly(CEVE): Control of the Number of PS Branches

Cl group per poly(CEVE)	$\bar{M}_n^{th}$	$\bar{M}_n^{exp}$ LS detector[b]	$\bar{M}_n^{exp}$ RI detector[a]	$M_w/\bar{M}_n$[a]	f[c]	$[n]$,[d] dL/g
0		10 400	10 400	1.02		
3	31 520		27 400			0.17
4	42 000	42 100	33 700	1.01	4.01	0.19
5	52 460	54 300	38 700	1.01	5.17	0.18_5
7	73 330	72 800	48 800	1.03	6.94	0.18
8	83 800	82 500	54 500	1.03	7.87	0.17_5
9	94 270	94 500	57 900	1.04	9.01	0.18_5
$\overline{5,8}$	62 930	67 500	47 700	1.21	6.43	0.18_5
$\overline{26}$	272 350	248 200	94 900	1.11	23.70	0.19

[a] Determined by SEC with linear PS as calibration standards. [b] $\bar{M}_w$ and $\bar{M}_n$ determined by light scattering were obtained in THF using dn/dc = 0.179 (at 633 nm, 25 °C). [c] Number of PS branches: $\bar{M}_n^{exp}$ LLS/$\bar{M}_n^{exp}$ PS branch. [d] Measured in THF at 25 °C.

Grafting of PSLi ($\bar{M}_n$ = 10 400 and $\bar{M}_w/\bar{M}_n$= 1.02) onto the different isometric oligomer fractions was achieved as described above. The characteristics of the corresponding poly(CEVE)-*g*-polystyrene graft copolymers are collected Table 2. As may be seen, the theoretical molar masses of the graft copolymers, calculated from those of the poly(CEVE) backbone and the PS graft, assuming one PS graft per CEVE unit, are in close agreement with the experimental "absolute" molar masses determined by SEC using laser light scattering detection. The experimental number of PS branches, $\bar{f}$, determined from the ratio $\bar{M}_n$ graft copolymer/$\bar{M}_n$ PS branch closely fits with the calculation assuming total substitution of chloride groups. These results both support that grafting is quantitative with respect to the chloroether functions and that the number of CEVE units determined by ^{1}H NMR for each oligomer is the correct one. The SEC chromatograms of the different graft copolymers (3−9 branches) can be compared with the corresponding graft copolymer obtained from the unfractionated poly(CEVE) ($\overline{DP}_n$ = 6, $\bar{M}_w/\bar{M}_n$ = 1.21) in Figure 3. Due to the difference of molar masses between the graft copolymers and the residual mono- and dimerized polystyrene chains, the graft copolymer fraction was easily freed from the low molar masses polystyrene by selective adsorption of the graft copolymers onto silica gel.[4] Although the dispersity of the unfractionated graft copolymer is quite narrow (1.21), as may be seen Figure 6, the use of isometric oligomers as reactive

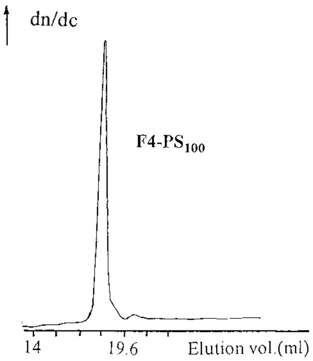


Figure 6. SEC chromatogram of a poly(CEVE)-*g*-polystyrene obtained from an isometric poly(CEVE) oligomer fraction (DP = 4) after purification.

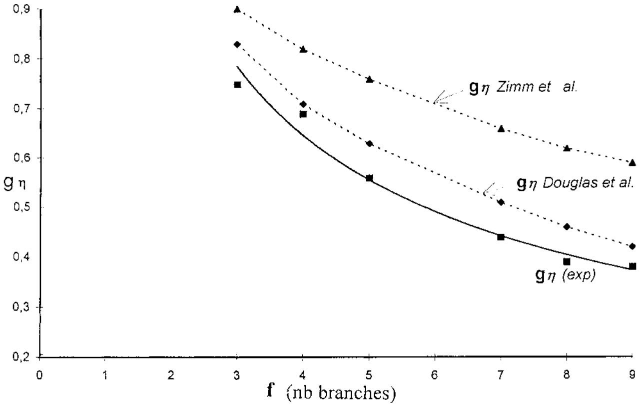


Figure 7. Evolution of g_η with the number of branches *f*. Comparison of experimental data (■) with values calculated using Zimm (▲) and Douglas (◆) empirical equations.

backbone significantly reduces the polymolecularity of the resulting graft copolymers ($\bar{M}_w/\bar{M}_n \leq 1.03$).

As shown in Table 2, the apparent molar mass of poly(CEVE)-*g*-polystyrene, calculated on the basis of linear polystyrene calibration, is much lower than the "absolute" molar mass, determined by SEC using multiangle laser light scattering detection (Table 2). This is consistent with the very compact dimensions of these polymers in solution as compared to those of the linear polystyrenes of the same molar mass.[8,9]

The experimental contraction factor g_η, which corresponds to the ratio of intrinsic viscosity of the branched polymers and of their linear conterparts of same molar mass, is plotted versus the number of branches *f* in Figure 7. Its variation with *f* can be compared with the empirical laws established by Zimm and Kilb[10] (eq 1) and Roovers and co-workers[11] (eq 2):

$$g_\eta = (2/f)^{3/2}[0.390(f-1) + 0.196]/0.586 \qquad (1)$$

$$g_\eta = [(3f-2)/f^2]^{0.58}[1 - 0.276 - 0.015(f-2)]/(1 - 0.276) \qquad (2)$$

As may be seen, experimental data fit quite closely with eq 2 developed by Roovers for star polymers.[11]

The double-logarithmic relationship between the intrinsic viscosity, measured in THF at 25 °C, and the $\bar{M}_w$ of the poly(CEVE)-*g*-polystyrene prepared from two unfractionated ($\overline{DP}_n$ = 6 and 26) and a series of isometric poly(CEVE) backbones (DP ranging from 3 to 9), is plotted in Figure 8. The log[*n*] remains constant for the whole series of samples in agreement with an α coefficient in the Mark–Houwink–Sakurada equation close to zero, clearly supporting that these comblike copolymers behave as very densely filled and nondraining rigid spheres.

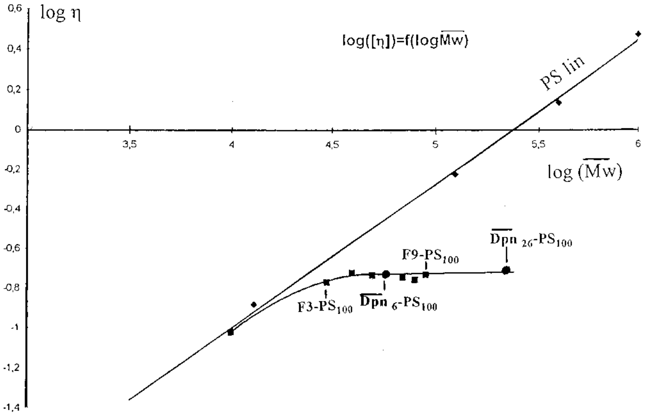


Figure 8. Logarithmic variation of the intrinsic viscosity (THF, 25 °C) with the molar mass for comblike copolymers with an increasing number of branches (3–9 [■], $\bar{6}$ and $\overline{26}$ [●]).

In conclusion, we have shown in this paper that starlike polymers with a precisely determined number of branches can be prepared by grafting PSLi chains onto isometric poly(CEVE). In the domain investigated, the selectivity of the process allows the quantitative substitution of chloride of the CEVE units by PS chains. Since poly(CEVE) fractions composed of oligomers with the same and unique degree of polymerization, presently named isometric, can be easily prepared by chromatographic fractionation of poly(CEVE) synthesized by living cationic polymerization, this method allows the unique preparation of a series of poly(CEVE)-*g*-polystyrenes with an exact number of branches that may be varied stepwise. This was achieved for *f* ranging from 3 to 9. However, depending on the $\overline{DP}_n$ of the poly(CEVE) used as starting materials, we may expect to prepare by this approach isometric graft copolymers with higher *f* values.

The graft copolymers exhibit in the domain examined the typical characteristics of star polymers. In the case of poly(CEVE) with longer backbone,[6] these graft copolymers, due to their compact structure, are expected to follow the typical behavior of polymacromonomers.[9,12]

Further studies on the synthesis of highly branched polymers of controlled structure, based on this grafting onto method, and their characterization are in progress.

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