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DESIGN OF NEW POLYMER ARCHITECTURES BY COMBINATION OF ANIONIC AND CATIONIC LIVING POLYMERIZATION TECHNIQUES

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Abstract

The grafting of polystyryl lithium onto poly(chloroethyl vinyl ether) chains has been investigated. The reaction proceeds cleanly and quantitatively thus allowing the synthesis of comblike polymers. Since the dimensions of the polystyrene branches and of the poly(chloroethyl vinyl ether) backbone can be controlled by living polymerizations, both the length and the number of branches of the graft copolymers can be tuned. The latter behave as star polymers. The possibility to initiate a new cationic polymerization of chloroethyl vinyl ether from polystyrene branches bearing acetal termini in order to prepare the corresponding stars with poly(chloroethyl vinyl ether-*b*- styrene) branches is also examined.

Finally access to hyperbranched polymers of controlled architecture and dimensions by deactivation of a second amount of polystyryl lithium onto the last blocks of poly(chloroethyl vinyl ether) is also reported.

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 in various domains.

An important research activity has been devoted in recent years to the preparation of polymers with special architecture and well-controlled structure and dimensions ; stars,

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combs, hyperbranched polymers, dendrimers, macrocycles, etc... Despite some important breakthroughs, the development of new synthetic procedures remains still an important challenge.

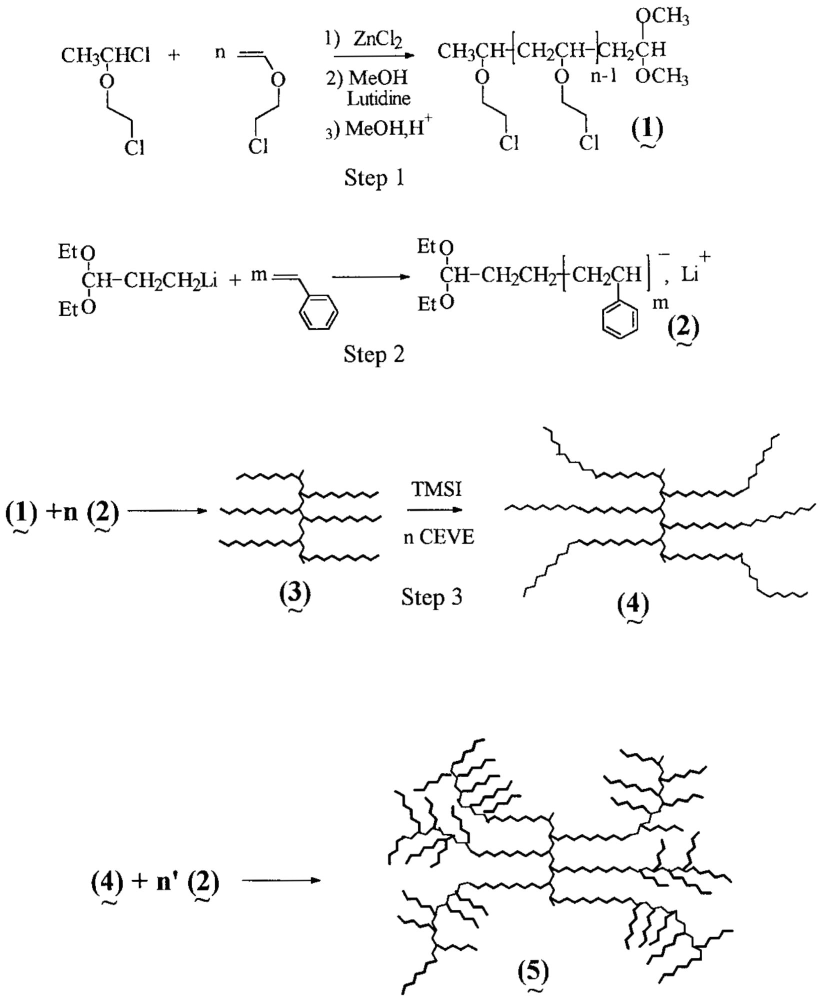
A general step-by-step route for the preparation of polystyrene and polybutadiene with a chain architecture of increasing segment density, based on the successive and repeated interconnection of poly(chloroethyl vinyl ether) (PCEVE) and polystyrene (PS) or polybutadiene elementary blocks has been recently explored in our group. One first interest of this strategy is that both the cationically and the anionically prepared blocks can be synthesized by living type-polymerizations, thus allowing the precise control of their dimensions. A second advantage deals with the high efficiency and selectivity of the coupling reaction between the carbanionic polymer ends and the chloroethyl ether functions of the PCEVE.

The application of this approach to the synthesis of poly(chloroethyl vinyl ether-*g*-styrene) copolymers [P(CEVE-*g*-S)] with star-like (1), comb-like and hyperbranched chain architectures, as well as the solution properties of these materials are described in this paper.

RESULTS AND DISCUSSION

Strategy

It consists in the use of PCEVE homopolymer (1), and then of PCEVE blocks of (4), as plurifunctional backbone for grafting living polystyryl (or polybutadienyl) lithium chains (2), see Scheme 1. The controlled synthesis of PCEVE by living cationic polymerization initiated from an organic (step 1) (2-3) or a macromolecular chain precursor (4-5) (step 3) has been described in detail in several papers. The grafting of PS chains is then achieved by adding dropwise the PSLi solution onto a known amount of CEVE units of (1) or (4) dissolved in dry toluene. Although reaction is fast at the beginning, the discoloration of the last PSLi aliquot requires generally several hours. To achieve a complete substitution of chlorine of CEVE, PSLi was added in slight excess until a persistent light-red coloration of the medium remains.



Scheme 1

Stars and comblike polystyrenes

This strategy was first applied to the synthesis of stars and comblike polystyrenes (3) possessing a well-controlled number of branches of same length.

Their preparation involves first the preparation of the poly(CEVE) backbone (1). CEVE polymerization was achieved in toluene, at low temperature, in the presence of αchloro(chloroethyl ethyl ether), denoted [RCl], as chain precursor and $ZnCl_2$ as catalyst. The characteristics of PCEVEs used as reactive backbone are given in Table 1. As it may be seen, the average $\overline{DP}_n$ of the polymers, determined by SEC, are in good agreement with theoretical values calculated from the ratio [CEVE] consumed/[RCl], whereas the molar masses distribution are narrow (<1,2) as expected for a living polymerization.

Table 1 : Synthesis and characteristics of poly(CEVE) backbones

RCl precursor (10^{-3} M)	CEVE (M)	$\overline{DP}_n$ th^{a}	$\overline{M}_n$ th	$\overline{M}_n$exp$^{b)}$	$\overline{DP}_n$exp$^{C)}$	$\overline{M}_w/\overline{M}_n$
71	0,50	7	777	650	6	1,18
15,6	0,47	30,2	3 250	3 100	26	1,03
8,5	0,51	60	6 422	6 140	56	1,03

a) polymerisations 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

The polystyryllithium grafts (2) were prepared in benzene, using sec-butyl lithium in the presence of an equimolar amount of tetramethylene diamine (TMEDA), as initiating system, at 5°C. The polymerization was then achieved at 25°C and a fraction of the PSLi solution was sampled out for characterization of the PS graft.

The SEC chromatogram of a crude graft copolymer is presented on Figure 1. The main signal (I), located in the high molar masses domain, corresponds to the poly(ethyl vinyl ether-g-styrene) graft copolymer (3). As it may be seen, the peak is unimodal and very narrow (<1,1), in agreement with a clean and homogeneous grafting of polystyryl branches onto the PCEVE backbone. A second population (II) (between 10 to 20% in weight depending on the runs), with $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ identical to that of the initial PSLi corresponds to the slight excess of carbanionic chains utilized as well as to PSLi deactivated by protonic impurities remaining in the poly(CEVE) solution. The population (III) may be attributed to a small amount of dimerized polystyrene (6) (<< 5% of the grafted polystyrene). The molar mass of the graft copolymers has been determined by SEC using refractive index detection (calibration with linear polystyrenes) and laser light scattering after measuring their specific dn/dc. The corresponding experimental $\overline{M}_w$ and $\overline{M}_n$ are collected in Table 2 where they can be compared to theoretical $\overline{M}_n$ calculated assuming one PS branch attached per CEVE unit of the PCEVE backbone. As it may be seen a good agreement is observed suggesting that the grafting is nearly complete, even for grafts with $\overline{M}_n$ as high as 15000. This supports the formation of graft copolymers with a comblike or "polymacromonomer" architecture.

6b

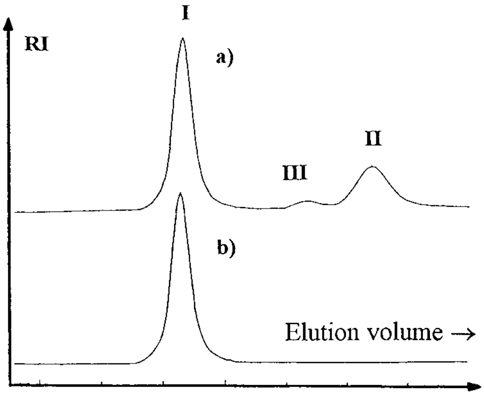


Figure 1 . SEC Chromatogram of a poly(CEVE-g-styrene) in THF : a) crude reaction product. I : poly(CEVE-g-styrene), $\overline{M}_{n\,SEC}$= 58500 ; II : deactivated polystyrene, $\overline{M}_{n\,SEC}$ = 5400 ; III : polystyrene dimer, $\overline{M}_{n\,SEC}$ = 11500. b) after fractionation by reprecipitation.

Table 2 : Characteristics of poly(CEVE-g-styrene) comblike copolymers : comparison of theoretical molar masses with apparent and absolute experimental molar masses

PCEVE	PSLi	Graft copolymer			
$\overline{DP}_n$exp[a)]	$\overline{M}_n$exp[a)]	$\overline{M}_n$ th	$\overline{M}_n$exp		$\overline{M}_w/\overline{M}_n$
			LS detector[b)]	DRI detector[a)]	
6	10 000	60 000	62 000	36 700	1,14
26	2 600	70 300	70 800	24 500	1,05
26	5 500	148 700	154 500	60 100	1,06
26	15 000	390 000	351 400	127 000	1,07
56	3 100	173 600	168 500	61 000	1,09

a) determined by SEC with linear PS as calibration standards

b) $\overline{M}_n$ from light scattering was determined in THF using a dn/dc =0,179 (633 nm, 25°C)

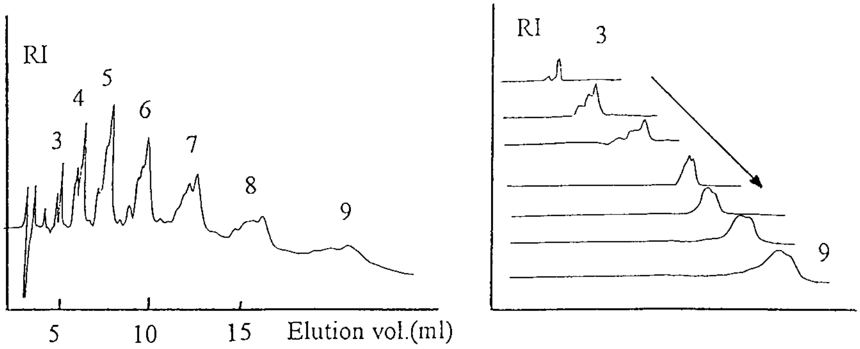
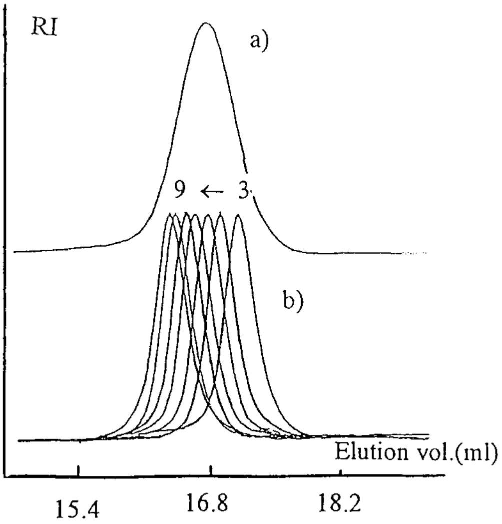


Figure 2 : HPLC analysis of a poly(CEVE) : a) crude oligomer ; b) after oligomer fractionation. Solvent THF/Hexane (15/85) ; column spherisorb Si60.



SEC analysis : a) unfractionated oligomer ; b) oligomer fractions with DP 3 to 9

Figure 3 : SEC chromatograms of a poly(CEVE), $\overline{DP}_n = 5.8$, $\overline{M}_w/\overline{M}_n = 1.2$ and of uniform oligomers with DP 3 to 9 see Table 3.

To investigate in more detail the selectivity of the grafting reaction and to prepare comblike polymers with an uniform number of branches, a PCEVE oligomer ($\overline{DP}_n$ = 5,8) was fractionated by HPLC chromatography to obtain a series of uniform oligomers with an exact number of monomer units. As it may be seen on Figure 2, chromatography performed on a silica column using an hexane/THF solvent mixture yields selectively pure PCEVE oligomers with DP ranging from 3 to 9 ; each oligomer series is characterized by a complex eluogram which may be interpreted by the influence of chain configuration on retention time. The number of CEVE units per oligomer was determined by ^{1}H NMR from the ratio of -CH_2-CH_2-Cl methylene protons and the H-acetal of the ω-end of the chain.

The characteristics of the corresponding P(CEVE-g-S) graft copolymers are collected in Table 3. The theoretical molar masses of the graft copolymers calculated from the molar mass of the PCEVE backbone and that of the PS graft, assuming one graft per CEVE unit, are in close agreement with experimental molar masses determined by SEC using light scattering detection. These results both support that grafting is quantitative with respect to the chloroether functions and that the calculated number of CEVE units per oligomer series is correct. The SEC chromatograms of the different graft copolymers (3 to 9 branches with PS graft $\overline{M}_n$= 10400 and $\overline{M}_w/\overline{M}_n$=1,02) can be compared with the corresponding graft copolymer obtained from the unfractionated PCEVE ($\overline{DP}_n$ = 5,8, $\overline{M}_w/\overline{M}_n$ = 1,2) in Figure 3. As it may be seen although the dispersity of the unfractionated graft copolymer is quite narrow (1,21) the use of uniform oligomers significantly reduce the polymolecularity.

Viscosity measurements performed on a P(CEVE-g-S) copolymer series with an increasing number of branches (uniform 3 to 9 and average $\overline{5,8}$ and $\overline{26}$), see Figure 4, show than they behave as typical star polymers (rigid spheres) characterized by an α coefficient close to zero in the Mark-Houwink equation. The experimental variation of the contraction factor g_v which represent the viscosity ratio between the branched polymers and their linear conterparts is in close agreement with the calculated values using the equation developed by Roovers for star polymers (7).

Table 3 : Poly(CEVE-*g*-styrene) graft copolymers : control of the number of branches

nb. of Cl-ethyl ether function (branches) per PCEVE oligomer	P(CEVE-*g*-S) graft copolymer			
	$\overline{M}_n$ th	$\overline{M}_n$exp		$\overline{M}_w/\overline{M}_n$ a)
		LS detector b)	RI detector a)	
0	10 400	10 400	10 400	1,02
3	31 600	-	27 400	-
4	42 100	42 100	33 700	1,01
5	52 600	54 300	38 700	1,01
7	73 600	72 800	48 800	1,03
8	84 100	82 500	54 500	1,03
9	94 700	94 500	57 900	1,04
$\overline{5,8}$	61 000	67 500	47 700	1,21
$\overline{26}$	273 550	248 200	94 900	1,11

a) determined by SEC with linear PS as calibration standards

b) $\overline{M}_n$ from light scattering was determined in THF using a dn/dc =0,179 (633 nm, 25°C)

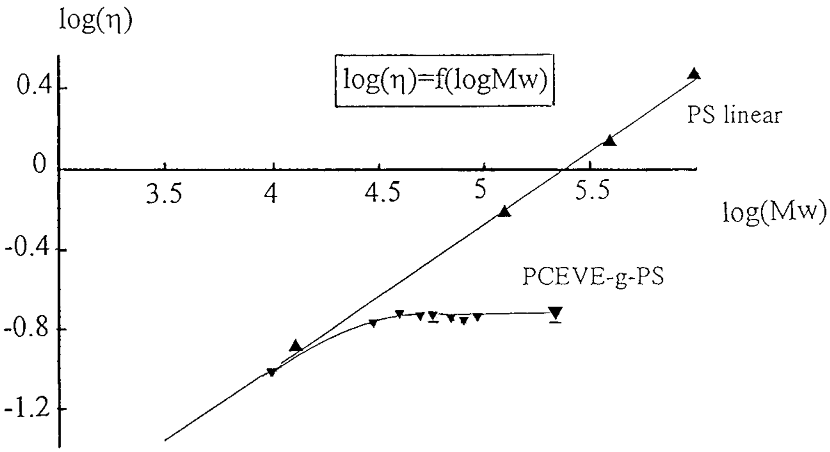


Figure 4. Variation of the intrinsic viscosity of linear (▲) and PCEVE-g-PS copolymers with an uniform (▼) and average ($\underline{▼}$) number of branches (PS with $\overline{M}_n$ = 10 400), see Tab.3.

Stars and comblike copolymers with poly(styrene-b-CEVE) branches

Since the living polystyryl chains have been initiated from a lithioacetal derivative, see scheme 1, the terminal acetal group of the PS branches can be used to initiate the cationic growth of new PCEVE blocks (4,5). With this aim, acetal endgroups were first transformed into α-iodoether termini in the presence of TMSI, and the CEVE polymerization was triggered by adding zinc chloride. As indicated by NMR and SEC analysis most of the PCEVE chains are anchored to the multifunctional PS precursor, thus yielding stars and comb-like copolymers (4) with P(CEVE-g-S) branches of controlled structure and dimensions. The small fraction of ungrafted PCEVE formed as side product was eliminated by selective precipitation and used to get an estimate of the PCEVE block length in the graft copolymer. The corresponding data, collected in Table 4, show the molar mass increase due to the growth of PCEVE blocks whereas polymolecularity of the final copolymers remains unimodal and very narrow.

Table 4 : Synthesis and characteristics of poly(CEVE) with (Styrene-*b*-CEVE) branches

$PCEVE_1$	PS	P(CEVE-*g*-S)	$PCEVE_2$	$P[CEVE_1\text{-}g\text{-}(S\text{-}b\text{-}CEVE_2)]$		
$\overline{DP}_n$ [a)]	$\overline{DP}_n$ [a)]	$\overline{M}_w$exp [b)]	$\overline{DP}_n$ [a)]	$\overline{M}_n$ th	$\overline{M}_w$exp [b)]	$\overline{M}_w/\overline{M}_n$
26	51	168 000	82	351 000	388 200	1,13
26	146	409 000	50	518 000	564 000	1,10
60	30	162 000	21	322 000	305 000	1,16

a) determined by SEC with linear PS as calibration standards
b) $\overline{M}_W$ determined in THF from light scattering

Hyperbranched architectures

Using the same approach, the chloroethyl ether units of the external poly(CEVE) blocks of the copolymers (4) were utilized as new electrophilic sites for grafting another generation of PS chains (or α-acetal PS chains) to form an hyperbranched polystyrene of first generation (5). Since acetal end groups are still present at the end of the PS branches this procedure can be repeated again. By this step-by-step procedure hyperbranched polystyrenes of second generation with molar masses up to 10^7 and narrow molar masses distribution (< 1,1) have been prepared.

The architecture and the behavior of the first generation products are already very intriguing. Some characteristics of these new polystyrene-based polymers are collected in Table 5. As it may be seen the molar masses are in satisfactory agreement with theoretical calculation assuming again one PS chain attached to each CEVE unit of the outer blocks. Moreover, the polydispersity of theses objects remains apparently extremely narrow.

Viscosity and light scattering measurements indicates that these macromolecules (8) are highly compact spheres with a radius of gyration which is much smaller than that of linear PS of the same molecular weight (about 1/5 to 1/10 of r_g of linears). Indeed the dimensions of the final macromolecules of first generation are determined by 4 chain parameters ; the PCEVE core and the first PS grafts which form the inner part of the sphere, the second PCEVE blocks and their PS grafts which constitute the outer part. Interestingly the size of these unimolecular particles seems to be influenced by the length of the first PS grafts which could be in extension and therefore generate an empty space inside the sphere whereas most of the mass made by the second PCEVE blocks and their PS grafts (around 95-99 % in weight) may constitute the shell of the sphere.

Table 5 : characteristics of hyperbranched poly[CEVE$_1$-*g*-(S$_1$-*b*-(CEVE$_2$-g-S$_2$))] copolymers

PCEVE	S$_1$	PCEVE$_2$	PS$_2$	P[CEVE$_1$-*g*-(S$_1$-*b*-(CEVE$_2$-g-S$_2$))]				
$\overline{DP_n}^{a)}$	$\overline{DP_n}^{a)}$	$\overline{DP_n}^{a)}$	$\overline{DP_n}^{a)}$	$\overline{M_n}$ th	$\overline{M_n}_{SEC}{}^{a)}$	$\overline{M_w}$exp$^{b)}$	$\overline{M_w}/\overline{M_n}$	r_g (nm)
26	51	82	52	11.600 000	460 000	9 500 000	1,06	25
26	146	50	52	7 300 000	-	5 700 000	1,33	30
60	30	55	37	13 250 000	500 000	10 350 000	1,05	28

a) determined by SEC with linear PS as calibration standards
b) $\overline{M_w}$ determined in THF from light scattering

Further characterization and detailed evaluation of the properties of these new macromolecular objects of well-controlled architecture and dimensions are in progress.

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