9504 *Macromolecules* **2000,** *33,* 9504−9511

Complex Macromolecular Architectures by Combining TEMPO Living Free Radical and Anionic Polymerization

Thodoris Tsoukatos, Stergios Pispas, and Nikos Hadjichristidis*

Department of Chemistry, University of Athens, Panepistimiopolis, Zografou, 15771 Athens, Greece

Received July 11, 2000; Revised Manuscript Received October 16, 2000

ABSTRACT: A combination of TEMPO living free radical (LFRP) and anionic polymerization was used for the synthesis of star, graft, block−graft, block−brush, and graft−block−graft copolymers of styrene and isoprene. For graft copolymers with polystyrene (PS) backbone and polyisoprene (PI) branches, living free radical copolymerization of styrene and *p*-chloromethylstyrene (CMS) was performed, followed by a linking reaction at −20 °C of the chloromethyl groups of the backbone with living 1,1-diphenylethylene end-capped polyisoprenyllithium (PI−DPELi). Similarly the reaction of the chloromethyl groups of a diblock copolymer of styrene and *p*-chloromethylstyrene, obtained by LFRP, with PI−DPELi gave a block−brush copolymer with polyisoprene branches. Reaction of low molecular weight *p*-chloromethylstyrene homopolymers (PCMS) with PI−DPELi lead to polyisoprene stars. Finally reaction of a (PS-*g*-PS)-*b*-(PS-*co*-PCMS) with PI−DPELi resulted to a graft−block−graft copolymer. All products were analyzed and molecularly characterized by size exclusion chromatography, low angle laser light scattering, membrane osmometry, ^{1}H NMR spectrometry, and viscometry. In all cases the molecular and compositional polydispersity was low ($M_w/M_n = 1.08−1.32$) and the linking efficiency was close to 100%.

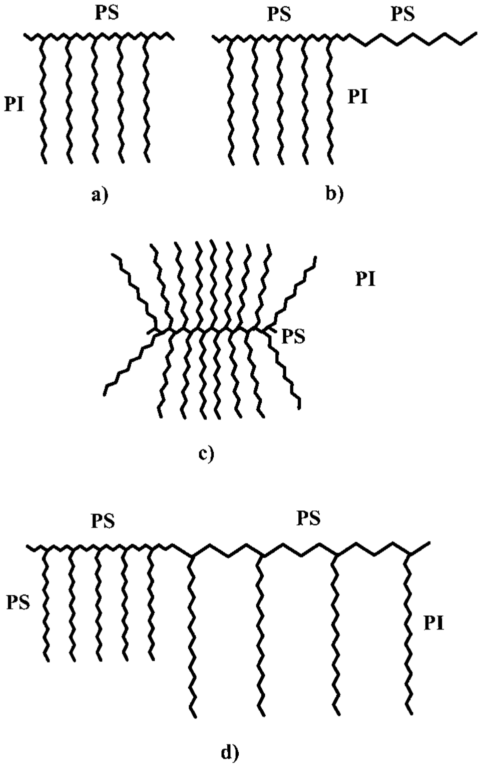
Introduction

During the past decade polymers with complex architectures (star, graft, block−graft, etc.) have been synthesized mainly by using ionic polymerization and an appropriate linking agent.[1] Recently great attention has been paid to living free radical polymerization (LFRP). Georges first reported living free radical polymerization of styrene by using initiators produced from nitroxide compounds, as TEMPO, and benzoylperoxide or azodiisobutylnitrile.[2,3] These initiators have been replaced by unimolecular initiators for better control over the molecular weight and the functionality of the polymer chain ends.[4−6] By using the unimolecular initiators, diblock[7−11] as well as graft,[12] star,[12] and hyperbranched polymers[13] were prepared. The main disadvantage of TEMPO living free radical polymerization is that its application is limited mainly to styrenic monomers. Additionally some limitations exist in respect to the architecture of the polymers that can be produced by this method. In an effort to tackle this problem, we used a combination of LFRP and anionic polymerization to create macromolecular architectures which are difficult to create by only one kind of polymerization (Chart 1). All materials were molecularly characterized by a combination of analytical techniques for structure verification. A combination of LFRP and anionic polymerization has been already used by Quirck but only to produce linear block copolymers of styrene and butadiene.[14]

Experimental Section

TEMPO Living Free Radical Polymerization. Materials. Styrene (Merck) and *p*-chloromethylstyrene (90%) (Aldrich) were freshly distilled over calcium hydride (Merck). Reagent grade acetic anhydride (Ferak) and 1-phenyl-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane (Binrad) were used as received.

Chart 1. (a) PS-*g*-PI Graft Copolymer; (b) (PS-*g*-PI)-*b*-PS Block−Graft or Block−Brush Copolymer; (c) PI Star Copolymer; (d) (PS-*g*-PS)-*b*-(PS-*g*-PI) Graft−Block−Graft Copolymer



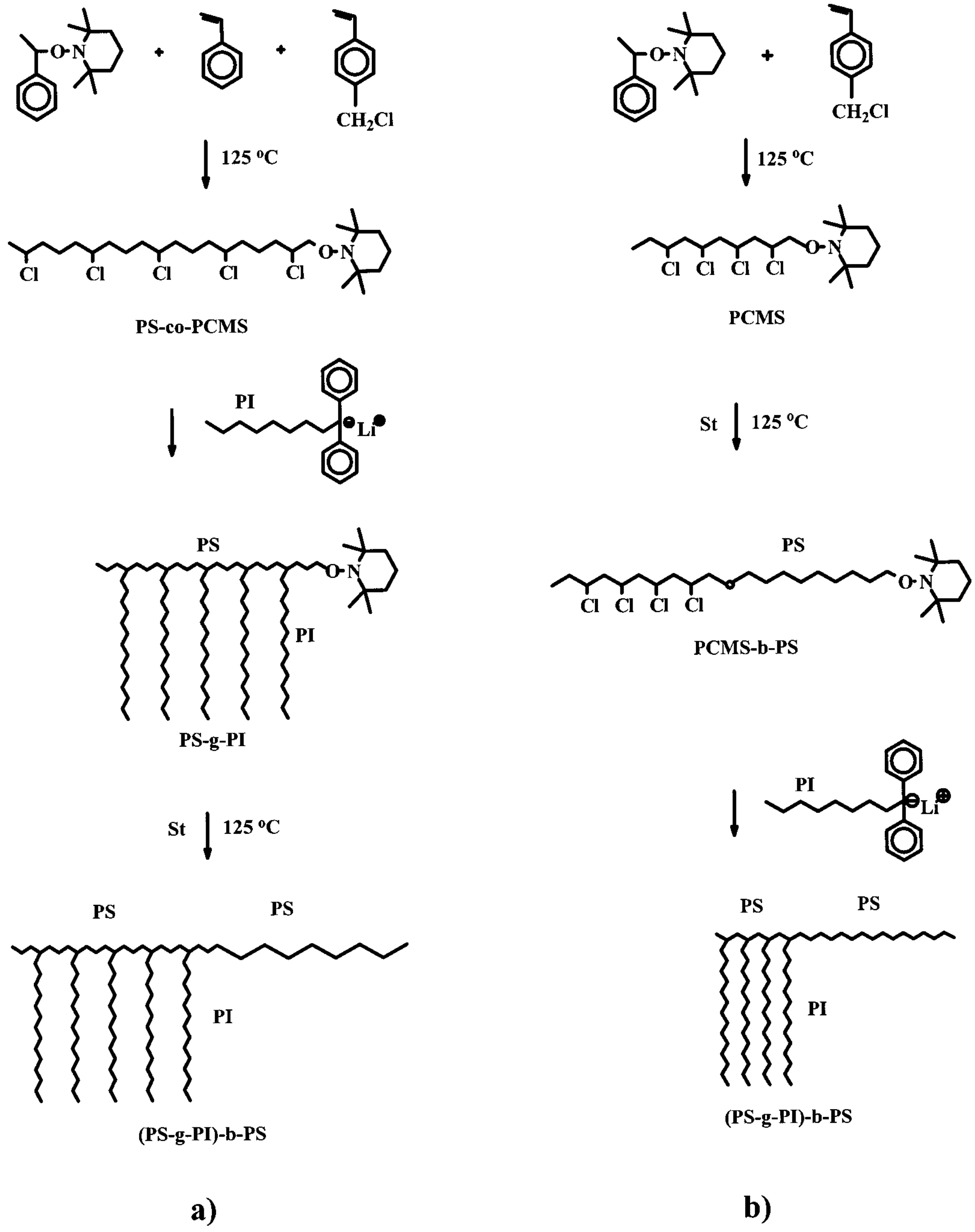
Copolymers of Styrene and *p*-Chloromethylstyrene (PS-*co*-PCMS). In a typical styrene (St) and *p*-chloromethylstyrene (CMS) copolymerization, 8.386 g (80.64 mmol) of St and 3.820 g (24.97 mmol) of CMS (31.3% w/w CMS) were placed in a glass ampule with 0.256 g (1.02 mmol) of 1-phenyl-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane (unimolecular initiator). Then 0.143 g of acetic anhydride (∼1% w/w referred to the monomers) was also added as an accelerator according to Hawker.[15] After three freeze−thaw cycles, the glass ampule

---

* To whom correspondence should be addressed (E-mail: hadjichristidis@chem.uoa.gr).

10.1021/ma0011946 CCC: $19.00

Scheme 1. (a) Synthesis of PS-*g*-PI Graft and (PS-*g*-PI)-*b*-PS Block−Graft Copolymers; (b) Synthesis of (PS-*g*-PI)-*b*-PS Block−Brush Copolymer



was sealed-off from the vacuum line and placed in an oil bath at 125 °C for 6 h. The resulted copolymer was dissolved in toluene and precipitated in methanol twice. The polymer was thoroughly dried under vacuum, until constant weight.

***p*-Chloromethylstyrene Homopolymers (PCMS).** In a typical polymerization, 0.023 g (0.09 mmol) of 1-phenyl-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane and 2.788 g (18.22 mmol) of *p*-chloromethylstyrene were placed in a glass ampule. Then, 0.025 g of acetic anhydride (∼ 1% w/w to CMS) was also added. After three freeze−thaw cycles the ampule was sealed-off from the vacuum line and was placed in an oil bath at 125 °C for 4 h. The polymer was diluted in toluene, filtered, and precipitated in methanol twice and dried under vacuum, until constant weight.

PCMS-*b*-PS. First, 0.611 g of PCMS (0.087 mmol) was dissolved in 7.879 g (75.76 mmol) of styrene and 0.091 g (∼ 1% w/w) of acetic anhydride. After three freeze−thaw cycles, the glass ampule was sealed-off from the vacuum line and placed in an oil bath at 125 °C for 5 h. The final polymer was fractionated with a toluene/methanol mixture to make sure that no residues of the starting PCMS homopolymer was left. The fractionated diblock copolymer was precipitated in methanol and dried under vacuum until constant weight.

(PS-*g*-PS)-*b*-(PS-*co*-PCMS). First, 0.774 g (0.009 mmol) of PS-*g*-PS (end-capped by TEMPO) was dissolved in 6.252 g of St, 0.594 g of CMS (8.67% w/w CMS), and 0.057 g of acetic anhydride. The mixture was placed in a glass ampule, and after three freeze−thaw cycles, it was sealed-off from the vacuum line and was immersed in an oil bath at 125 °C for 5 h. The product was diluted in toluene, filtered, and fractionated with a toluene/methanol mixture to isolate the (PS-*g*-PS)−(PS-*co*-PCMS) from any residues of the starting PS-*g*-PS. The final polymer was precipitated in methanol and dried under vacuum until constant weight.

Anionic Polymerization. Materials. Isoprene (Aldrich) was stirred overnight over calcium hydride (Merck) and distilled twice over *n*-BuLi (Merck) under vacuum. It was left over *n*-BuLi for half an hour at 0 °C. Then the monomer was

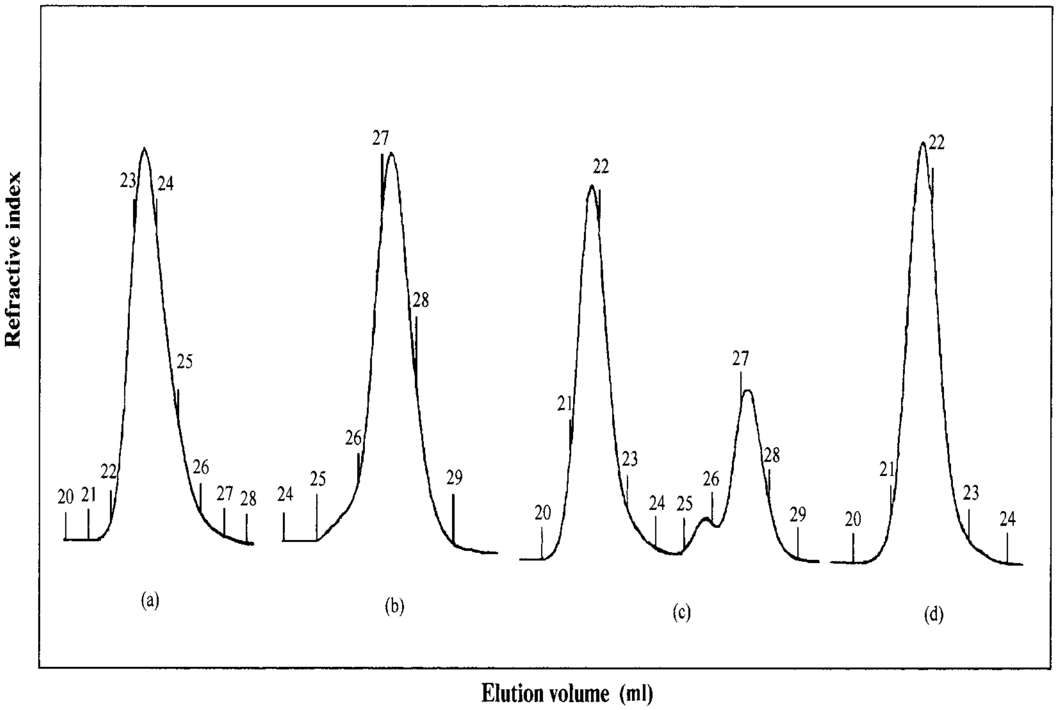


Figure 1. SEC monitoring of the synthesis of graft copolymer: (a) PS-*co*-PCMS copolymer; (b) PI branch; (c, d) PS-*g*-PI graft copolymer before (c) and after (d) fractionation.

Table 1. Molecular Characteristics of Graft Copolymers and Homopolymer

	backbone PS-*co*-PCMS					branch		graft					
sample[a]	$10^{-3}M_{n,th}$[b]	$10^{-3}M_w$[c]	M_w/M_n[d]	% w/w CMS[e]	N_{Cl}[f]	$10^{-3}M_w$[c]	M_w/M_n[d]	$10^{-3}M_n$[g]	$10^{-3}M_w$[c]	M_w/M_n[d]	X[h]	% w/w PS[e]	f[i]	f[j]
(PS-*g*-PI 30−10/15)	23	30	1.11	5.3	10	19	1.04	150	200	1.07	9	17	86	84
(PS-*g*-PI 30−20/15)	24	32	1.21	9.2	19	16	1.04	283	328	1.08	19	11	97	95
(PS-*g*-PI 50−100/3)	42	44	1.26	32.8	94	2.7	1.07	290	330	1.12	106	24	112	99
(PS-*g*-PI 15−30/3)	11	14	1.19	33.3	30	3	1.07	80	100	1.09	29	24	94	83
(PS-*g*-PS 15−30/3)	11	14	1.19	33.3	30	3	1.10	92	110	1.13	32		105	

[a] For example, sample PS-*g*-PI 30−10/15 means a graft copolymer with PS 30K as backbone and 10 PI branches of 15K. [b] $M_{n,th} = \alpha m_{St+CMS}/100 \times \text{moles}_{initiator}$ (where α = 90−95% in all cases). [c] By LALLS in THF at 25 °C. [d] Polydispersity index by SEC in THF at 30 °C. [e] By ^{1}H NMR in $CDCl_3$ at 30 °C. [f] Number of chlorine atoms by ^{1}H NMR. [g] By membrane osmometry in toluene at 35 °C. [h] Number of branches given by the relationship: $X = (M_{wGraft} - M_{wBackbone})/M_{wBranch}$. [i] f is the grafting efficiency determined by the ratio: $f = X/N_{Cl}$ (%). [j] f is the grafting efficiency determined by NMR (%).

distilled into glass ampules equipped with break-seals and stored under vacuum at −20 °C until use. 1,1-Diphenylethylene (Aldrich) was purified by reacting with a small quantity of *n*-BuLi for several hours. During this period the bloody red color of DPELi anions was formed. It was then distilled and diluted with benzene in glass ampules under vacuum and stored at −20 °C until use. THF, benzene, and *sec*-BuLi were purified as described elsewhere.[16]

In a typical anionic polymerization, isoprene is polymerized in benzene (10% w/v) in a glass reactor by using a predetermined amount in moles of *sec*-BuLi as the initiator. After 24 h, a sample is taken for characterization of the branch. Then DPE is added, and an orange color appears. A 1.5−2 molar excess of DPE over PILi was used in order to make sure that all living chains are end-capped with DPE. The color turns dark red when a quantity of THF is added, to produce a mixture of THF:benzene of at least a 30:70 v/v ratio (in order to avoid freezing of the solvent when lowering the temperature at −20 °C and also to accelerate the end-capping by DPE). Finally the polymer from LFRP (PCMS, PS-*co*-PCMS, PCMS-*b*-PS, (PS-*g*-PS)-*b*-(PS-coPCMS)), which was dried overnight on a vacuum line and diluted in THF (10% w/v) in a glass ampule, is added to the PI−DPELi solution at −20 °C. An excess of PI−DPELi is needed to make sure that all chlorine atoms reacted and were replaced by PI chains. Samples were withdrawn during the course of the coupling reaction in order to determine the end of the reaction. Then degassed methanol is added to deactivate the residual living PI−DPELi chains. Fractionation with a mixture of toluene/hexane as solvents and methanol as a nonsolvent is necessary to isolate the desired product (star, graft, block−graft, block−brush, graft−block−graft) which is precipitated in stabilized, with 2,6-di-*tert*-butyl-*p*-cresol, methanol and dried under vacuum.

For the synthesis of the PS-*g*-PS comb, an anionically produced polystyrene end-capped by DPE (PSDPE-Li) reacted with PS-*co*-PCMS at −20 °C, following a procedure similar to the case of the synthesis of the PS-*g*-PI graft copolymer. Fractionation with toluene as solvent and methanol as a nonsolvent is necessary to isolate the PS-*g*-PS comb from the excess PS branch.

Molecular Characterization. Size Exclusion Chromatography (SEC). Number and weight-average molecular weights (M_n and M_w respectively) and polydispersities (M_w/M_n) of polymers were determined by SEC at 30 °C, using tetrahydrofuran as the eluent at a rate of 1 mL/min. SEC analysis was performed with a Waters system equipped with a Waters 501 HPLC pump, four Waters Styragel columns having a porosity range 10^3−10^6 Å, and a Waters 410 differential refractometer. Calibration curves were prepared with standard polystyrene samples covering the range from 1800 to 560 000.

Low-Angle Laser Light Scattering (LALLS). Absolute weight-average molecular weights of polymers were obtained by static light scattering measurements, using a Chromatix

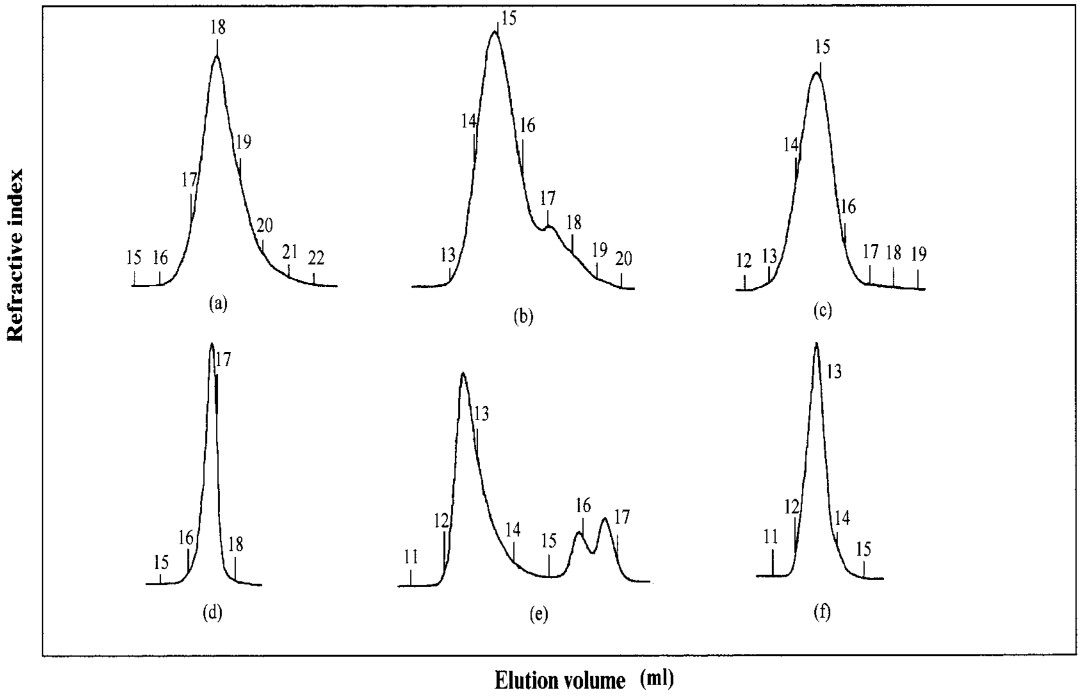


Figure 2. SEC monitoring of the synthesis of block−graft copolymer: (a) PCMS homopolymer; (b, c) PCMS-*b*-PS before (b) and after (c) fractionation; (d) PI branch; (e, f) (PS-*g*-PI)-*b*-PS block−graft copolymer before (e) and after (f) fractionation.

KMX-6 low angle (6−7°) laser light scattering (LALLS) photometer operating at wavelength $\lambda = 633$ nm. THF, freshly distilled from Na, was the solvent in all cases. dn/dc values required for M_w determination were measured with a KMX-16 differential refractometer at 25 °C, operating at the same wavelength and calibrated with aqueous NaCl standard solutions.

Viscosity Measurements. Intrinsic viscosities $[\eta]$ of the star polyisoprenes were determined in toluene at 35 °C in a Schott Ubbelohde viscometer 531 01 (capillary diameter i.d. = 0,53 mm). Flow times for the solvent ($t_0 = 200$ s) and five polymer concentrations, below the overlap concentration, $c^* \sim [\eta]^{-1}$,[17] were measured in a setup consisting of a Schott Gerate CT 1450 thermostated bath and a Schott Gerate AVS410 control and measuring unit. Huggins and Kraemer plots were used in order to determine $[\eta]$, k_H, and k_K.

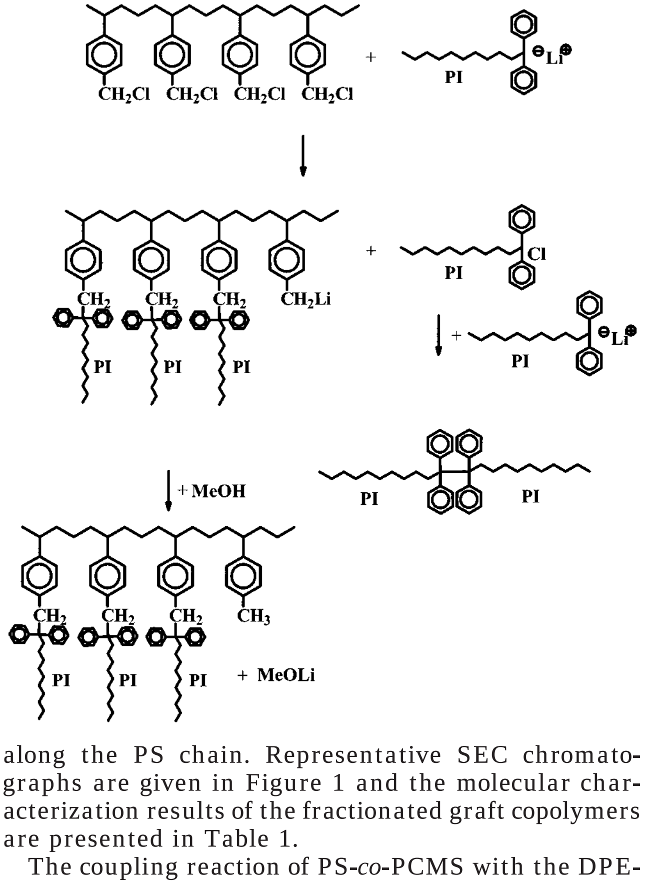
NMR Measurements. The composition of the copolymers and the grafting efficiency were obtained by ^{1}H NMR spectroscopy (Bruker-AC 200 instrument) in CDCl$_3$ at 30 °C. All chemical shifts refer to CDCl$_3$ (7.27 ppm). The characteristic intensities of styrene units at 6.4−7.2 ppm and isoprene units at 4.8−5.5 ppm were used for composition determination. The characteristic peak of CH$_2$Cl protons at 4.5 ppm was used to determine the composition of the PS-*co*-PCMS copolymers.

Results and Discussion

Graft Copolymers. Graft copolymers, with polystyrene (PS) backbone and polyisoprene (PI) branches, were synthesized by following the grafting onto methodology, according to the basic reactions shown in Scheme 1a.

The PS-*co*-PCMS copolymers, synthesized from styrene (St) and chloromethylstyrene (CMS) by LFRP to conversions about 90−95%, possess molecular weights very close to the expected ones. The PCMS content in the copolymer, determined by ^{1}H NMR, was found to be about the same as its content in the feed mixture. The reactivity ratios for CMS:St are as expected to be the same for LFRP and conventional free radical polymerization[18] (St/CMS: 0.72/1.08 at 60 °C).[19] This means that the chlorine atoms are randomly distributed along the PS chain. Representative SEC chromatographs are given in Figure 1 and the molecular characterization results of the fractionated graft copolymers are presented in Table 1.

Scheme 2



The coupling reaction of PS-*co*-PCMS with the DPE-capped polyisoprenyllithium at −20 °C gives a small percentage (4−5%) of dimer as is evident in Figure 1c. It seems that due to the presence of many chlorine atoms, a small percentage of chlorine−lithium exchange reactions[20] occur (Scheme 2) despite the fact that the coupling reaction was accomplished in low temperature (−20 °C).[20−21]

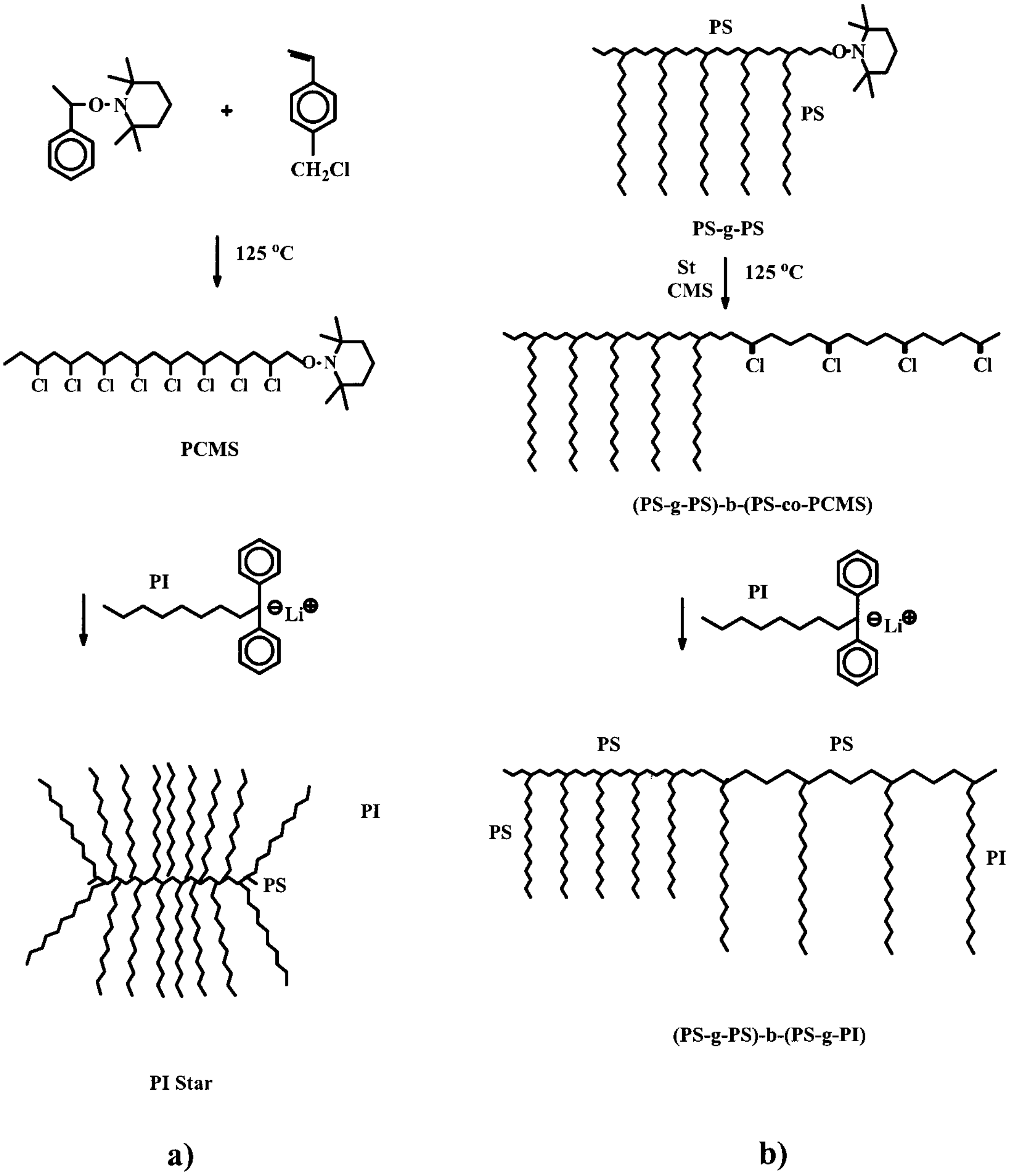
Table 2. Molecular Characteristics of Block−Brush and Block−Graft Copolymers

	PCMS-*b*-PS backbone				branch		block−brush					
sample 1[a]	$10^{-3}M_w$[b]	M_w/M_n[c]	% w/w CMS[d]	N_{Cl}[e]	$10^{-3}M_w$[b]	M_w/M_n[c]	$10^{-3}M_w$[b]	M_w/M_n[c]	X[f]	% w/w PS[d]	f[g]	f[h]
	118	1.24	14	108	13	1.06	1430	1.09	101	6.5	93	95

	PS-*g*-PI				block−graft		
sample 2[i]	$10^{-3}M_w$[b]	M_w/M_n[c]	X[f]	% w/w PS[d]	$10^{-3}M_w$[b]	M_w/M_n[c]	% w/w PS[d]
	200	1.07	9	17.4	1000	1.26[j]	57.4

[a] Prepared by procedure b (see text). [b] By LALLS in THF at 25 °C. [c] Polydispersity index by SEC in THF at 30 °C. [d] By ^{1}H NMR in $CDCl_3$ at 30 °C. [e] Number of chlorine atoms by ^{1}H NMR. [f] Number of branches given by the relationship: $X = (M_{wGraft} - M_{wBackbone})/M_{wBranch}$. [g] f is the grafting efficiency determined by the ratio: $f = X/N_{Cl}$ (%). [h] f is the grafting efficiency determined by NMR (%). [i] Prepared by procedure a (see text). [j] Bimodal peak.

Scheme 3. (a) Synthesis of PI Star; (b) Synthesis of (PS-*g*-PS)-*b*-(PS-*g*-PI) Graft−Block−Graft Copolymer



To make sure that all chlorine atoms were completely replaced by PI side chains an excess of about 50% of living branch was used. The excess was always confirmed by the deep red color of the solution. The reaction was monitored by SEC and also by the change in the color of the solution which turned from deep red to an orange-red color at the end of the reaction. Finally it has to be noticed that despite the DPE-capping and the low temperature the reaction is relatively fast. A couple of hours are enough for the final product to be produced.

The advantage of the grafting onto procedure is that the backbone, the branch and the final graft can be characterized independently. Thus, the number of branches in the graft copolymer can be easily deter-

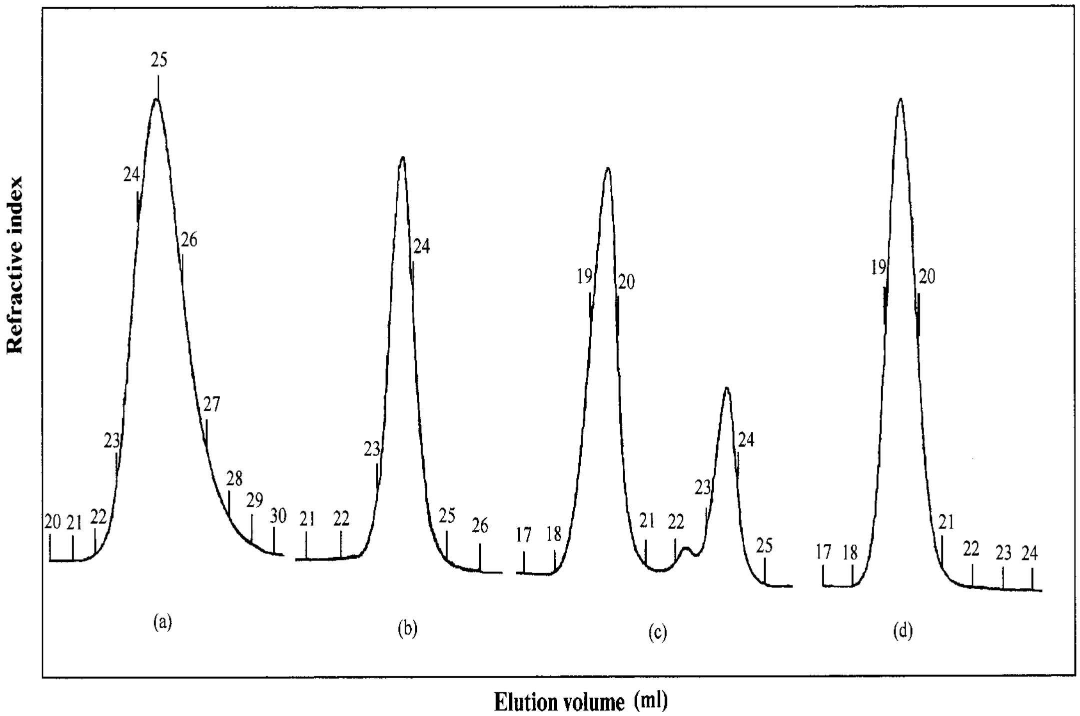


Figure 3. SEC monitoring of the synthesis of PI star: (a) PCMS homopolymer; (b) PI branch; (c, d) PI star before (c) and after (d) fractionation.

Table 3. Molecular Characteristics of PI Stars

	backbone			branch		star					
sample	$10^{-3}M_{\mathrm{w}}$[b]	$M_{\mathrm{w}}/M_{\mathrm{n}}$[c]	N_{Cl}[d]	$10^{-3}M_{\mathrm{w}}$[b]	$M_{\mathrm{w}}/M_{\mathrm{n}}$[c]	$10^{-3}M_{\mathrm{w}}$[b]	$M_{\mathrm{w}}/M_{\mathrm{n}}$[c]	X[e]	% w/w PS[f]	f[g]	f[h]
(70/5)[a]	11	1.45	72	5	1.03	360	1.12	70	0.7	97	99
(70/10)	11	1.45	72	9.3	1.03	640	1.12	68	1	94	95
(140/5)	21	1.44	137	5	1.03	750	1.17	146	0.7	106	109
(140/10)	21	1.44	137	9.3	1.03	825	1.08	86	1	63	64
(200/5)	32	1.65	209	5	1.03	1150	1.21	224	0.6	107	109
(200/10)	32	1.65	209	9.3	1.03	1760	1.17	186	1.3	89	89

[a] For example sample (70/5) is a PI star with 70 PI branches of 5K. [b] By LALLS in THF at 25 °C. [c] Polydispersity index by SEC in THF at 30 °C. [d] Number of chlorine atoms by ^{1}H NMR. [e] Number of branches given by the relationship: $X = (M_{\mathrm{wStar}} - M_{\mathrm{wBackbone}})/M_{\mathrm{wBranch}}$. [f] Determined by ^{1}H NMR in $CDCl_3$ at 30 °C. [g] f is the grafting efficiency determined by the ratio: $f = X/N_{\mathrm{Cl}}$ (%). [h] f is the grafting efficiency determined by NMR (%).

mined. In all cases, the grafting efficiency was near 100% (Table 1) as confirmed by ^{1}H NMR and by molecular weight characterization. The polydispersity of all graft copolymers determined by SEC are between 1.07 and 1.13 and very close to the ones obtained from LALLS and membrane osmometry. The produced materials are comparable, in respect to their molecular characteristics, to the ones obtained by grafting of anionically produced branches to chloromethylated polystyrenes.[22] However a three-stage procedure is necessary in the latter case compared to our two stage procedure.

Block–Graft Copolymers. Block–graft copolymers were synthesized, by following two different procedures, as shown in Scheme 1.

The Graft-First Procedure. A random copolymer of St and CMS is produced by LFRP and is used as the backbone. After the DPE-capped PI branches were grafted onto this copolymer, the second PS block of the backbone was obtained by LFRP, using the terminal alkoxyamine (Scheme 1a).

The Diblock Backbone First Procedure. Using TEMPO LFRP, a linear diblock copolymer (PCMS-*b*-PS) is synthesized and used as the backbone. Then living DPE-capped PI branches are linked to the chloromethyl groups of the diblock. In this case every monomeric unit of the one PS block possess one branch. Therefore, this material is a block–brush copolymer (Scheme 1b).

Representative SEC chromatographs are given in Figure 2, and the molecular characteristics of the fractionated samples are shown in Table 2.

In procedure a, the formation of the second block of the backbone is confirmed by the increase in the molecular weight and in the styrene content in the copolymer (Table 2).

In procedure b, the PCMS homopolymer shows higher molecular weight distributions ($I = 1.30-1.50$) than a PS synthesized by living free radical polymerization, following the same procedure. A typical CMS polymerization proceeded faster than a styrene one. An explanation could be that, due to the electron-withdrawing chlorine atom, the energy of the bond between carbon and oxygen (from TEMPO) decreases. That means that the alkoxyamine C–O bond dissociates faster in the case of *p*-chloromethylstyrene and the polymerization goes faster.

The coupling reaction of the fractionated PCMS-*b*-PS ($I = 1.24$) with an excess of PI–DPELi was also performed at −20 °C. The rate of the coupling reaction was smaller in this case in comparison with simple graft

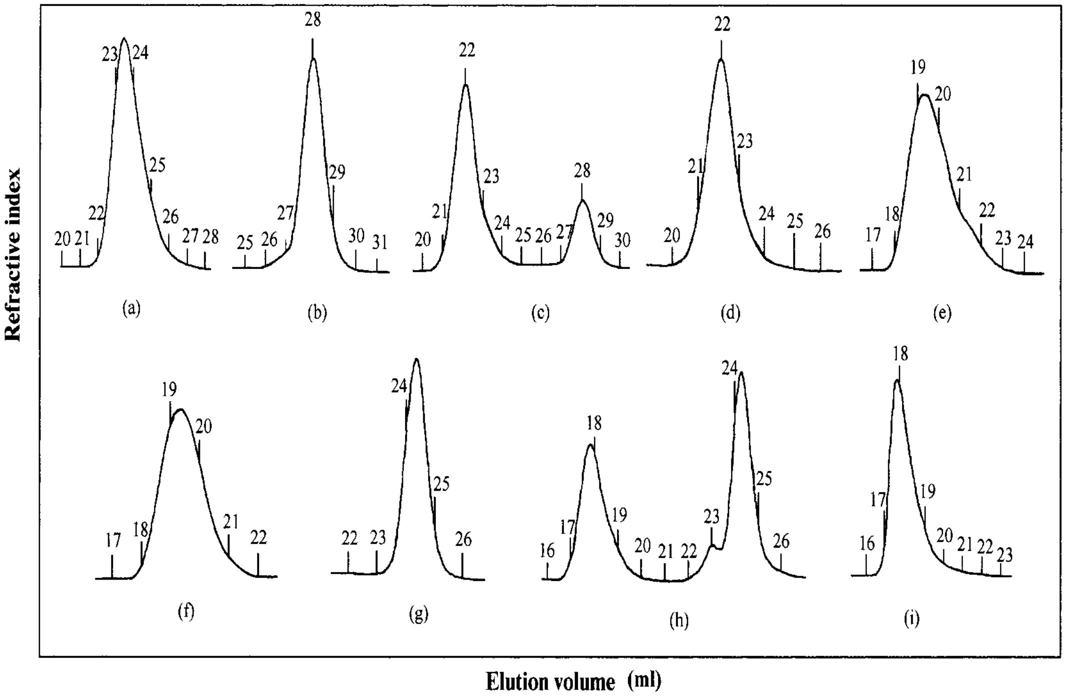


Figure 4. SEC monitoring of the synthesis of graft−block−graft copolymer: (a) PS-*co*-PCMS copolymer; (b) PS branch; (c, d) PS-*g*-PS comb before (c) and after (d) fractionation; (e, f) (PS-*g*-PS)-*b*-(PS-*co*-PCMS) block−graft before (e) and after (f) fractionation; (g) PI branch; (h, i) (PS-*g*-PS)-*b*-(PS-*g*-PI) graft−block−graft before (h) and after (i) fractionation.

copolymers. That is because many chlorine atoms are placed in neighboring monomers in the PCMS block and steric hindrance is much larger in this case.

The difference in structure between these two block−grafts is that the first one has a PI polymer chain for nearly every monomer coming from the PCMS block (block-brush), while the second one has a few PI polymer chains randomly distributed along the backbone (block−graft).

Stars. A series of star polymers were synthesized according to the reactions shown in Scheme 3a. Representative SEC chromatographs are given in Figure 3, and molecular characteristics of fractionated stars are given in Table 3.

All the coupling reactions of the PI−DPELi with the PCMS homopolymer were performed at −20 °C. The rate of the coupling reaction was much smaller than that of the grafts. Instead of some hours, days and even weeks in some cases were necessary for completion of the coupling reaction. The rate was also smaller as the number of chlorine atoms was higher. For samples (200/5) and (200/10) we had to increase the reaction temperature to room temperature after 1 week at −20 °C, to accelerate the reaction. For sample (200/5) with the smaller PI branch, it took some days at room temperature until no significant change could be observed. Sample (200/10) with the larger PI branch took 2 weeks more at room temperature to be completed. As a conclusion, the rate is faster for small PCMS homopolymers with small PI branches and slower for longer PCMS homopolymers and for longer branches. The percentage of formed dimer was smaller than 5% in all cases.

The grafting efficiency was lower for large numbers of chlorine atoms and for longer branches and ranged between 90 and 100%. In most cases, all chlorine atoms were replaced by PI−DPELi chains, despite the increased steric hindrance from the DPE and from the fact that the chlorine atoms were placed on each monomer.

Table 4. Viscometric Results for PI Stars in Toluene at 35 °C

sample	$[\eta]_{star}$ (mL/g)	k_H	$[\eta]_{lin}$ (mL/g)	g'^{a}	$g'_Z{}^{b}$	$g'_R{}^{c}$	R_v (nm)
(70/5)	18.6	1.18	222.4	0.084	0.224	0.077	10.2
(70/10)	31.6	0.48	340.5	0.093	0.227	0.079	14.7
(140/5)	19.1	1.31	382.9	0.050	0.155	0.043	13.1
(140/10)	26.4	1.34	410.9	0.064	0.201	0.065	15.1
(200/5)	22.7	0.93	525.3	0.043	0.126	0.030	16.0
(200/10)	29.0	1.10	719.8	0.040	0.138	0.035	20.0

[a] $g' = [\eta]_{star}/[\eta]_{lin}$. [b] $g'_Z = (2/f_w)^{3/2}(0.390(f_w - 1) + 0.196)/0.586$. [c] $\log g'_R = 0.36 - 0.80 \log f_w$.

The PS content of the final star polymers is very small (∼ 1%). It can be assumed that these copolymers are actually polyisoprene stars with a small linear PS core. The synthesis of star-branched polymers is evidenced by the extremely low values of $g' = [\eta]_{star} / [\eta]_{lin}$, where $[\eta]_{star}$ and $[\eta]_{lin}$ are the intrinsic viscosity of the star and linear PI respectively with the same molecular weight under the same conditions. $[\eta]_{star}$ was determined in a good solvent (in toluene at 35 °C) and $[\eta]_{lin}$ values were calculated by the Mark−Houwink relationship, (1).[23]

$$[\eta]_{lin} = 0.0172 M_w^{0.74} \quad (1)$$

The experimental g' values were compared (Table 4) with the Zimm and Kilb[24] theoretical values of g'_{ZK} calculated from eq 2, as well as with the g'_R given by

$$g'_{ZK} = (2/f_w)^{3/2}(0.390(f_w - 1) + 0.196)/0.586 \quad (2)$$

Roovers for good solvents based on experimental results of star polymers with low polydispersity index (≤1.10), calculated from eq 3.[25] Measured g' values were much

$$\log g'_R = 0.36 - 0.80 \log f_w \quad (3)$$

Table 5. Molecular Characteristics of (PS-*g*-PS)-*b*-(PS-*g*-PI) Copolymer

(PS-*g*-PS)-*b*-(PS-*co*-PCMS) backbone					PI branch		(PS-*g*-PS)-*b*-(PS-*g*-PI)					
$10^{-3}M_n$[a]	$10^{-3}M_w$[b]	M_w/M_n[c]	% w/w CMS[d]	N_{Cl}[e]	M_w[b]	M_w/M_n[c]	M_w[b]	M_w/M_n[c]	X[f]	% w/w PS[d]	f[g]	f[h]
205	255	1.32	10.3	172	7	1.03	1450	1.32	171	13	99	105

[a] By membrane osmometry in toluene at 35 °C. [b] By LALLS in THF at 25 °C. [c] By SEC in THF at 30 °C. [d] Determined by ^{1}H NMR in $CDCl_3$ at 30 °C. [e] Number of chlorine atoms by ^{1}H NMR. [f] Number of branches given by the relationship: $X = (M_{wg-b-g} - M_{wBackbone})/M_{wBranch}$. [g] f is the grafting efficiency determined by the ratio: $f = X_w/X_{wCl}$ (%). [h] f is the grafting efficiency determined by NMR (%).

lower than that predicted by the theory of Zimm and Kilb, as g' for good solvents is lower than that of Θ conditions and the relationship of Zimm and Kilb is valid only for Θ conditions. g'_R values given by the relationship of Roovers for good solvents agreed quite well with our experimental results. That lead to the conclusion that the linear PS core is almost negligible comparing to the big number of PI branches, making these star copolymers behave like PI star homopolymers. Viscometric radii were also calculated by relationship 4, and they were increasing as the number of

$$R_v = (3/10\pi N_A)^{1/3}(M_w[\eta])^{1/3} \qquad (4)$$

chlorine atoms and the size of the branch were increasing (Table 4).

Graft−Block−Graft Copolymer. One graft−block−graft copolymer was prepared according to the reactions shown in Scheme 3b. SEC chromatographs from different stages of the synthesis are given in Figure 4, and molecular characteristics are given in Table 5.

A PS-*g*-PS comb homopolymer was used as the starting material and not a PS-*g*-PI, to make sure that the new part of the backbone is created at the end of the first one and not from a radical produced at a double bond of the PI branch after heating. When polystyrylithium was used end capped with DPE at low temperature, no noticeable amount of dimer was formed. This is probably due to the increased steric hindrance of the polystyrene branch in comparison with the polyisoprene one, a factor that decreases the rate of the coupling and the chlorine−lithium exchange reactions. The terminal alkoxyamine is very stable at low temperatures, even during the coupling reaction, as was also reported by Quirk.[14,26] The reason for the incomplete reinitiation of the PS-*g*-PS-TEMPO to (PS-*g*-PS)-*b*-(PS-*co*-PCMS), as is observed from Figure 4e, could be that during the LFRP not all of the produced PS-*co*-PCMS (and PS-*g*-PS) chains are end-capped by TEMPO (usually <90%).[27]

Conclusions

A combination of anionic and TEMPO living free radical polymerization proved a powerful method for the successful synthesis of well-defined complex structures like stars, grafts, and block−grafts and for new structures like block−brush and graft−block−graft copolymers. Synthesis was based on the incorporation of chloromethyl groups in the backbone by living free radical polymerization of *p*-chloromethylstyrene or its copolymerization with styrene followed by a coupling reaction with a living polymer, created by anionic polymerization. Isoprene was used in our case but other monomers like styrene, butadiene and methacrylates could be used as branches too. Dimer formation was limited (<5%), by performing the coupling reaction at low temperature and by end-capping living PI branches with DPE. Grafting efficiency was quantitative in all cases, except from the case of a large PCMS homopolymer as a backbone, reacting with a high molecular weight branch.

References and Notes

(1) Pitsikalis, M.; Pispas, S.; Mays, W. J.; Hadjichristidis, N. *Adv. Polym. Sci.* **1998**, *135*, 1.
(2) Georges, M.; Veregin, R.; Kazmaier, P.; Hamer, G. *Macromolecules* **1993**, *26*, 2987.
(3) Georges, M. K.; Veregin, R. P.; Kazmaier, P. M.; Hamer, G. K. *Trends Polym. Sci.* **1994**, *2*, 66.
(4) Puts, R. D.; Sogah, D. Y. *Macromolecules* **1996**, *29*, 3323.
(5) Sogah, D. Y.; Puts, R. D.; Trimble, A.; Sherman, O. *Polym. Prepr.* **1997**, *38* (1), 731.
(6) Benoit, D.; Grimaldi, S.; Finet, J. P.; Tordo, P.; Fontanille, M.; Gnanou, Y. *Polym. Prepr.* **1997**, *38* (1), 729.
(7) Bertin, D.; Boutevin, B. *Polym. Bull.* **1996**, *37*, 337.
(8) Kazmaier, P.; Daimon, K.; Georges, M.; Hamer, G.; Veregin, R. *Macromolecules* **1997**, *30*, 2228.
(9) Wendler, U.; Bohrisch, J.; Jaeger, W.; Rother, G.; Dautzenberg, H. *Macromol. Rapid. Commun.* **1998**, *19*, 185.
(10) Listigovers, N. A.; Georges, M. K.; Odell, P. G.; Keoshkerian, B. *Macromolecules* **1996**, *29*, 8992.
(11) Georges, M. K.; Hamer, G.; Listigovers, N. A. *Macromolecules* **1998**, *31*, 9087.
(12) Hawker, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 13, 1456.
(13) Hawker, C.; Fréchet, M. J.; Grubbs, B. R.; Dao, J. *J. Am. Chem. Soc.* **1995**, *117*, 10763.
(14) Kobatake, S.; Harwood, J.; Quirk, R. P. *Macromolecules* **1998**, *31*, 3735.
(15) Malmstrom, E.; Miller, R.; Hawker, G. *Tetrahedron* **1997**, *53*, 45, 15225.
(16) Morton, M.; Fetters, L. *Rubber Chem. Technol.* **1975**, *48*, 359.
(17) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: Evanston, IL, 1971.
(18) MacLeod, J. P.; Hamer, K. G.; Lukose, P.; Georges, K. M. Chapter 3 from *Functional Polymers-Modern Synthetic Methods and Novel Structures* edited by Patil, O. A.; Schulz, N. D.; Novak, M. B.
(19) Brandrup, J. In *Polymer handbook;* Immergut, E. H., Ed.; American Cyanamid Company, 1967, private communication.
(20) Gauthier, M.; Möller, M. *Macromolecules* **1991**, *24*, 4548.
(21) Kee, R. A.; Gauthier, M. *Macromolecules* **1999**, *32*, 6478.
(22) Pitsikalis, M.; Sioula, S.; Pispas, S.; Hadjichristidis, N.; Cook, C, D.; Li, J.; Mays, W. J. *J. Polym. Sci., Part A: Polymer Chem.* **1999**, *37*, 4337.
(23) Hadjichristidis, N.; Roovers, J. *J. Polym. Sci., Part B: Polym. Phys.* **1974**, *12*, 2521.
(24) Zimm, H.; Kilb, W. *J. Polym. Sci.* **1959**, *37*, 19.
(25) Roovers, J. in M. K. Mishra and, S. Kobagashi, Eds.; *Star and Hyperbranched Polymers*; Marcel Dekker Inc.: New York, 1998.
(26) Kobatake, S.; Harwood, J.; Quirk, R. P.; Priddy, D. B. *Macromolecules* **1999**, *32*, 10.
(27) Malmstrom, E.; Hawker, C. *Macromol. Chem. Phys.* **1998**, *199*, 923.

MA0011946