Synthesis of Model Multigraft Copolymers of Butadiene with Randomly Placed Single and Double Polystyrene Branches

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ABSTRACT: Model multigraft copolymers of butadiene (Bd) and styrene (St) with randomly placed trifunctional, poly(Bd-*g*-St), and tetrafunctional branch points, poly(Bd-*g*-St_2), were synthesized by hydrosilylation of polybutadiene (~92 wt % 1,4) with $HSiMe_2Cl$ and $HSiMeCl_2$, respectively, followed by reaction of the resultant silicon−chloride groups along the backbone with polystyryllithium (PSLi). The extent of hydrosilylation was controlled by appropriate adjustment of the [silane]/[C=C] ratio. Characterization carried out by size exclusion chromatography (UV and RI detector), low-angle laser light scattering, differential refractrometry, and NMR spectroscopy indicated that the synthesized branched molecules have a high degree of molecular and compositional homogeneity.

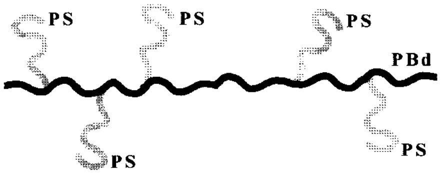
Introduction

By using controlled chlorosilane chemistry and anionic polymerization techniques, we synthesized model graft copolymers having one[1,2] or two branches[3] in well-defined positions along the backbone. Graft copolymers with more than two branches have been prepared,[4] although the branches were randomly placed along the chain. Roovers[5] reported a method for preparing multigraft copolymers with polystyrene backbone, by controlled chloromethylation of the phenyl rings, followed by transformation of the C−Cl to C−$OSiMe_2Cl$ (in order to avoid metal−halogen exchange) and reaction with living polyisoprene. By this method the number of branches can be controlled but not their position along the backbone.

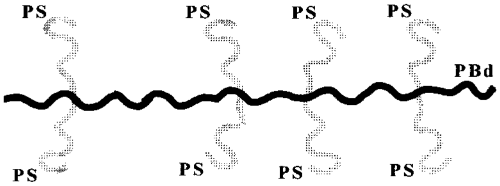
In the case of multigrafts with polydiene backbone, where the beneficial aromatic rings are absent, the preparation relies either on the hydrosilylation of the vinyl side groups,[6−8] followed by reaction of the resultant SiCl groups along the backbone with the living branch or alternatively, on the metalation[9,10] of the polydiene backbone followed by in situ polymerization of the branches.

Cameron[11] succeeded in incorporating PS or poly(α-methylstyrene) branches on a polybutadiene chain (45 wt % vinyl content) after complete hydrosilylation of the vinyl groups, reaction with the living branches, and neutralization of the remaining Si−Cl groups with *n*-BuLi. Judging from the size exclusion chromatography (SEC) traces, control of the number of branch points was not achieved. Möller[12] by hydrosilylating completely the PBd backbone and the grafts emanating from every previous generation of grafts succeeded in preparing “graft on graft” polybutadiene. Roovers and Hadjichristidis[13] reported a method of preparing poly(isoprene-*g*-styrene) by lithiation of the polyisoprene backbone with *s*-BuLi−TMEDA mixture and in situ polymerization of styrene with the multifunctional initiator produced. The multifunctional initiator is contaminated by monofunctional species, thus hindering the controlled incorporation of the branches.

Chart 1



Poly(Bd-g-St)
Graft Copolymers with single branches
(Trifunctional branch points)



Poly(Bd-g-St_2)
Graft Copolymers with double branches
(Tetrafunctional branch points)

In this paper we report a method of controlling the extent of hydrosilylation with $HSiMe_2Cl$ and $HSiMeCl_2$ of PBd (~92 wt % 1,4) and thus the number of branch points, in the presence of platinum divinyltetramethyldisiloxane complex[14,15] (Pertrach PC 072) by varying the [silane]/[C=C] ratio. By using the resultant chlorosilylated PBd, we have synthesized multigraft copolymers with double PS branches (tetrafunctional branch point) for the first time, and with single PS branches (trifunctional branch point, Chart 1).

We symbolize the samples as RMG-*x*-*y*-*z*, where *x* is the functionality of the branch point, *y* is the number of branches per backbone chain, and *z* is the volume fraction of the multigraft; e.g., RMG-3-5-18 corresponds to the random multigraft copolymer with trifunctional branch points, five branches along the backbone, and 18% volume fraction of PS.

Experimental Section

Synthesis of Multigraft Copolymer with Randomly Placed Trifunctional Branch Points (Single Branches). The PBd backbone was prepared in benzene with *s*-BuLi as initiator using high-vacuum techniques in evacuated, *n*-BuLi-washed, and benzene-rinsed reactors. Details of the reagent

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Table 1. Molecular Characteristics of Trifunctional Multigraft Copolymers and Their Precursors

sample	$10^{-4}M_n{}^a$ PBd	$10^{-4}M_w{}^b$ PBd	$10^{-4}M_n{}^c$ PS	$10^{-4}M_w{}^b$ PS	$10^{-5}M_n{}^a$ RMG	$10^{-5}M_w{}^b$ RMG	$M_w/M_n{}^d$ RMG	no. of branch points[e]
1	9.7	10.1	0.51	0.54	2.60	2.75	1.06	32
2	9.7	10.1	0.44	0.46	1.98	2.12	1.07	23
3	9.7	10.1	0.41	0.44	1.22	1.27	1.04	6
4	8.7	9.2	0.45	0.47	1.00	1.06	1.06	3

[a] Membrane osmometry in toluene at 35 °C. [b] Low-angle laser light scattering in THF at 25 °C. [c] Vapor pressure osmometry in toluene at 35 °C. [d] Calculated from M_w and M_n values of multigraft copolymers. [e] Calculated from M_w and M_n values of PBd backbone, PS branch, and multigraft copolymers.

Table 2. Molecular Characteristics of Tetrafunctional Multigraft Copolymers and Their Precursors

sample	$10^{-4}M_n{}^a$ PBd	$10^{-4}M_w{}^b$ PBd	$10^{-4}M_n{}^c$ PS	$10^{-4}M_w{}^b$ PS	$10^{-5}M_n{}^a$ RMG	$10^{-5}M_w{}^b$ RMG	$M_w/M_n{}^d$ RMG	no. of branch points[e]
5	10.1	10.3	0.52	0.54		3.24		41
6	10.1	10.3	0.46	0.49	1.38	1.45	1.05	8

[a] Membrane osmometry in toluene at 35 °C. [b] Low-angle laser light scattering in THF at 25 °C. [c] Vapor pressure osmometry in toluene at 35 °C. [d] Calculated from M_w and M_n values of multigraft copolymers. [e] Calculated from M_w and M_n values of multigraft copolymers and their precursors.

purification to the standards required for anionic polymerization, are described elsewhere.[16]

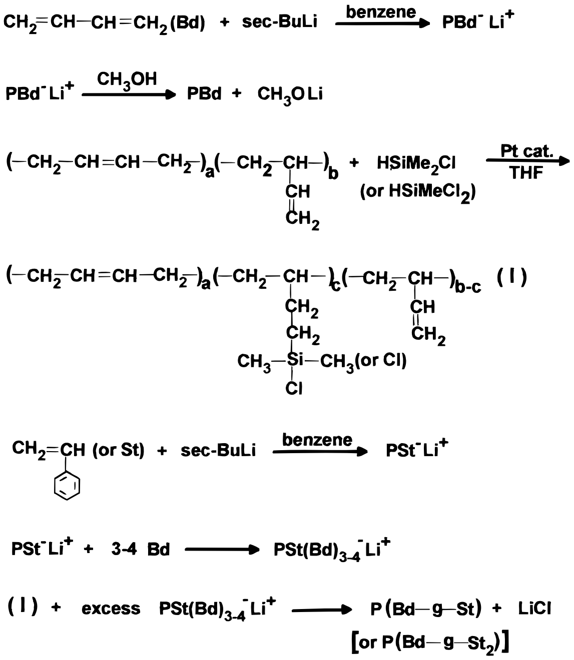
The backbone was dissolved in tetrahydrofuran (THF) in a round-bottom flask equipped with a condenser, communicating with the atmosphere through a $CaCl_2$ filled tube, to which 3−4 drops of platinum divinyltetramethyldisiloxane complex in xylene (Karstedt's catalyst) was added. The solution was dried overnight with 1.5−2 mL of trimethylchlorosilane to destroy any impurity that could react with the chlorosilane compound. After chlorodimethylsilane was added, the temperature of the mixture was slowly raised to 70 °C. There was an induction period[17,18] varying between 1 and 6 h, followed by a rapid reaction being obvious by the change of the color of the solution. The reaction was allowed to proceed for at least 24 h, in all the experiments. We performed a few exploratory experiments where the same PBd was allowed to react with $HSiMe_2Cl$ and $HSiMeCl_2$ for 1, 2, and 3 days. The resulting hydrosilylayed polybutadienes were reacted with the same living PS and the M_w of the graft copolymers determined by low-angle laser light scattering was found to be the same as the one given in Tables 1 and 2 determined after 24 h. On the basis of these kinetic results, we allowed all hydrosilylation reactions to proceed for 24 h. THF and chlorosilanes were removed in the high-vacuum line by pumping for 3−5 days. The randomly functionalized polybutadiene was dissolved in benzene, sealed under vacuum, and subdivided into ampules for the preparation of a series of multigraft copolymers of varying branch lengths with a constant number of branches per backbone.

A 25% excess of living polystyryllithium was intentionally added during each grafting reaction, to force it into completion. After 3 weeks, the excess living arm was terminated with methanol. The polymers were protected against oxidation by 2,6-di-*tert*-butyl-*p*-cresol. Fractionation was carried out by adding methanol to a solution of the product in toluene. The fractionation was repeated until no arm or other undesirable byproducts were shown to be present by SEC. The polymers were finally precipitated in methanol containing antioxidant, dried, and stored under vacuum in the dark.

Synthesis of Multigraft Copolymers with Randomly Placed Tetrafunctional Branch Points (Double Branches). In this case, the hydrosilylation was carried out with dichloromethylsilane instead of chlorodimethylsilane. To relieve steric hindrances and facilitate the addition of two polystyryllithium arms per branch point, their living ends were capped with three to four units of butadiene before the coupling reaction with the multifunctional backbone.

Characterization. Size exclusion chromatography experiments were carried out at 30 °C in THF using a Waters Model 510 differential pump, Waters Model 470 differential refractometer, and Waters Model 486 absorbance detector in series with a three Phenomenex columns set having a continuous porosity range from 50 to 10^6 Å.

Scheme 1



The weight-average molecular weight of the backbone, of the branches, and of the final multigraft copolymers was determined by a Chromatix KMX-6 low-angle laser photometer (LALLS) equipped with a He−Ne laser operating at 633 nm at 35 °C in THF. The refractive index increment d*n*/d*c*, was measured in THF at 25 °C by a Chromatix KMX-16 differential refractometer operating at 633 nm and calibrated with aqueous NaCl solutions.

The PBd backbones analyzed by ^1H NMR and ^{13}C NMR (Bruker AC 200) spectroscopy in $CDCl_3$ at 30 °C were found to have the following microstructure: 8 wt % 1,2, 50 wt % *cis*-1,4, and 42 wt % *trans*-1,4.

Results and Discussion

The basic reactions for the synthesis of graft copolymers with single, P(Bd-*g*-St), and double branches, P(Bd-*g*-St_2), are given in Scheme 1.

The usual sharp acceleration observed during hydrosilylation of small molecules was absent in our case due to the low vinyl content (~8 wt %) and the high molecular weight of the PBd backbone. Many parameters, such as solvent, type of the silane, and concentration of hydrosilylation mixture, may exert a strong

Table 3. Extent of Hydrosilylation of PBd with $HSiMe_2Cl$ and $HSiMeCl_2$

[silane]/[C=C]	extent of hydrosilylation[a] with $HSiMe_2Cl$ (%)	extent of hydrosilylation[a] with $HSiMeCl_2$ (%)
0.60:1.0	20.5 (1)	27.0 (5)
0.48:1.0	15.0 (2)	
0.18:1.0	5.4 (A)	6.8 (C)
0.15:1.0	3.6 (3)	5.4 (6)
0.13:1.0	2.4 (4)	
0.11:1.0	1.5 (B)	3.0 (D)
0.06:1.0		1.2 (E)

[a] Calculated by the relation: M_w(graft) − M_w(backbone)/M_w(branch) (M_w determined by LALLS). In parentheses we present the number of the sample of Tables 1 and 2 that the results refer to. We also include the results of the following multigraft copolymers: A = RMG-3-15, B = RMG-3-5, C = RMG-4-18, D = RMG-4-10, and E = RMG-4-4. The molecular characteristics of these copolymers are presented in Tables 6 and 7.

influence on the kinetics of the hydrosilylation.[19,20] At low [silane]/[C=C] ratio and Pt concentration a very long induction period was noticed, in agreement with Sauvet's observations.[21]

During the induction period the platinum divinyltetramethyldisiloxane complex bonds with the oxygen, thus forming colloidal platinum complexes, which are the actual hydrosilylation promoters. This explains why hydrosilylation needs traces of oxygen to get started.[20] Furthermore, oxygen prevents the irreversible colloid agglomeration (colloids of larger particle size have reduced activity) and makes the Pt/SiH complex more electrophilic. The hydrosilylation reaction was carried out in boiling THF instead of benzene, because of the increased solubility of oxygen in THF. Furthermore, fewer side products are formed in boiling THF due to its low boiling point.

A few exploratory hydrosilylation experiments were carried out by varying the [silane]/[C=C] ratio in order to optimize the conditions for controlling the extent of hydrosilylation. After coupling the hydrosilylated PBd, we determined the molecular weight of the graft copolymer, and the results are presented in Tables 1 and 2. By calculating the number of branch points per backbone, we obtained the extent of hydrosilylation. These data are given in Table 3. From these results it is obvious that (a) when the [silane]/[C=C] ratio decreases, the extent of hydrosilylation also decreases and (b) by use of $HSiMeCl_2$ instead of $HSiMe_2Cl$ the intermediate Pt/SiH complex becomes more reactive and the extent of hydrosilylation is increased.

The hydrosilylation of PBd with $HSiCl_3$ is expected to be easier because of the presence of three chlorines. The resulting hydrosilylated PBd is a potential macrocoupling agent for the synthesis of graft copolymers with triple branches, pentafunctional branch points.

The SEC chromatograms of the hydrosilylated PBd, recorded immediately after neutralization with methanol, was almost indistinguishable from the parent PBd. It was noticed that the chromatogram was changing with time due to the outgoing cross-linking reaction of the $SiOCH_3$ groups (Figure 1).

Although we observed a decrease of the 1,2 peak and the appearance of the $Si-CH_3$ peak after the hydrosilylation, NMR spectra of the neutralized hydrosilylated PBd were unreliable for any quantitative analysis of the hydrosilylated sites due to the high molecular weight of the backbone and the relatively small number of sites. Lower molecular weight of backbone and higher number of graft sites are necessary to determine the number of branch points before grafting. The only effective method then to calculate the number of hydrosilylated sites is to determine the molecular weight of the PBd backbone, PS branch, and graft copolymer.

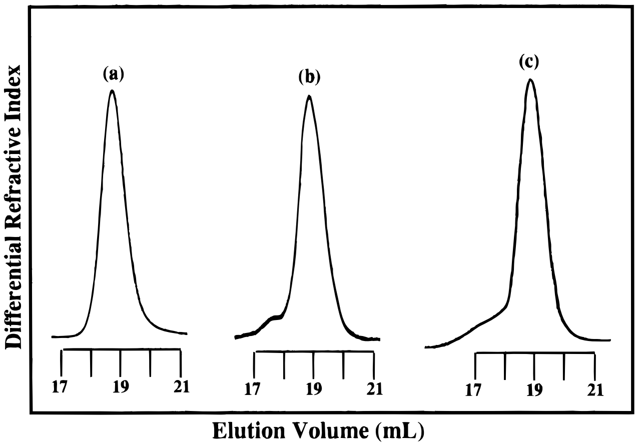


Figure 1. SEC chromatograms of hydrosilylated PBd backbone recorded: (a) immediately, (b) 1 day, and (c) 2 days after neutralization with methanol.

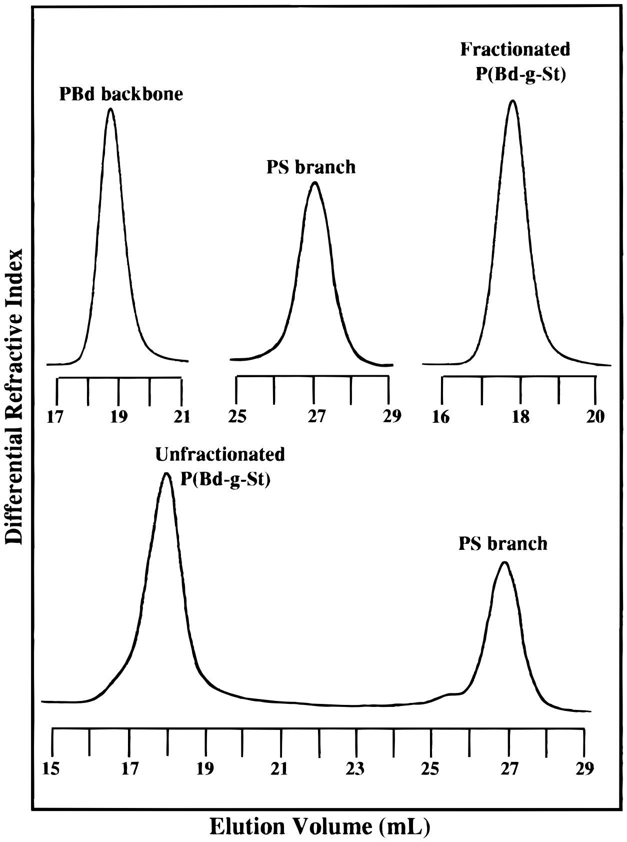


Figure 2. SEC chromatograms of the precursors and the final graft copolymer RMG-3-5-18.

The synthesis of all samples was monitored by SEC. Typical examples are given in Figures 2 and 3. After coupling with living PS in the SEC chromatogram of the final product, small peaks on the left side of the linear branch precursors appeared. These peaks correspond to side products from the reaction of the living branch with disilicon compounds $ClMe_2Si-SiMe_2Cl$ and $Cl_2MeSi-SiMeCl_2$, as was confirmed by the molecular weight values corresponding to these peaks by using SEC calibrated with PS standards. The disilicon com-

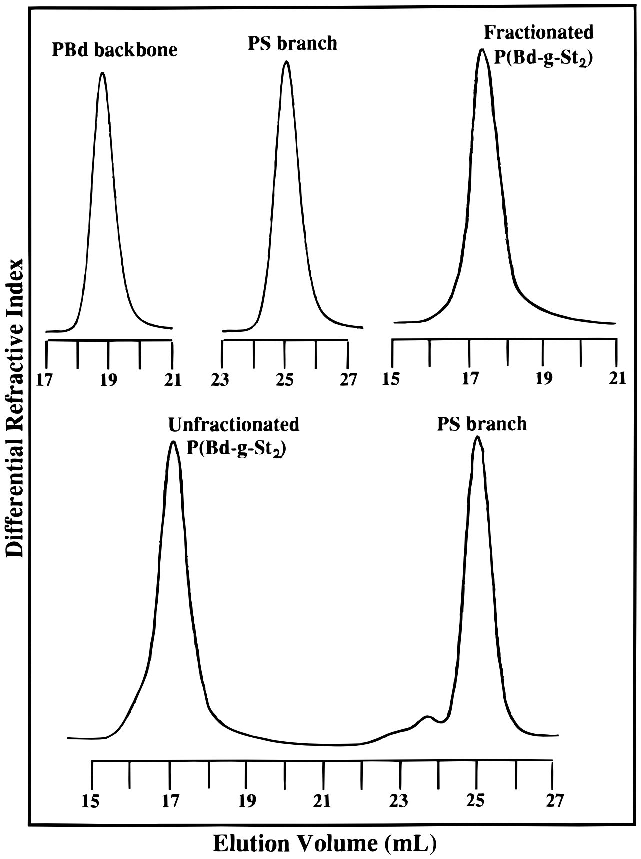


Figure 3. SEC chromatograms of the precursors and the final graft copolymer RMG-4-4-43.

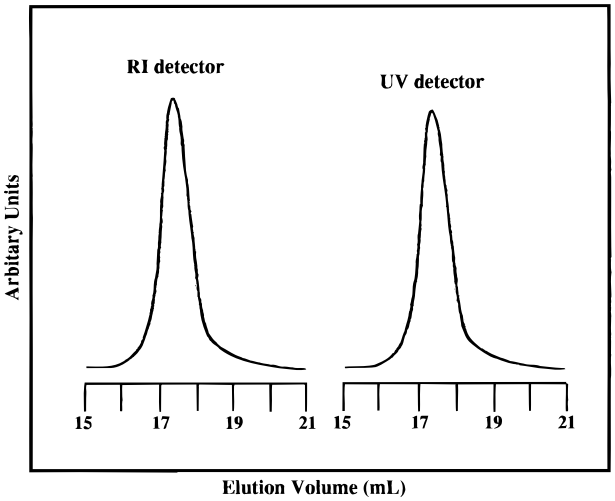


Figure 4. SEC (UV/RI) chromatograms of fractionated graft copolymer RMG-4-4-43.

Table 4. Weight Percent PS of the Poly(Bd-*g*-St) Copolymers

sample	^{1}H NMR[a]	UV−SEC[b]	(d*n*/d*c*)[c]	calcd[d]
RMG-3-5-18	21	20	20	20
RMG-3-5-34	37	36	36	37
RMG-3-5-41	44	44	42	43
RMG-3-5-48	50	52	51	53
RMG-3-5-62	64	64	66	66
RMG-3-15-48	50	50	51	53
RMG-3-15-63	65	65	65	67
RMG-3-15-72	74	74	75	75

[a] In $CDCl_3$ at 30 °C. [b] SEC in THF at 30 °C. [c] Calculated from $(dn/dc) = w(dn/dc)_{PS} + (1 - w)(dn/dc)_{PBd}$, where w is the unknown wt % PS. [d] Calculated from the molecular weight of the precursors and the graft copolymers.

Table 5. Weight Percent of the Poly(Bd-*g*-St$_2$) Copolymers

sample	^{1}H NMR[a]	UV−SEC[b]	(d*n*/d*c*)[c]	calcd[d]
RMG-4-4-16	17	17	18	19
RMG-4-4-28	29	29	30	30
RMG-4-4-43	45	45	46	48
RMG-4-4-61	62	63	64	64
RMG-4-10-31	35	35	35	35
RMG-4-10-45	46	45	46	48
RMG-4-10-61	63	62	64	64
RMG-4-10-77	79	78	78	80
RMG-4-18-46	51	51	52	53
RMG-4-18-65	69	69	68	70
RMG-4-18-74	78	77	76	78

[a] In $CDCl_3$ at 30 °C. [b] SEC in THF at 30 °C. [c] Calculated from $(dn/dc) = w(dn/dc)_{PS} + (1 - w)(dn/dc)_{PBd}$, where w is the unknown wt % PS. [d] Calculated from the molecular weight of the precursors and the graft copolymers.

Table 6. Molecular Characteristics of Trifunctional Multigraft Copolymers and Their Precursors

sample	$10^{-5}M_w$[a] PBd	$10^{-4}M_w$[a] PS	$10^{-5}M_w$[a] RMG	M_w/M_n RMG (SEC)[b]	(d*n*/d*c*)[c]	no. of branch points[d]
RMG-3-5-18	1.98	1.02	2.47	1.06	0.145	4.9
RMG-3-5-34	1.98	2.32	3.14	1.06	0.154	5.0
RMG-3-5-41	1.98	3.14	3.53	1.06	0.157	4.9
RMG-3-5-48	1.98	4.16	4.20	1.06	0.162	5.3
RMG-3-5-62	1.98	7.38	5.77	1.07	0.170	5.1
RMG-3-15-48	1.78	1.28	3.78	1.05	0.162	15.6
RMG-3-15-63	1.78	2.39	5.37	1.06	0.170	15.0
RMG-3-15-72	1.78	3.63	7.18	1.06	0.175	15.0

[a] Low-angle laser light scattering (LALLS) in THF at 25 °C. [b] Size exclusion chromatography in THF at 30 °C. [c] Differential refractometry in THF at 25 °C. [d] Calculated from M_w values of the graft copolymers and their precursors.

pounds are formed by the bimolecular reaction of $HSiMe_2Cl$ and $HSiMeCl_2$ in the presence of Pt catalyst.[20] A little gelling was also observed due to the formation of Si−O−Si, as explained in Figure 1. The side products were eliminated along with the linear branch precursors by fractionation (Figures 2 and 3). SEC chromatograms recorded by RI and UV detectors were very narrow ($M_w/M_n < 1.1$), almost identical (an example is given in Figure 4), meaning that the molecular and compositional homogeneity of the prepared samples is very high. The experimentally determined and calculated composition of the fractionated samples are given in Tables 4 and 5, whereas the molecular characteristics of the precursors and the fractionated samples are presented in Tables 6 and 7. The good agreement between the values determined by NMR, UV, and d*n*/d*c* wt % PS content and those calculated from the M_w of the backbone and of the branches supports the SEC/RI−UV results.

The case of the graft copolymers with double branches needs further clarification in order to prove the complete substitution of both chlorine atoms by PS branches. A plausible method would be the molecular characterization, by SEC of the remaining PS after breaking the double bonds of the PBd backbone with *m*-chloroperbenzoic and periodic acid.[22] This would lead to the detection of single and double PS branches, if incomplete substitution would have occurred. Nevertheless, in our case this is not feasible due to the prior capping of PSLi with butadiene, which would lead to single branches only.

Table 7. Molecular Characteristics of Tetrafunctional Multigraft Copolymers and Their Precursors

sample	$10^{-5}M_w{}^a$ PBd	$10^{-4}M_w{}^a$ PS	$10^{-5}M_w{}^a$ RMG	M_w/M_n RMG (SEC)[b]	$(dn/dc)^c$	no. of branch points[d]
RMG-4-4-16	1.98	0.55	2.45	1.06	0.144	4.3
RMG-4-4-28	1.98	1.13	2.84	1.05	0.151	3.8
RMG-4-4-43	1.98	2.16	3.83	1.05	0.159	4.3
RMG-4-4-61	1.98	4.45	5.54	1.06	0.169	4.0
RMG-4-10-30	1.98	0.52	3.05	1.06	0.153	10.3
RMG-4-10-45	1.98	0.95	3.78	1.05	0.160	9.5
RMG-4-10-61	1.98	1.82	5.47	1.06	0.169	9.6
RMG-4-10-77	1.98	3.81	9.82	1.06	0.177	10.3
RMG-4-18-46	1.78	0.53	3.77	1.07	0.162	18.8
RMG-4-18-65	1.78	1.15	6.03	1.07	0.170	18.5
RMG-4-18-74	1.78	1.78	8.08	1.07	0.176	17.7

[a] Low-angle laser light scattering (LALLS) in THF at 25 °C. [b] Size exclusion chromatography in THF at 30 °C. [c] Diferrential refractometry in THF at 25 °C. [d] Calculated from M_w values of the graft copolymers and their precursors.

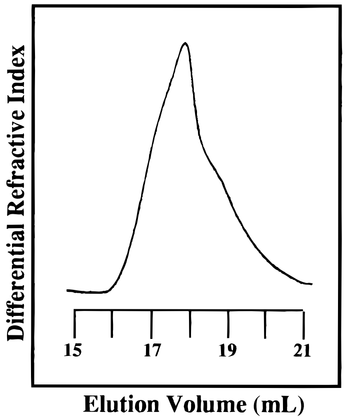


Figure 5. SEC chromatogram of graft copolymer prepared without capping the living branch with butadiene.

To ensure the full substitution of the chlorine atoms per branch point, a large excess of the living PSLi capped with three to four butadienes was used to relieve steric hindrance and force the reaction into completion. The following arguments indicate the complete substitution: (a) narrow molecular weight distribution of the graft copolymers when capping was performed, unlike the very broad distribution (Figure 5), when no capping was taken place, caused by incomplete substitution; (b) invariant with the time SEC chromatograms, proving that no SiCl groups were left on the backbone after the grafting reaction; (c) good agreement between the number of different molecular weights of the branches of the graft copolymers prepared by the same batch of PBd backbone (Table 7).

In conclusion, the combined characterization results show that the multigraft copolymers with single and double branches have a high degree of homogeneity. In a forthcoming paper the morphological study of these materials will be presented.

By using the same method, we have prepared comb PBds and, by hydrogenation, the corresponding polyethylenes.[23]

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