Selective Grafting of Block Copolymers

Miroslav Janata, Lubomír Lochmann,* Jiří Brus, Petr Holler, Zdeněk Tuzar, and Pavel Kratochvíl

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

Bardo Schmitt, Wolfgang Radke, and Axel H. E. Müller

Institute of Physical Chemistry, University of Mainz, D-55099 Mainz, Germany

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ABSTRACT: Synthesis of nonpolar block copolymers selectively grafted in one block with 4-methylstyrene is described, using a novel two-step method: (i) multisite metalation of the more reactive block by a superbase, prepared from 3-(lithiomethyl)heptane and potassium *tert*-pentoxide, and (ii) use of the metalated intermediate as a multifunctional initiator for anionic "grafting from" 4-methylstyrene. Various degrees of grafting (up to ca. 50%) were obtained in the reactive block. Also, other characteristics of the grafted block copolymers may be changed in a wide range, such as type and length of starting blocks or structure and length of the introduced grafts. Thus, a great variety of polymeric structures is available by this method. Molecular weight, molecular weight distribution, and molecular size of the copolymers in tetrahydrofuran were determined by static and dynamic light scattering and by size exclusion chromatography coupled with concentration (RI and UV), viscosity, and light scattering detectors.

Introduction

A novel method for multisite functionalization of nonpolar polymers has been developed recently. It involves two steps: (i) multisite metalation of the polymer by a superbase (SB) and (ii) reaction of the metalated intermediate with an electrophile *in situ*. SB of the second generation, made of 3-(lithiomethyl)heptane and 3 equiv of potassium *tert*-pentoxide, was used in the metalations.[1−4] Various polymers were functionalized by this method, such as homopolymers (polystyrene (PS)[5,6] or polyether dendrimers[7,8]) or diverse block copolymers.[9] Using this method, it is possible to selectively substitute the more acidic block in the block copolymer A−B, if the difference in C−H acidities of the blocks is sufficiently high (pK(A) − pK(B) > 2). Various functional groups have been introduced into the polymers, e.g., $-C_{12}H_{25}$, $-Si(CH_3)_3$, $-CH_2OH$, $-COOH$. The degree of substitution, i.e., the ratio of the number of functionalized repeat units to the number of all repeat units susceptible to substitution, may be varied in a wide range, typically between 1 and 0.1, by the molar ratio SB/repeat unit. Molecular weights of (co)polymers functionalized by this method are mostly quite close to the calculated values. The molecular weight distribution data show that some slight broadening occurs in the functionalization and this tendency is more pronounced if functionalization is carried out to a higher degree.[6,8,9]

Some polymers were previously metalated using other bases, e.g., styrene homo- or copolymers with butyllithium in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine[10,11] or polybutadiene with butyllithium and metal alkoxides.[12] The SB described above seems to be superior to those bases because of higher reactivity, selectivity, and efficiency.

The multisite-metalated polymer obtained should also be effective as a multifunctional initiator of anionic polymerization, as shown by grafting styrene from a polyether dendrimer in a preliminary experiment.[13] This concept was now extended to block copolymers. The possibility of metalating selectively the more acidic block of a block copolymer enables us to synthesize diverse polymer structures by grafting just the one block.

Numerous methods for grafting of polymers were described;[14−16] however, their use is often limited to specific materials or to cases where regioselectivity of grafting is not important. The procedure presented here for grafting polymers and, in particular, block copolymers offers a convenient alternative for selective "grafting from".

Experimental Section

Materials. Crystalline potassium *tert*-pentoxide was prepared by reaction of potassium metal with *tert*-pentyl alcohol in a heptane−tetrahydrofuran (THF) mixture (2:1 v/v). 3-(Lithiomethyl)heptane was prepared by reaction of Li powder (containing 2% Na) with 3-(chloromethyl)heptane in cyclohexane at 50 °C: The purity of these organometallic compounds is essential for a successful metalation of polymers. *tert*-Pentyl alcohol, 3-(chloromethyl)heptane, and trimethylchlorosilane (TMS-Cl) were distilled with calcium hydride. Cyclohexane, benzene, and 4-methylstyrene were distilled from dibutylmagnesium *in vacuo* prior to use, THF was distilled from Na anthracenide. All operations with the organometallics were carried out under an argon atmosphere.

Block Copolymers Used for Grafting: (i) Polyisoprene-*block*-polystyrene, in which the polyisoprene block was fully hydrogenated after polymerization (PIH-*b*-PS), i.e.,Shellvis-50, Shell Co., $w_{PS} = 0.42$; (ii) polystyrene-*block*-poly(4-methylstyrene) (PS-*b*-P(4-MS)), $w_{4-MS} = 0.53$ or 0.09, prepared by anionic polymerization. For other parameters of starting copolymers; see Table 1. All copolymers were dried *in vacuo* and stored under argon before use.

Metalation of Block Copolymers (Typical Procedures). (i) PIH-*b*-PS. A cyclohexane solution of 3-(lithiomethyl)heptane (0.015 mol) was added to a stirred solution of potassium *tert*-pentoxide in heptane (0.045 mol) at room temperature. After 1 min the mixture was cooled to 0 °C and a solution of the copolymer (amount given in Table 2) in cyclohexane was added at once. The concentration of the solutions was adjusted so as to obtain a final concentration of 0.10 mol of average repeat units of the copolymer per liter. The mixture was then stirred for 3 h at the same temperature.

(ii) PS-*b*-P(4-MS). (This copolymer requires another procedure in order to maintain the high selectivity in metalation.)

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A cyclohexane solution of 3-(lithiomethyl)heptane (0.015 mol) was added to a stirred solution of the block copolymer in benzene at room temperature. The solution was cooled to 7 °C, and a solution of potassium *tert*-pentoxide in cyclohexane (0.015 mol) was added dropwise within ca. 5 min. The mixture was stirred for another 3 h at the same temperature. A sample of the metalation mixture was quenched with TMS-Cl; the silylated copolymer was isolated and used for determination of the degree of metalation by ^{1}H NMR.

Grafting of the Metalated Copolymers. A calculated amount of 4-MS was then added to the solution of the metalated copolymer, and the resulting mixture was stirred for 2 h at room temperature. The grafting was quenched with an excess of TMS-Cl, and the product was isolated by precipitation into methanol. The homopolymer of 4-MS, which was formed in an appreciable amount in the grafting of PIH-*b*-PS, was separated from the grafted copolymer by fractional precipitation from a benzene solution by dropwise addition of methanol. In this way, pure grafted block copolymer could be isolated.

Physical Methods. NMR. NMR spectra were measured using a Bruker DPX 300 spectrometer with internal deuterium stabilization at 298 K.

^{1}H NMR spectra were measured at the frequency of 300.1 MHz with an external standard hexamethyldisiloxane (HMDS). ^{29}Si NMR spectra were measured at a frequency of 59.6 MHz with the same external standard. The DEPT pulse sequence was used to increase the sensitivity: number of data points 32 K, number of FID accumulations 4000−12 000, relaxation delay 5 s, mixing pulse $\theta = 23°$, polarization transfer time $t =$ 48 ms (which corresponds to a coupling constant $^2J_{\mathrm{H-C-Si}} =$ 10.4 Hz).

Size Exclusion Chromatography (SEC). The SEC characterization was performed in THF at room temperature at a flow rate of 0.5 mL/min using three 5 m, PSS-SDV-gel columns (10^3, 10^5, 10^6 Å, 30 cm each) and the following detectors: RI (Bischoff Model 8110), diode array UV (Applied Biosystems S 1000), multiangle light scattering (Wyatt Technology DAWN-F-DPS operated using a He/Ne laser at 633 nm), and viscosity (Viscotek H 502 B). Two valves allowed us to incorporate the light scattering and/or viscosity detector if needed. Data evaluation was performed using WinGPC software (V 3.0 b61, PSS, Mainz, Germany) except for SEC/LS analysis where Win-Astra software (V. 4.1, Wyatt Technology) was used. The values obtained relate only to the high-molecular-weight portions of the polymers. The determination of copolymer composition is based on the assumption that the response of a detector can be expressed as the sum of the responses of the two components. Using two detectors, it is possible to solve the resulting set of linear equations to yield the concentrations of the two components. The concentrations necessary for the evaluation of the light scattering and viscosity data were not corrected for changes in the refractive index increment with elution volume since the copolymer composition was found to be nearly independent of elution volume for the derivatives of PIH-*b*-PS (see Results). This was also assumed for derivatives of PS-*b*-P(4-MS), for which no copolymer composition could be evaluated due to low differences in the response factors.

Static Light Scattering (SLS). Measurements of molecular weights (M_w) and radii of gyration (R_G) of copolymers were performed in THF solution on a Sofica instrument equipped with a He/Ne laser. Data were treated by a standard Zimm method. Refractive index increments of copolymers were determined using a Brice-Phoenix differential refractometer.

Dynamic Light Scattering (DLS). The measurements were made using an ALV 5000, multibit, multitau autocorrelator and an argon ion laser ($\lambda_0 = 514.5$ nm). The data were processed by a standard cumulant method. Hydrodynamic radii (R_H) were calculated from the Stokes−Einstein equation.

Results and Discussion

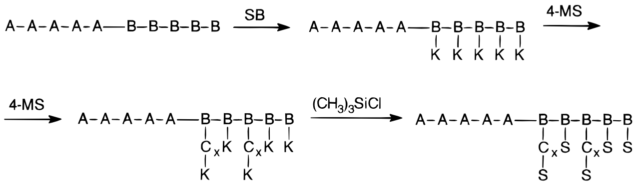
Several AB-type block copolymers were selectively grafted with 4-methylstyrene (4-MS) in one block only using a novel method. The more acidic block of the starting block copolymer is first multisite metalated by a superbase (SB) under specific conditions. The selectively polymetalated copolymer then acts as a multifunctional initiator for the anionic polymerization of 4-MS according to Scheme 1. The SB used was prepared in cyclohexane−heptane solution from 3-(lithiomethyl)heptane and 1 or 3 equiv of potassium *tert*-pentoxide.[1,2] In the metalation of PS-*b*-P(4-MS) copolymers, benzene was also present in order to ensure the selectivity of substitution.[9]

Table 1. Properties of Starting Block copolymers

starting block copolymer AB[a]	contents of B units, % wt	molecular weight × 10^{-3} [b]				
		M_n	M_w	M_w/M_n	M_w[c]	$[\eta]$,[b] mL·g^{-1}
PIH-*b*-PS	42	92	94	1.02	95	78
PS-*b*-P(4-MS) I	53	107	117	1.04	126	54
PS-*b*-P(4-MS) II	9	146	150	1.03	158	63

[a] For abbreviations, see Experimental Section. [b] SEC values using concentration and viscosity detectors (universal calibration). [c] Determined by SLS.

Scheme 1



K = potassium, C_x = poly(4-methylstyrene), S = $(CH_3)_3Si$-, pK(A) - pK(B) > 2

Block copolymers used in these experiments are listed in the Experimental Section and Table 1. In the PIH-*b*-PS copolymer, both the benzylic and aromatic hydrogens are more acidic than the aliphatic ones and, thus, the polystyrene blocks are metalated exclusively. It was shown earlier[6] that metalation of aromatic sites in PS is preferred to the metalation of benzylic sites, although the latter hydrogens are more acidic. Their reactivity is obviously reduced for steric reasons in the kinetically controlled reaction. In the two PS-*b*-P(4-MS) copolymers, the poly(4-methylstyrene) blocks are metalated selectively under the conditions used,[9] as the methyl group is the most reactive site in the copolymer.

The starting copolymers were metalated to various degrees, using mole ratios SB/B units between 0.5 and 1.5. The degree of metalation (DM) of the copolymers was estimated in a sample of the metalation mixture quenched with TMS-Cl. The content of TMS groups in the copolymer, which is equal to the number of potassium atoms introduced into the copolymer in the metalation step, was determined using ^{1}H NMR spectroscopy. The efficiency of metalation E (E = DM × B × 100/SB, where B/SB is the mole ratio of B repeat units and superbase) ranged mostly around 70% (Table 2).

In this way, block copolymers selectively grafted in one block with 4-MS were prepared in good yields. The conversion of 4-MS in the grafting was better than 95%. In grafting of PS-*b*-P(4-MS) copolymers, only a small amount of 4-methylstyrene homopolymer (<10% by weight) was formed and, therefore, these copolymers were analyzed as such. In contrast, the amount of 4-methylstyrene homopolymer (with molecular weights below 10 000) in the grafting of PIH-*b*-PS copolymer was considerable (40−70% by weight relative to the reacted 4-MS). The homopolymer was separated from the grafted copolymer by fractional precipitation from benzene solution by addition of a small amount of methanol.

Table 2. Preparation and Properties of AB Block Copolymers Selectively Grafted in Block B with 4-Methylstyrene (4-MS)

	reaction conditions				grafted block copolymers						
no.	starting AB[a]	contents of B units, % wt	SB/B units mole ratio	ratio of 4-MS added[b]	contents of grafts,[c] % wt	contents of 4-MS homopolymer,[d] % wt	degree of metalation[e]	efficiency of metalation,[f] %	degree of grafting[g]	efficiency of grafting,[h] %	$\overline{\mathrm{DP}}$ of 4-MS grafts[i]
1	PIH-*b*-PS	42	0.5	6.7	(i) 32 (ii) 32	3	0.37	74	0.17	46	2.5[k]
2	PIH-*b*-PS	42	1.5	14.7	(i) 62 (ii) 58	4	0.89	89[l]	0.52	58	4.5
3	PS-*b*-P(4-MS) I	53	0.5	6		3	0.43	86	0.26	61	10
4	PS-*b*-P(4-MS) I	53	1.0	5.2		10	0.67	67	0.32	47	11
5	PS-*b*-P(4-MS) II	9	0.8	15.1		10	0.46	58	0.34	74	20

[a] For abbreviations, see Experimental Section. [b] Ratio of 4-MS added = [4-MS$_{\mathrm{added}}$]/([B-units] × degree of metalation). [c] Graft contents in the grafted block copolymer determined by (i) ^{1}H NMR and (ii) SEC using two concentration detectors. An almost constant composition of the samples within the elution range of the high-molecular-weight part of the copolymer was observed. [d] Determined by SEC (molecular weights after fractional precipitation 4000−7000). [e] Degree of metalation = number of TMS groups/B unit, determined by ^{1}H NMR. [f] Efficiency of metalation = degree of metalation × 100/ratio ([SB])/[B units]). [g] Degree of grafting = number of grafts/B unit, determined by ^{29}Si NMR. [h] Efficiency of grafting = degree of grafting × 100/degree of metalation. [i] $\overline{\mathrm{DP}}_{\mathrm{grafts}}$ = [4-MS$_{\mathrm{grafted}}$]/([B units] × degree of grafting). [k] Preliminary value. [l] Relative to 1 equiv of SB.

The grafted copolymer could then be isolated in the pure state (homopolymer contents below 4% by weight). The partition of 4-methylstyrene between the homopolymer and grafted copolymer was calculated using ^{1}H NMR spectra and SEC eluograms. The preparation conditions and properties of grafted block copolymers are summarized in Table 2.

The amount of 4-MS "grafted from" the PIH-*b*-PS block copolymer was determined by two independent methods: (i) ^{1}H NMR and (ii) SEC coupled with two concentration detectors. Here, an almost constant composition of the grafted block copolymer within the elution range of the high-molecular-weight portion of the copolymer was observed. Both methods gave close values and, therefore, seem to be reliable (Table 2).

The structure of the grafted block copolymers may be varied in a broad range due to a great flexibility of the method. The degree of grafting, i.e., the ratio of grafted B units to all B units, may be controlled first of all by the degree of metalation. However, only a fraction of the metalated sites is able to add 4-MS and, therefore, the efficiency of grafting, i.e., the ratio of grafted sites to all metalated sites, is less than 100%. Nevertheless, degrees of grafting as high as ca. 74% could be reached in some cases, which means that almost three-fourths of the B units in the copolymer bear a grafted oligo- or poly(4-methylstyrene) chain (Table 2). The average degree of grafting was calculated using data from ^{29}Si NMR spectra of the grafted copolymers, as the ratio of signals ($b_1 + b_2 + c_l$)/($d_1 + d_2$) for the PIH-*b*-PS copolymer and ($b_1 + b_2 + c_1$)/c_2 in the case of PS-*b*-P(4-MS) copolymers (Figure 1a,b. For assignment of signals, see below).

Yet other parameters of the grafted block copolymers may be widely varied, such as the length of the grafts and the lenghts of blocks in the original block copolymer. The degree of polymerization of the grafts can be calculated from the relation DP$_{\mathrm{grafts}}$ = [4-MS grafted]/([B units] × degree of grafting); the values thus obtained for the polymers prepared are given in Table 2. They were kept low intentionally to make analyses of the products more accurate. Longer grafts can be prepared as well. Block copolymers with various lengths of blocks A and B can be used in the process, determining the overall shape of the product. Thus, grafted block copolymers derived from a copolymer with a long A block and short B block may give rise to structures resembling a bottle-brush and, the other way round, a starting copolymer with a short A block and long B block may be grafted to a "mouselike" structure having a big body with a short tail. Indeed, very diverse polymer structures may be synthesized by this method.

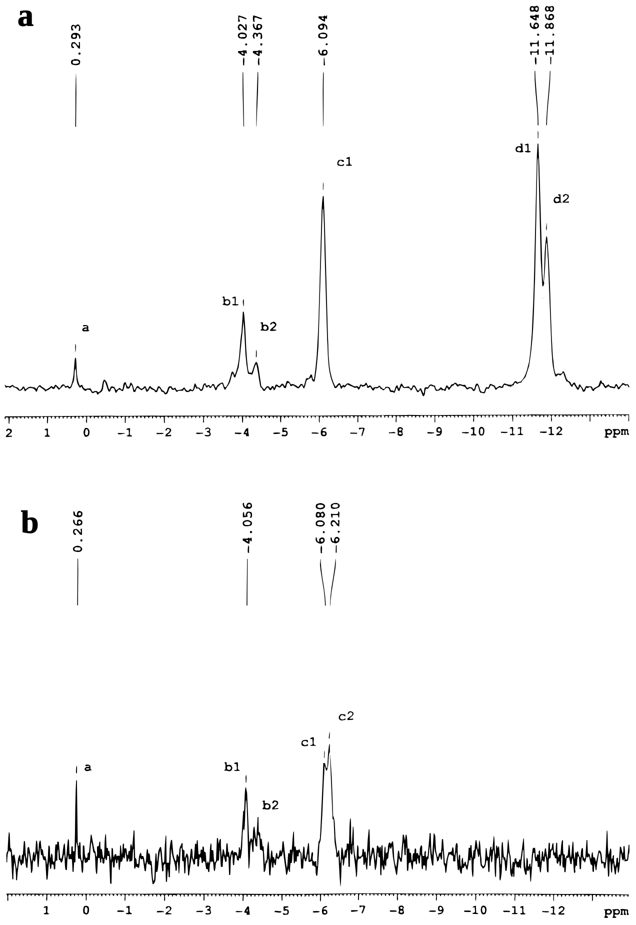


Figure 1. ^{29}Si NMR spectra of grafted block copolymers in CDCl$_3$: (a) PIH-*b*-PS selectively grafted in the PS block with 4-methylstyrene; (b) PS-*b*-P(4-MS) selectively grafted in the 4-MS block with 4-methylstyrene.

The grafting was quenched by addition of an excess of TMS-Cl, and therefore, all sites originally bearing potassium atoms, either at the end of the grafts or in the block B, which did not initiate the grafting, were substituted with TMS groups (Scheme 1). Therefore, valuable information on the structure of these grafted

Table 3. Molecular Characteristics of Grafted Block Copolymers

	SLS		DLS			SEC			
no.[a]	$10^{-3}M_w$	R_G, nm	R_H, nm	PD[b]	ρ[c]	$10^{-3}M_w$[d]	M_w/M_n[d]	$10^{-3}M_w$[e]	$[\eta]$, mL·g^{-1}
1	206	34.5	8.6	0.05	0.13	193	1.33	190	66
2	306	<15.0	9.6	0.11	0.14	297	1.30	291	55
3	490	25.5	14.0	0.18	0.07	585	1.64	552	50
4	890	31.0	18.0	0.21	0.06	1 090	2.27	907	48
5	230	14.5	9.4	0.10	0.11	297	1.16	297	47

[a] Cf. Table 2. [b] Polydispersity by a standard cumulant method. [c] Average volume fractions of segments. [d] By SEC using concentration and viscosity detectors and universal calibration. [e] By SEC using concentration and light scattering detectors.

block copolymers could be obtained from their ^{29}Si NMR spectra; typical spectra being shown in Figures 1a,b. The signals were assigned by comparison with spectra of model compounds as follows: (1) signals d_1 and d_2 (at −11.648 and −11.868 ppm) correspond to TMS groups linked to carbon atoms in aromatic rings of PIH-*b*-PS, probably in meta and para positions; (2) signals c_1 and c_2 (around −6 ppm) correspond to TMS groups bonded to benzylic carbons in $-CH(C_6H_4CH_3)$ groupings at the end of the 4-MS grafts and in $-CH_2(C_6H_4-)$ groupings in the main chain of the PS-*b*-P(4-MS) copolymer, not used in the grafting, respectively; (3) signals b_1 and b_2 (around −4 ppm) are related to another form of the growth center in the grafts, which is being investigated; (4) signals slightly below 0.3 ppm are probably due to impurities. The total absence of signals d_1 and d_2 (TMS group on an aromatic ring) in the spectrum of grafted PS-*b*-P(4-MS) copolymers (Figure 1b) confirms the high regioselectivity of the metalation of the copolymers. In our case, the metalation is directed exclusively to the methyl groups on aromatic rings (cf. ref 9).

The parameters of the grafted block copolymers obtained from NMR spectra are only average values. The distribution of the grafted sites among block copolymer molecules, as well as the distribution of the lengths of the grafts (DP_{grafts}) are of special interest. In some cases, an indication of these distributions can be obtained from SEC eluograms of grafted block copolymers: molecular weight distribution of some grafted block copolymers is not substantially broader than that of the starting block copolymer. Therefore, it seems probably that distributions of the grafted sites among copolymer molecules and distribution of DP of grafts are also narrow; i.e., most macromolecules have parameters quite close to the mean values. Molecular weight distributions of some other grafted block copolymers are broad and, therefore, no conclusion on the distribution of the grafts can be made.

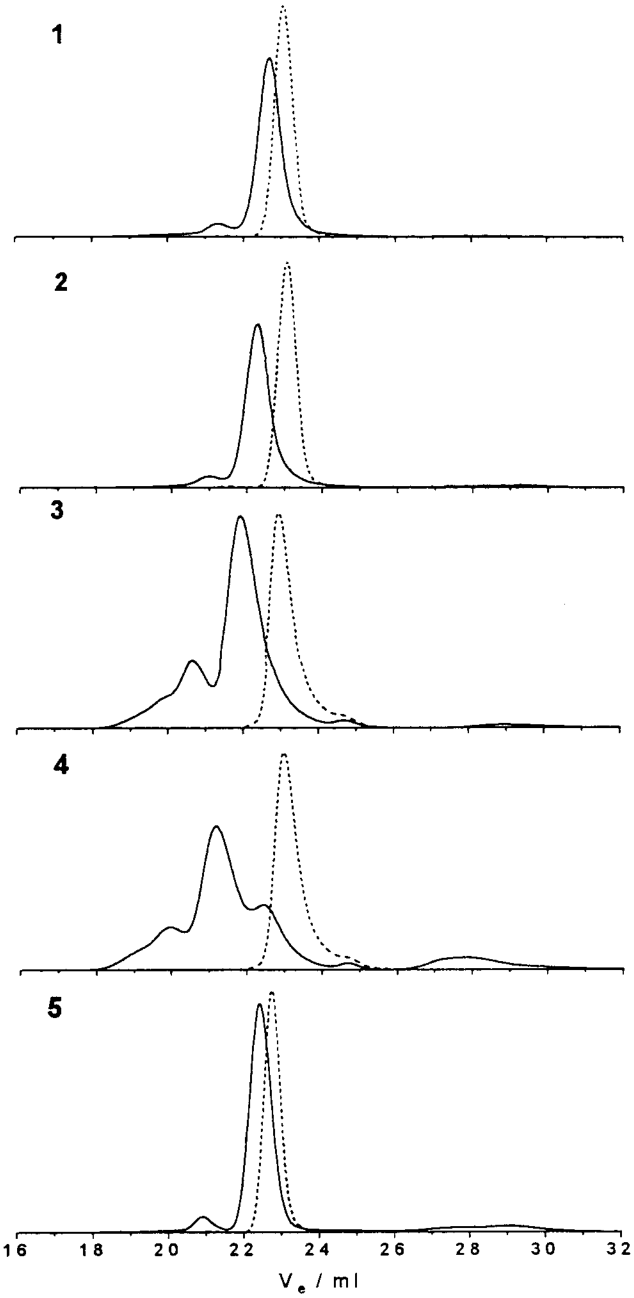


Figure 2. SEC eluograms of grafted block copolymers (RI detector), samples 1−5 (Table 2). Signals at V_e > 26 mL correspond to the 4-MS homopolymer. Dotted lines correspond to the starting block copolymer.

Molecular weights of the starting block copolymers as well as of their grafted derivatives were determined by SEC using various detectors including RI, UV, light scattering, and viscosity detectors and by static light scattering (SLS), as shown in Tables 1 and 3. Eluograms of some copolymers are demonstrated in Figure 2. The molecular weight of the block copolymers increased after grafting with 4-MS, and the values found by three independent methods (SLS and SEC with two sets of detectors) are the same within experimental error. In contrast, molecular weights obtained by SEC with concentration detectors (RI and UV) and with a PS calibration gave results that differed increasingly from the correct values with the increasing degree of polymer branching. Generally, the molecular weight distribution became broader after grafting. The effect was more pronounced with PS-*b*-P(4-MS) copolymers bearing long 4-MS blocks (samples 3 and 4) than with the copolymer containing a short 4-MS block (sample 5). Grafted PIH-*b*-PS copolymers (samples 1 and 2) exhibited almost the same, relatively narrow molecular weight distribution regardless of the degree of grafting. The intrinsic viscosity of the grafted copolymers is lower than that of the unsubstituted block copolymers although their MW is higher, indicating a strong contraction of the grafted polymer chain due to the branched structure.

As already mentioned, M_w values of the grafted copolymers from SLS and SEC do not differ appreciably (Table 3), although both methods are subject to their inherent experimental errors. Due to possible heterogeneity in chemical composition and differences in contrast values (i.e., in the refractive index increments) of both blocks,[17] which may play a major role in the case of grafted PIH-*b*-PS copolymers, MW values from SLS are, strictly speeking, only apparent values. SEC with either combination of detectors can also show slightly erroneous results.[18] In our case (Table 3), the potential sources of error are obviously not operative and can be disregarded.

Molecular weights of copolymers 2 and 4 with higher degrees of grafting are expectedly substantially higher than those of copolymers 1 and 3 with lower degrees of grafting (Table 3), although the degrees of polymerization of grafts in both PIH-*b*-PS or PS-*b*-P(4-MS) (2.5 and 4.5 or 14 and 15, respectively; see Table 2) are quite close. Similar values of $[\eta]$ in both pairs indicate that the copolymers have degrees of grafting high enough to show a low dependence of $[\eta]$ on M. A small portion of copolymer molecules with a high molecular weight (as SEC eluograms indicate) have less influence on the overall M_w values determined by both SEC and SLS and more influence on the size values (R_G and R_H from SLS and DLS) since these are the *z*-averages. Moreover, R_G values may be strongly influenced by a heterogeneity in chemical composition.[19] For these reasons, the otherwise meaningful ratio R_H/R_G[20] has only a small significance here and is not discussed.

The average volume fraction of polymer segments in a given macromolecule in dilute solution, ρ, within a sphere with a radius of R_H can be estimated. For comparison, ρ is of the order of magnitude 0.03−0.05 for a linear polymer coil and 0.3 for a copolymer micelle.[21,22] The ρ values in Table 3 are somewhere in between: for grafted copolymers based on PIH-*b*-PS and PS-*b*-P(4-MS) II, the values are somewhat higher; for those based on the PS-*b*-P(4-MS) I (Table 1), copolymer they lie lower. It would be premature to interpret the results; a more thorough study, involving additional experimental methods, is in progress.

Conclusions

The presented method for grafting of block copolymers offers a broad choice for synthesis of nontraditional polymer structures and extends the processes hitherto available. Particular noteworthy is the high degree of grafting and selectivity of grafting obtainable in this way. In a further extension, the grafted block copolymers may be selectively multisite-substituted with various functional groups using a similar process (ref 9) and thus another class of polymers can be obtained.

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