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Selective Grafting of Block Copolymers. 2. Multimetalated (Co)polymers as Initiators for Grafting Process. Model Metalation Studies

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ABSTRACT: Metalation of polystyrene, poly(4-methylstyrene), and their block copolymers is described using either superbases (made of organolithium compounds and potassium *tert*-pentoxide) or *sec*-butyllithium complexed with *N,N,N′,N′*-tetramethylethylenediamine as metalating agents. Depending on the type and concentration of the metalating agent, different sites in the above polymers were metalated. Generally, only the most acidic and the most accessible hydrogen atoms in polystyrene (aromatic protons) and poly(4-methylstyrene) (methyl group protons) were selectively metalated using the above metalating agents at metalation ratios lower than unity. At higher metalation ratios, nonselective metalation occurred, and also other positions in the polymers (backbone, aromatic protons in poly(4-methylstyrene)) were metalated. To distinguish positions of metalation, functionalization of metalated polymers with chlorotrimethylsilane and subsequent ^{29}Si NMR analysis of polymer-bonded trimethylsilyl groups were applied.

Introduction

Graft copolymers are of great interest, because they are able to join vastly different properties of individual polymers in one molecule. Thus, graft copolymers are useful in the compatibilization of polymer blends or for introducing new properties, which are not inherent to the parent polymers.

Several procedures can be used for the preparation of graft copolymers by the anionic technique;[1] one of them is the "grafting from" method. In this method, reactive sites are generated along the polymer chain, which are able to initiate polymerization of an appropriate monomer, giving rise to graft polymers. Anionic initiating centers in the polymer backbone can be generated by hydrogen−metal exchange (metalation) provided that the parent (co)polymer contains sufficiently acidic hydrogen atoms that can be abstracted by the metalating reagent. At present, two general types of metalating agents are commonly used; either superbases[2,3] made of an organolithium compound and potassium *tert*-alkoxide or organolithium compounds complexed with a tertiary amine.[4]

To prepare defined graft copolymers using the "grafting from" technique, we wanted to know the location of metalated sites, i.e., the centers for subsequent grafting, in the starting (co)polymer. Moreover, we preferred selective metalation and, consequently, selective grafting of the starting (co)polymer due to more uniform structure of the resulting graft copolymer. Therefore, prior to grafting of some nonpolar block copolymers, we investigated metalation and functionalization of relevant homopolymers as models with the emphasis on the structural analysis of resulting polymeric products. The reaction conditions were selected with respect to those applied later in the synthesis of graft copolymers.[5]

Experimental Section

Materials. Cyclohexane, benzene, styrene (S), 4-methylstyrene (4-MS), and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) were distilled from dibutylmagnesium; tetrahydrofuran (THF) was distilled from sodium anthracenide prior to use. *tert*-Pentyl alcohol, 2-ethylhexyl chloride, and chlorotrimethylsilane (TMS-Cl) were distilled with calcium hydride. Crystalline potassium *tert*-pentoxide (*t*-PeOK) was prepared by reaction of potassium metal with *tert*-pentyl alcohol.[6] 2-Ethylhexyllithium (EtHexLi) and butyllithium (BuLi) were prepared by reaction of lithium powder (containing 2% Na) with 2-ethylhexyl chloride and butyl bromide, respectively.[6] *sec*-Butyllithium (*s*-BuLi, 1.3 M solution in cyclohexane, Aldrich) and (trimethylsilyl)methyllithium (TMSMeLi, 1 M solution in pentane, Fluka) were used as received. The concentration of alkyllithiums used was determined by direct titration at room temperature with 2-butanol in toluene using 1,10-phenanthroline as indicator.[7] Superbases "2-ethylhexylpotassium" (EtHexK)[6] and "phenylpotassium" (PhK)[8] were prepared by reaction of EtHexLi with *t*-PeOK at room temperature in cyclohexane and benzene, respectively. Superbase "(trimethylsilyl)methylpotassium" was prepared in the similar way by reaction of (trimethylsilyl)methyllithium with *t*-PeOK in THF at −78 °C. All operations with organometallics were carried out under purified argon.

Starting Model Polymers. Polystyrene (PS, $M_n = 4400$, $M_w/M_n = 1.24$) and poly(4-methylstyrene) (P(4-MS), $M_n = 5500$, $M_w/M_n = 1.07$) were prepared by anionic polymerization in THF at −78 °C using *s*-BuLi as initiator and degassed methanol as terminator. The block copolymer composed of the above polymers ($M_n = 120\,000$, $M_w/M_n = 1.11$, $w_{4-MS} = 0.30$) was prepared in the same way, polymerizing styrene as the first monomer followed by polymerization of 4-methylstyrene.

Metalation Reactions (Typical Procedures). (i) Superbases as Metalating Agents. 0.8 M cyclohexane solution (12 mL) of 2-ethylhexyllithium (1.202 g, 0.01 mol) was added to a stirred 1 M cyclohexane solution (30 mL) of potassium *tert*-pentoxide (3.787 g, 0.03 mol, *t*-PeOK/EtHexLi = 3) at room temperature. After 2 min, a solution of PS (1.04 g, 0.01 mol, EtHexLi/S = 1) in cyclohexane (62 mL) was added. The metalation ratio, i.e., the molar ratio of alkyllithium compound (EtHexLi) to monomeric units of the starting polymer, was varied in a broad range with typical values 0.5, 1 (given example), 1.5, and 2. The concentration of the solutions was adjusted so as to obtain a final polymer concentration of ca. 1% w/v. The mixture was stirred for 3 h at room temperature, quenched with the solution of TMS-Cl (7.60 mL, 0.06 mol, TMS-Cl/(EtHexLi + *t*-PeOK) = 1.5) in THF (5 mL), and precipitated in methanol. The silylated PS was then dried at 40 °C under vacuum.

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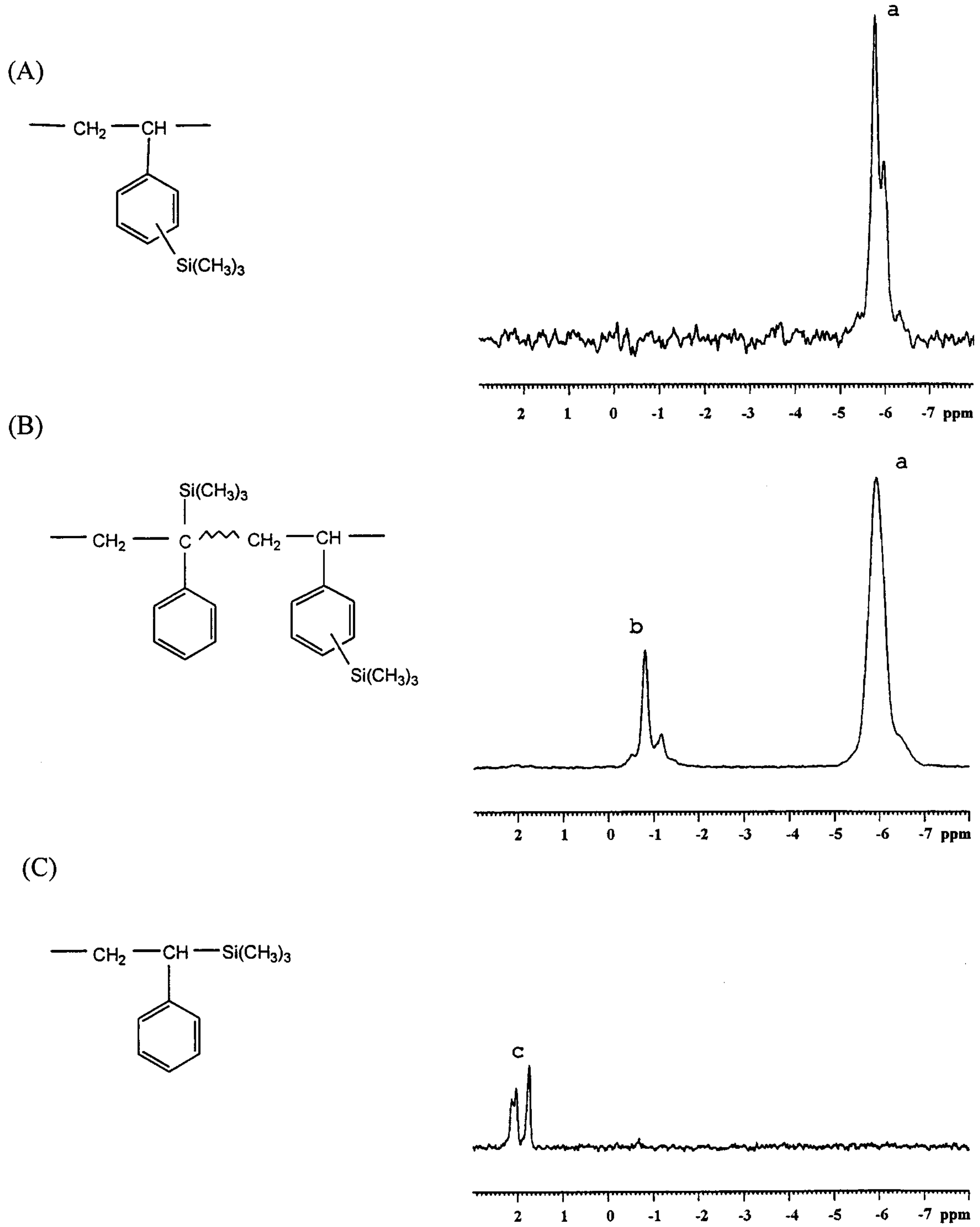


Figure 1. ^{29}Si NMR spectra of silylated PS prepared from the corresponding metalated precursor, using following metalating agents: (A) EtHexK/S < 1 or *s*-BuLi/TMEDA, (B) EtHexK/S ≥ 1, (C) living PS from anionic polymerization as precursor. Abbreviation in the spectra corresponds to TMS groups bonded in the ring (a), in the backbone (b), and at the ω-chain end (c).

The metalation and silylation of P(4-MS) and PS-*b*-P(4-MS) (in both cases EtHexLi/4-MS = 0.5−2) were carried out in a similar way. If exclusive metalation of methyl groups in the latter two polymers in high yields was desirable (see Results and Discussion), a benzene solution of the polymers was used. The ^{29}Si NMR spectra of silylated PS and P(4-MS) are given in Figures 1 and 2, respectively.

In one special case, (trimethylsilyl)methylpotassium was used as metalating agent. 1 M cyclohexane solution (30 mL) of potassium *tert*-pentoxide (0.03 mol) was added to THF solution (10 mL) of polystyrene (0.52 g, 0.005 mol) and cooled to −78 °C. Then 1 M pentane solution (10 mL) of (trimethylsilyl)methyllithium (0.01 mol, TMSMeLi/S = 2, *t*-PeOK/TMSMeLi = 3) was added; the mixture was stirred for 5 h at −78 °C, quenched with an excess of TMS−Cl, and precipitated in methanol. The isolated polymer was dried at 40 °C under vacuum. No signal was found in the ^{29}Si NMR spectrum of this polymer.

(ii) *s*-BuLi−TMEDA Complex as Metalating Agent. 1.3 M cyclohexane solution (7.7 mL) of *s*-BuLi (0.64 g, 0.01 mol) followed by TMEDA (1.51 mL, 0.01 mol, *s*-BuLi/TMEDA = 1) was added to a stirred solution of PS (1.04 g, 0.01 mol, *s*-BuLi/S = 1) in cyclohexane (94 mL) at room temperature so as to reach the final polymer concentration of ca. 1% w/v. The metalation ratio was varied in a broad range with typical values 0.5, 1 (given example), 1.5, and 2. The mixture was stirred for 3 h at room temperature, quenched with the solution of TMS-Cl (1.9 mL, 0.015 mol, TMS−Cl/*s*-BuLi = 1.5) in THF (2 mL),

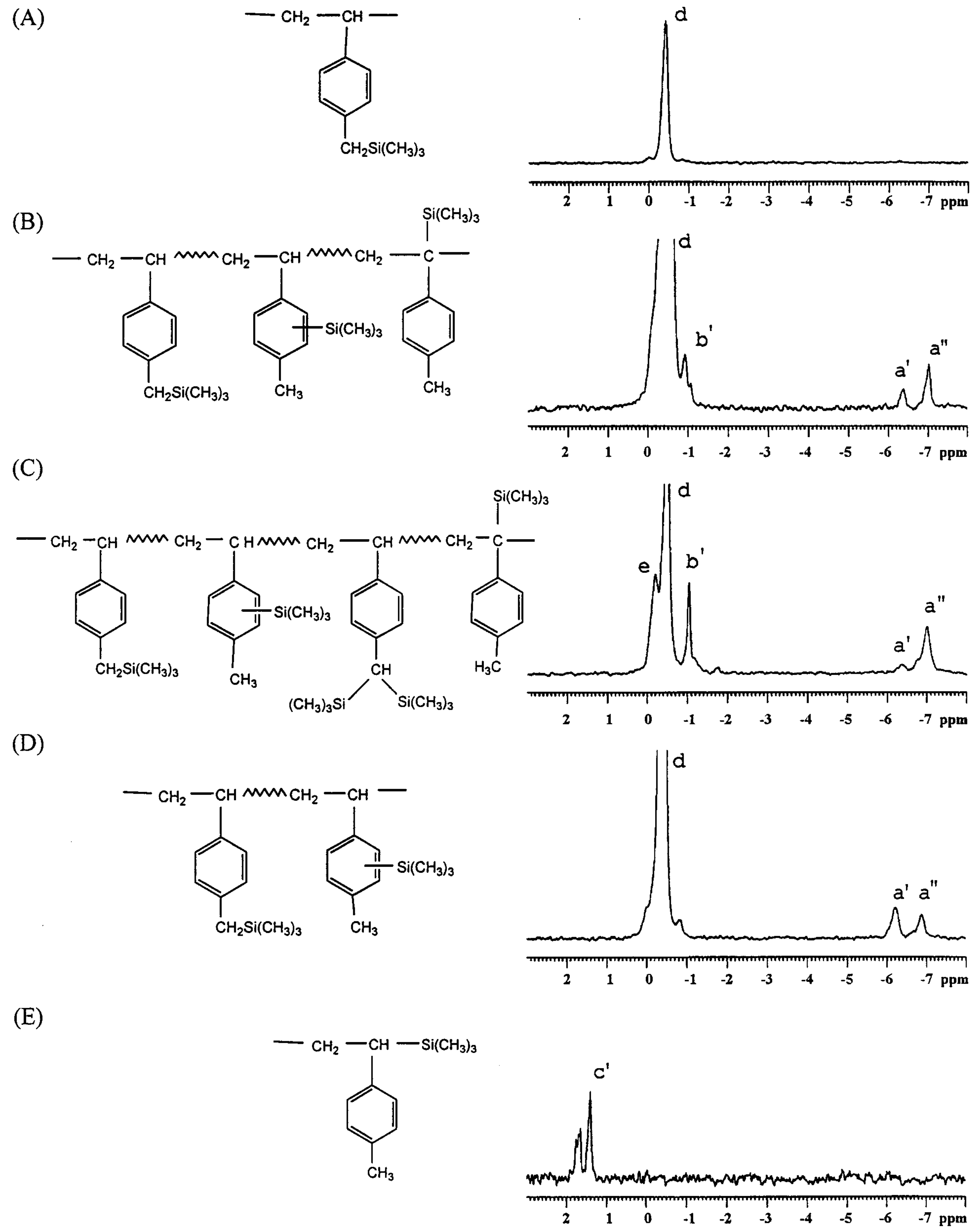


Figure 2. ^{29}Si NMR spectra of silylated P(4-MS) prepared from the corresponding metalated precursor, using following metalating agents: (A) EtHexK/4-MS < 1 or PhK/4-MS ≤ 2, (B) $1 \leq$ EtHexK/4-MS < 2, (C) EtHexK/4-MS ≥ 2, (D) *s*-BuLi/TMEDA, (E) living P(4-MS) from anionic polymerization as precursor. Abbreviation in the spectra corresponds to TMS groups bonded in the ring (a′, a″), in the backbone (b′), at the ω-chain end (c′), in the benzylic position [d (one TMS group); e (two TMS groups)].

and precipitated in methanol. The silylated PS was then dried at 40 °C under vacuum. The metalation and silylation of P(4-MS) and PS-*b*-P(4-MS) (in both cases *s*-BuLi/4-MS = 0.5−2) were carried out in the similar way. The ^{29}Si NMR spectra of silylated PS and P(4-MS) are given in Figures 1 and 2, respectively.

In one special case, the BuLi−TMEDA complex was used as metalating agent. Silylated P(4-MS) with trimethylsilyl group selectively bonded in benzylic positions, prepared according to above-described procedure with superbase EtHexK as metalating agent (EtHexK/4-MS = 0.5), was used as starting material (see Scheme 1). 1.1 M hexane solution (9.1

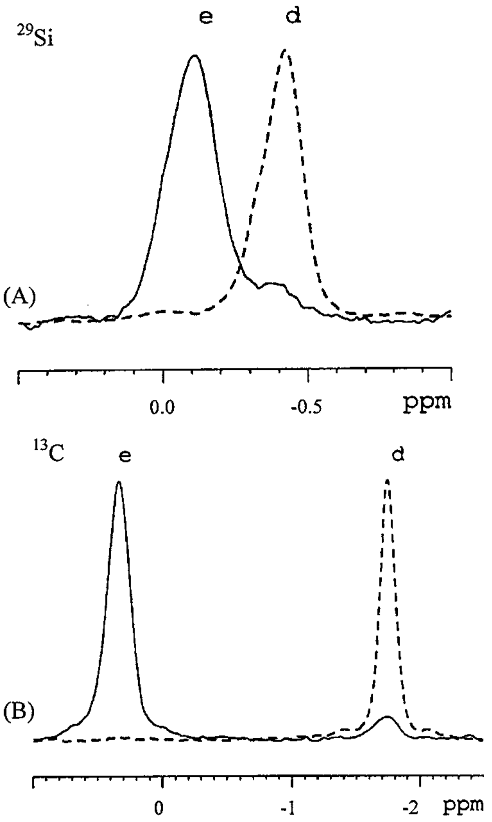
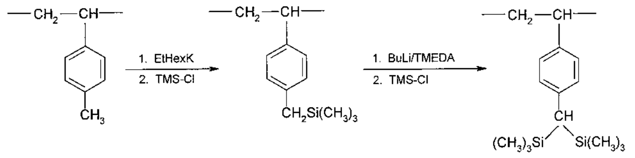


Figure 3. ^{29}Si and ^{13}C NMR spectra of silylated P(4-MS). Chemical transformation of P(4-MS) with one TMS group in the benzylic position (broken line, signal *d*) to P(4-MS) with two TMS groups in benzylic position (full line, signal *e*). See Scheme 1 and Results and Discussion.

Scheme 1



mL) of butyllithium (0.01 mol) followed by TMEDA (1.51 mL, 0.01 mol) was added to a stirred solution of silylated P(4-MS) (1.18 g, BuLi/4-MS = 1) in cyclohexane (118 mL). The mixture was stirred for 3 h at room temperature, quenched with an excess of TMS-Cl/THF, and precipitated in methanol. The silylated polymer was then dried at 40 °C under vacuum. The ^{29}Si and ^{13}C NMR spectra of this polymer are given in Figure 3.

Analytical Methods. NMR. ^{29}Si and ^{13}C NMR spectra were measured in $CDCl_3$ in 5 mm glass tubes using a Bruker DPX 300 spectrometer at frequencies of 50.6 and 75.4 MHz, respectively, with an internal deuterium lock. The number of data points was 32K, repetition delay 5 s, temperature 297 K, and the number of FID accumulations 4000−12 000. The DEPT pulse sequence was used to increase sensitivity of measurement of ^{29}Si NMR spectra. The mixing pulse was set to $\theta = 23°$ and polarization transfer time to $\tau = 48$ ms (this corresponds to coupling constant $^{2}J_{\mathrm{H-C-Si}} = 10.4$ Hz). ^{13}C NMR spectra were measured using a standard pulse sequence with inverse gated decoupling and repetition delay of 10 s. Hexamethyldisiloxane (HMDS) was used as an internal standard for calibration of the ^{29}Si and ^{13}C NMR scale, the chemical shifts of appropriate nuclei having the value 6.0 and 2.0 ppm, respectively, referred to tetramethylsilane (TMS).

Size Exclusion Chromatography (SEC). The starting model polymers and some products were characterized by SEC in THF at room temperature at a flow rate of 1 mL/min using two PSS-Plgel columns (5 μ; 10^3 and 10^5 Å) and RI and UV detectors. Polystyrene standards and Mark−Houwink constants for the PS/THF system ($K = 0.000\,117$, $a = 0.717$)[9] were used to calculate molecular weights and molecular weight distributions.

Results and Discussion

The aim of this study was to investigate the selectivity of metalation reactions on model homopolymers of low molecular weight, i.e., to find which sites were metalated depending on the metalating agent used and on reaction conditions. These findings should clarify some uncertainties of the exact position of metalation and grafting of block copolymers[10] composed of similar structure and thus be helpful in the preparation of block copolymers selectively grafted in defined positions.

Low-molecular-weight polystyrene, poly(4-methylstyrene), and their block copolymer (see Experimental Section) were used as model compounds in this study. These model polymers were metalated either by superbases “2-ethylhexylpotassium” and “phenylpotassium” or by a 1:1 (mol/mol) complex of *sec*-butyllithium with TMEDA under various reaction conditions. The superbases were prepared from 2-ethylhexyllithium and potassium *tert*-pentoxide in cyclohexane (EtHexK) or benzene (PhK). Unless stated otherwise, 3 M excess of potassium *tert*-pentoxide was always used in the above reaction. 2-Ethylhexyllithium was preferred to the commonly used butyllithium, because 2-ethylhexylpotassium formed through the lithium−potassium exchange is, in contrast to butylpotassium, highly soluble in aliphatic hydrocarbons. Depending on the metalation ratio and the solvent used, different numbers of monomer units and different sites in the polymer chain were metalated. For analytical reasons, multimetalated polymers were then quenched with an excess of chlorotrimethylsilane to introduce trimethylsilyl (TMS) groups at all sites originally bearing potassium or lithium atoms.

In addition, low-molecular-weight polystyrene and poly(4-methylstyrene) with trimethylsilyl group linked only to the polymer ω-chain end were prepared by anionic polymerization of the appropriate monomers and termination with TMS-Cl. They represent a model of growing PS and P(4-MS) grafts terminated with TMS-Cl in the graft copolymer, prepared by “grafting from” technique.[5]

TMS-Cl was chosen as quenching agent because of its high reactivity and minimum extent of side reactions in the reaction with organometallic compounds. Moreover, the resonances of TMS groups bonded to carbon atom appear as signals in the region from −0.5 to +0.5 ppm in the ^{1}H NMR spectrum, i.e., in the range of chemical shifts usually not occupied by any other species present in the silylated polymer. However, in some cases, different types of silylated species in the silylated polymer cannot be distinguished by their ^{1}H NMR chemical shifts. In contrast, the range of chemical shifts in ^{29}Si NMR spectrum is generally much broader than in ^{1}H NMR, and moreover, since the signals of TMS groups of silylated polymer are the only signals present in this spectrum, they can provide more detailed and unique information about the metalated sites in the polymer. For these reasons, the silylated model (co)polymers were studied mainly using ^{29}Si NMR, sometimes in combination with ^{13}C NMR.

A. Metalation of Polystyrene. Generally, two different types of hydrogens in PS are susceptible to attack by a metalating agent. Both aromatic and backbone methine protons can be metalated simultaneously because of their nearly equal thermodynamic acidity;[11] however, due to steric restrictions in the polymer chain, the ring-metalated derivatives are preferred.[12,13] The formation of ring-silylated and backbone-silylated polystyrenes, both resulting from the metalation and subsequent silylation, has been reported in the literature.[12,13]

Superbases as Metalating Agents. Using superbase EtHexK in cyclohexane at room temperature, we revealed that both rings and the backbone of PS can be metalated, depending on the metalation ratio used. At lower metalation ratios, EtHexK/S < 1, only aromatic protons were metalated. Namely, a signal of only one type of TMS group appeared at ca. −6 ppm in the ^{29}Si NMR spectrum of the silylated PS (Figure 1A, signal *a*). As the signal of TMS group in the corresponding monomeric model, phenyltrimethylsilane, is located at −5 ppm in the ^{29}Si NMR spectrum,[14] we attributed the signal *a* to TMS groups bonded in the PS ring. Since metalation of the ring is possible in para, meta, and ortho positions, the splitting of this signal is probably due to the above ring isomers.

On the other hand, at higher metalation ratios, EtHexK/S ≥ 1, in addition to the above signal, a new absorption corresponding to another type of TMS group emerged as a multiplet signal in the range from −1 to −1.5 ppm in the ^{29}Si NMR spectrum of the silylated PS (Figure 1B, signal *b*). This indicates that not only aromatic protons but also methine protons in the backbone were metalated (see structure in Figure 1B), which is consistent with earlier conclusions[13] based on ^{1}H NMR analysis of silylated PS. In contrast to our results, no backbone metalation was found by Nemes et al.,[15] based on the ^{13}C NMR analysis of carboxylated polystyrene prepared by metalation of PS and subsequent carboxylation with CO_2. However, a different superbase, i.e., prepared from butyllithium and potassium *tert*-butoxide and insoluble in hydrocarbon solvents, was used in the mentioned study. Thus, the solubility of superbase can play an important role in the metalation of sterically hindered polymer backbone.

Another metalating agent, (trimethylsilyl)methylpotassium in THF, reportedly[16] metalates cumene at low temperatures exclusively in the α-position of the side chain. Therefore, we applied a similar procedure using this agent, prepared in situ from (trimethylsilyl)methyllithium and potassium *tert*-pentoxide, to PS in an attempt to prepare backbone-metalated PS. No signal of TMS groups was found after silylation in ^{29}Si NMR spectrum of the corresponding polymer. Thus, in contrast to cumene, no metalation of PS occurred under otherwise similar conditions. That is why methods other than direct metalation must be probably used to prepare pure backbone-metalated PS free of ring-metalated isomers.

***s*-BuLi−TMEDA Complex as Metalating Agent.** Using *s*-BuLi−TMEDA in cyclohexane at room temperature instead of EtHexK, we revealed that only aromatic protons of PS were metalated regardless of the metalation ratio used. Namely, only the signal of TMS groups bonded in the ring (located at ca. −6 ppm; see above) appeared in the ^{29}Si NMR spectrum of the corresponding silylated polymer (Figure 1A).

The above results indicate that the metalation of PS by superbases gives rise to more different products than that by *s*-BuLi−TMEDA, but it offers a broader variability in the selection of reaction conditions. On the other hand, when exclusively ring-metalated PS in a simple process is required, metalation by the latter agent is the method of choice.

For completion of our results and as a model of growing styrene chains in the grafting process, we prepared living PS by anionic polymerization and terminated it with TMS-Cl. Resulting ω-silylated polystyrene exhibits multiplet signal of the TMS group located at 1.5−2.5 ppm in the ^{29}Si NMR spectrum (Figure 1C, signal *c*). This multiplicity has been attributed[17] to the tacticity of styrene units at the chain end.

B. Metalation of Poly(4-methylstyrene). The ring-bonded methyl group is the most acidic site in the polymer,[11] and therefore, it should be metalated preferentially. Thus, P(4-MS) with TMS group only in benzylic positions should arise after the silylation (see structure in Figure 2A). In other words, the ^{29}Si NMR spectrum of selectively metalated and subsequently silylated P(4-MS) should exhibit only the signal of the given type of TMS groups. Unfortunately, metalation of P(4-MS) leads to this ideal result mostly under specific reaction conditions characterized by the presence of benzene.[18] In other cases, it often lacks selectivity, and silylated P(4-MS) with TMS groups bonded in different positions results after silylation as described below.

Superbases as Metalating Agents. Using EtHexK in cyclohexane, we revealed that the metalation of P(4-MS) is highly selective only at low metalation ratios, i.e., EtHexK/4-MS < 1. Namely, a signal of only one type of TMS group located at ca. −0.4 ppm appeared in the ^{29}Si NMR spectrum of the silylated polymer (Figure 2A, signal *d*). As the signal of TMS group in the corresponding monomeric model, benzyltrimethylsilane, appears at 0.4 ppm in the ^{29}Si NMR spectrum,[14] we attributed the signal *d* in Figure 2A to TMS groups bonded exclusively in the benzylic positions.

We further disclosed that various positions in P(4-MS) can be metalated at higher metalation ratios, i.e., EtHexK/4-MS ≥ 1. At metalation ratios 1 ≤ EtHexK/4-MS < 2, not only methyl groups but also aromatic protons and backbone were metalated. The ^{29}Si NMR spectrum of the corresponding silylated polymer (Figure 2B) reveals the presence of the signals of three types of TMS groups located at ca. −0.4 ppm (signal *d*), −1 ppm (signal *b′*), and in the region of −6 to −7 ppm (signals *a′* and *a″*). The signal *d* corresponds to TMS group bonded in the benzylic position (see above). The chemical shift of the signal *b′* is nearly the same as that of the signal *b* in the backbone-silylated PS (compare with Figure 1B). Therefore, we speculate that also backbone methine protons in P(4-MS) were metalated. The chemical shifts of the signals *a′* and *a″* correspond to TMS groups bonded in the ring (compare with Figure 1A). Since both meta and ortho positions in P(4-MS) can be metalated, we speculate that the signals *a′* and *a″* correspond to the above ring isomers.

At metalation ratios EtHexK/4-MS ≥ 2, in addition to signals mentioned above, a new signal of another type of TMS groups emerged at ca. −0.2 ppm in the ^{29}Si NMR spectrum of the corresponding silylated polymer (Figure 2C, signal *e*). The number of types of acidic hydrogen atoms that can be metalated in P(4-MS) is limited; due to the complete absence of this signal in the ^{29}Si NMR spectrum of silylated PS prepared under otherwise identical conditions, we assume that also *geminal* dimetalation of methyl group occurred, leading to *geminally* disilylated product after silylation (see structure in Figure 2C). Our conclusion is supported by the following evidence: (i) The signal of TMS groups in the corresponding monomeric model, i.e., phenylbis(trimethylsilyl)methane, is also shifted downfield (1.6 ppm)[19] to the signal of TMS group in benzyltrimethylsilane (0.4 ppm)[14] in the ^{29}Si NMR spectrum. (ii) A very facile *geminal* dimetalation of methyl group in toluene with the rate comparable to monometalation was described.[20] (iii) The signal proposed for *geminal* TMS groups in benzylic position of P(4-MS) was confirmed by us experimentally by selective metalation of methylene protons between aromatic ring and benzylic TMS group in the silylated P(4-MS) (see Scheme 1). These hydrogen atoms in the α-position to the silicon atom are more acidic than hydrogen atoms in methyl group on the ring due to the delocalization of negative charge into antibonding orbitals of the Si−C bonds. It was claimed[21] that metalation of 4-methylbenzyltrimethylsilane by *n*-BuLi−TMEDA in cyclohexane occurs exclusively at the methylene carbon and not at the methyl group. Therefore, we applied the same procedure to P(4-MS) with TMS group only in the benzylic positions, which was prepared under the conditions described above (EtHexK/4-MS < 1, see Experimental Section and Scheme 1). Indeed, the peak at −0.4 ppm corresponding to TMS group in the benzylic position of the starting polymer nearly vanished in favor of the peak at −0.2 ppm in the product, as can be seen in the ^{29}Si NMR spectrum (Figure 3A). This chemical shift can be seen more distinctly in the ^{13}C NMR spectrum (Figure 3B), where the signal of benzylic TMS group of the starting polymer (at −1.7 ppm) disappeared in favor of the signal at 0.4 ppm. The position of the new peak in both ^{29}Si and ^{13}C NMR spectra matches exactly the position of the peak proposed for *geminal* TMS groups in P(4-MS) metalated by a high excess of EtHexK. Moreover, the described changes in ^{13}C NMR spectra of the above polymer are in excellent agreement with the location of TMS groups in ^{13}C NMR spectra of monomeric models, benzyltrimethylsilane (−2.2 ppm)[14] and phenylbis(trimethylsilyl)methane (0.5 ppm).[19] Thus, *geminal* dimetalation of the methyl group in P(4-MS) seems to be proved.

If selective metalation of P(4-MS) exclusively on methyl groups and simultaneously high metalation yield were required, superbase "phenylpotassium" in benzene must be used. In contrast to EtHexK in cyclohexane, we could apply higher metalation ratios (PhK/4-MS = 2) to achieve higher yield of P(4-MS) metalated on methyl groups without the danger of ring or backbone metalation, as only the signal of TMS group in the benzylic positions appeared in the ^{29}Si NMR spectrum of the silylated polymer (Figure 2A). At higher metalation ratios, PhK/4-MS > 2, in addition to the above signal, the signal of *geminally* bonded TMS groups with very low intensity appeared in the ^{29}Si NMR spectrum (not shown).

***s*-BuLi−TMEDA Complex as Metalating Agent.** We revealed that metalation of P(4-MS) by this complex in cyclohexane does not lead to the product selectively metalated on the methyl group even at low metalation ratios, i.e., *s*-BuLi/4-MS < 1. Methyl groups were metalated preferentially (≥90% mol), but some ring metalation also occurred (Figure 2D). The content of ring-metalated product seems to be independent of the metalation ratio used since it remains below 10 mol % even at higher metalation ratios, i.e., *s*-BuLi/4-MS ≥ 1. No products corresponding to metalation in other positions were detected under the given conditions (*s*-BuLi/TMEDA = 1:1) regardless of the metalation ratio. On the other hand, it was noted[22] that metalation of toluene by a similar complex with nonequivalent ratio of metalating components (BuLi/TMEDA > 1) leads also to the product of *geminal* dimetalation of methyl group. For this reason, we metalated P(4-MS) by the complex *s*-BuLi/TMEDA = 2:1 under otherwise similar reaction conditions. No product of *geminal* dimetalation and, moreover, no difference in the selectivity of metalation were found in comparison with the metalating system *s*-BuLi/TMEDA = 1:1. Thus, the metalation of P(4-MS) by the above complex seems to be little sensitive to the *s*-BuLi/TMEDA ratio.

As a model of growing 4-methylstyrene chains in the grafting process, we prepared living P(4-MS) by anionic polymerization and terminated it with TMS-Cl. Resulting *ω*-silylated poly(4-methylstyrene) exhibits multiplet signal of TMS group located at 1.4−1.8 ppm in the ^{29}Si NMR spectrum (Figure 2E, signal *c*′). This multiplicity corresponds to the tacticity of 4-methylstyrene units at the chain end.

C. Metalation of Poly(styrene-*block*-4-methylstyrene). The selective metalation of methyl groups in P(4-MS) block leaving all other positions unaffected was a challenge for us. However, we found that some metalating agents which caused selective metalation of P(4-MS) homopolymer exhibited low selectivity in the metalation of its block copolymer with styrene.

Thus, using superbase EtHexK in cyclohexane, both methyl groups in the P(4-MS) block and aromatic protons in the PS block were metalated (in molar ratio 4:1) even at low metalation ratios, i.e., EtHexK/4-MS < 1. The same positions were metalated (in molar ratio 1:1) by the *s*-BuLi−TMEDA complex, i.e., with no enhanced preference for the metalation of the methyl group as in the above case. Only the metalating agent, superbase "phenylpotassium" in benzene, was able to metalate given block copolymer exclusively on methyl groups in the P(4-MS) block and is, therefore, the agent of choice in this case.

In some cases, the metalation of the block copolymer can differ from that of corresponding individual homopolymers. As a consequence, the regioselectivity of metalation of one block in the block copolymer can be diminished or increased depending on the type of the second block.[23−25] Different steric requirements of the block copolymers in comparison with the homopolymers and, as a consequence, different accessibility of acidic hydrogen atoms in homopolymers and copolymers can be responsible for such a different behavior. Nevertheless, the positions of the signals of TMS groups in ^{29}Si and ^{13}C NMR spectra corresponding to the individual types of reaction centers are nearly the same in the case of both block copolymers and the corresponding homopolymers. Thus, the structural information obtained from the model metalations can be used in the synthesis of selectively grafted block copolymers by the "grafting from" method. Detailed knowledge of the location of reactive (metalated) centers in the (co)polymer is important in the synthesis of more complex polymer structures by anionic techniques.

Conclusions

Significant differences in regioselectivity of metalation, using superbases and organolithiums complexed with TMEDA as metalating agents, were confirmed on the basis of model metalations of polystyrene and poly(4-methylstyrene). After the functionalization of metalated sites in the (co)polymer with trimethylsilyl groups, ^{29}Si NMR alone or in combination with ^{13}C NMR turned out to be a powerful tool for distinguishing trimethylsilyl groups bonded in different positions in the (co)polymer, and thus, valuable information about the metalated sites was obtained.

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