Controlled Functionalization of Polystyrene: Introduction of Reactive Groups by Multisite Metalation with Superbase and Reaction with Electrophiles

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ABSTRACT: The controlled functionalization of polystyrene using a process of metalation with a potassium superbase followed by reaction with electrophiles is described. The method is advantageous because metalation is extremely efficient, occurring rapidly even at room temperature, and the degree of functionalization can be controlled over a very broad range. Functionalization with trimethylsilyl groups allows effective monitoring and quantification of the metalation process. Other examples of modification include the introduction of small dendritic fragments by reaction with a dendron having an aldehydic focal point or the introduction of carboxylic acid pendant groups. This method, which has little effect on the polydispersity of the polymer, has broad applicability for the functionalization of a wide spectrum of polymers containing active hydrogens and may also be used to prepare randomly branched or star structures.

Introduction

A novel approach to the functionalization of polyether dendritic macromolecules[1−3] or linear polymers[4] has been described recently. This method involves metalation of the parent polymer by a superbase (SB) followed by a reaction with an electrophile. The modified superbase prepared from (3-lithiomethyl)heptane and an excess of potassium alkoxide[5,6] appears to be of particular interest for the metalation of hydrocarbon polymers such as polystyrene (PS) because it is fully soluble in aliphatic hydrocarbons. The metalation of polystyrene by reagents obtained by complexing butyllithium with polyamines such as tetramethylethylenediamine (TMEDA) has been known for some time[7−9] but the kinetics of the process and the degree of metalation are frequently difficult to control. The use of the modified superbase in the metalation of polystyrene is now investigated in detail and compared with the metalation with other reagents.

Experimental Section

Materials. Polystyrene of molecular weight 20 400 with a polydispersity index $M_w/M_n = 1.04$ was obtained from Pressure Chemical Co. (3-Lithiomethyl)heptane and potassium *tert*-pentoxide were prepared according to ref 5 and used to prepare the superbase;[5,6,10] 3,5-bis(benzyloxy)benzaldehyde, [G-1]-CHO, was prepared as previously described.[11] Organic halides were vacuum distilled in the presence of calcium hydride prior to use. THF was distilled from sodium anthracenide and cyclohexane with butyllithium, both under an inert atmosphere. Diazomethane was prepared from DIAZALD (Aldrich Chemical Co.).

Characterization of the Products. Proton NMR spectra were recorded in $CDCl_3$ on a Bruker WM 300 instrument using the solvent signal as internal reference. Size exclusion chromatography was performed with a Model 510 HPLC pump connected to a U6K injector (Millipore Waters Chromatography) to three 300 mm × 8 mm i.d. PL GEL columns (Mixed C, 100 Å, and 500 Å, Polymer Laboratories) thermostated at 30 °C. The separation was monitored by a differential viscometer (Viscotek Corp.) and a differential refractometer Refractomonitor IV (Milton Roy); column calibration was achieved using 18 polystyrene standards, each injected three times to ensure accuracy of data.

Procedures: Typical Procedure for PS Metalation and Reaction with Electrophiles. (A) Low Extent of Functionalization (for Concentration of 4 Styrene Units/SB). A round bottom flask fitted with a magnetic stirring bar and a three-way stopcock was filled with 10 mL of cyclohexane, 5.04 mL of a 1 M solution of potassium *tert*-pentoxide in cyclohexane (5.04 mmol), and 1.95 mL of 0.863 M (3-lithiomethyl)heptane solution in cyclohexane (1.68 mmol). After 2 min of stirring at room temperature, a solution of 0.700 g of polystyrene (6.72 mmol of styrene units) in 15.9 mL of cyclohexane was added and stirred for 1 h (final [PS] = 0.20 mol/L). Within a few minutes, an orange precipitate, which later became orange-red, separated. Then 0.01 mol of the electrophile was added (deuterium oxide, TMSCl, or dodecyl bromide in the form of a ca. 20% solution in dry THF) to the metalation mixture. Alternatively, an aliquot of the mixture was taken by a syringe that contained a THF solution of the electrophile. After 15 min, the substituted polystyrene was isolated by precipitation in methanol (for the dodecyl derivative 1% LiCl in methanol). The solid was washed with methanol and water and then dried in vacuum at room temperature for 12 h.

(B) High Extent of Functionalization. For the metalation of polystyrene to higher degrees of functionalization, the procedure was essentially the same; however, the concentration of polystyrene in the final mixture was only 0.15 mol/L. All operations with organometallics were done in an atmosphere of purified argon.

Carboxylated Polystyrene. The metalation mixture prepared according to the general procedure above was diluted with the same volume of dry hexane and siphoned onto ca. 100 g of crushed, dry solid carbon dioxide. After reaching room temperature, the polycarboxylic salt was converted into free acid in the following way: 35 mmol of TMSCl was added and the mixture was refluxed for 2 h under an inert atmosphere. The mixture was then concentrated to ca. one-third of the original volume under vacuum (to remove excess of TMSCl), 20 mL of water was added, and the mixture was refluxed for 1 h. Then the remaining organic solvent was removed under vacuum. The white solid was filtered off, washed with water, and dried in vacuum. It was then dissolved in 20 volumes of THF and precipitated into 200 volumes of hexane. The free polyacid was filtered, washed, and dried under vacuum for 12 h at room temperature.

Esterification of the Polyacid. The polyacid (0.074 g) was dissolved in 2 mL of THF, and a solution of diazomethane

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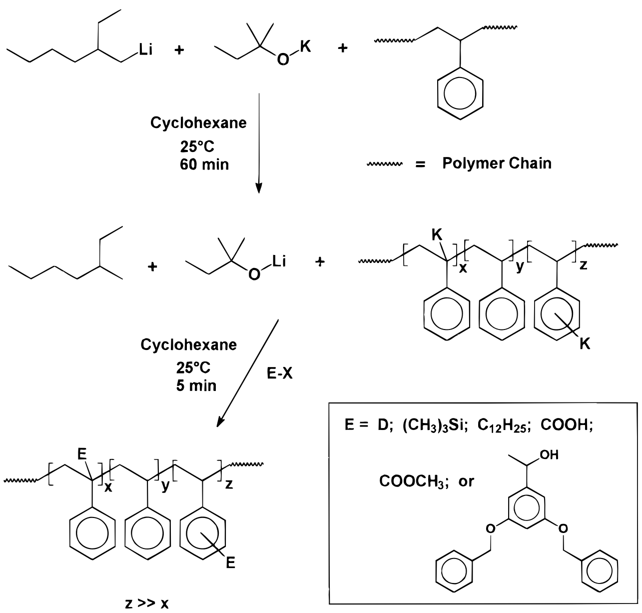
Table 1. Preparation of Multisite Substituted Polystyrenes

styrene units[a] superbase	E Group (atom) introduced	yield (mol %)	*n* (ratio of styrene units/E)[b]	effectiveness[c] of substitution (%)	mol wt of substituted PS × 10^{-3}		
					M_n(calcd)[d]	M_n(found)	M_w/M_n
4	D	94			20.4	21.8	1.11
4	$Si(CH_3)_3$	93	5.3	75	23.1	29.6	1.08
4	$C_{12}H_{25}$	97	6.5	62	25.1	29.4	1.18
4	$COOCH_3$	64	4.1	98	23.2	25.4	1.15
4	CH(OH)-[G-1][e]	84	6.1	66	30.6	36.4	1.14
1	D	90			20.5	19.1	1.09
1	$Si(CH_3)_3$	91	1.5	6.7	29.8	35.7	1.15
1	$C_{12}H_{25}$	75	1.6	61	40.5	60.0	1.86[f]
1	$COOCH_3$	78	1.2	83	28.0	27.6	1.39
1	CH(OH)-[G-1][e]	99	2.7	37[g]	52.4	51.4	1.37

[a] Expressed as a molar ratio. The polystyrene used had $M_n = 20\,400$, $M_w/M_n = 1.03$. [b] *n* is the average number of styrene units per unit of electrophile group E incorporated (calculated from ^{1}H NMR data). [c] Effectiveness = [styrene units/superbase] × 100/*n*. [d] M_n(calcd) = 196[104.1 + mol wt (E) $-1/n$]. [e] G-1 is a 3,5-bis(benzyloxy)phenyl moiety; for structure, see lower right-hand corner of box in Scheme 1. [f] The polymer has a broad polymodal molecular weight distribution. [g] Only one equivalent of aldehyde electrophile was used for this reaction.

Scheme 1



in diethyl ether was added until the evolution of nitrogen ceased and the yellow color of excess diazomethane persisted for 30 min. The solution was concentrated to one-half of its original volume, and the polyester was precipitated in hexane and reprecipitated from a THF solution into methanol.

Reaction of Polymetalated Polystyrene with [G-1]-CHO. [G-1]-CHO (3,5-bis(benzyloxy)benzaldehyde, 0.100 g, 0.31 mmol) dissolved in 3 mL of THF was added with stirring at room temperature. To 5.0 mL of the metalation mixture prepared according to the general procedure (containing 1.00 mmol of styrene units with 0.25 mmol of metalated sites. The mixture was stirred for 1 h, and then 0.5 mL of methanol was added, giving rise to a yellow solution. The substituted polystyrene was isolated from this solution by precipitation into 120 mL of hexane with a few pieces of solid carbon dioxide (to neutralize the bases). The solid was filtered, washed with hexane and water, and dried under vacuum, yielding 0.163 g of crude substituted polystyrene, *i.e.*, 109% mol (impurities). For purification, the product was precipitated twice from THF solution in hexane. The higher substituted polystyrene (styrene units/SB = 1) was precipitated once more from THF solution into methanol containing 1% LiCl.

Results and Discussion

Superbase prepared from (3-lithiomethyl)heptane and 3 equiv of potassium *tert*-pentoxide metalates polystyrene smoothly in cyclohexane at room temperature (Scheme 1). The metalated polystyrene, containing potassium substituents at a multiplicity of sites, separates within a few minutes as an orange precipitate. It is likely that this precipitate contains not only the metalated polystyrene but also its adduct with the excess of potassium alkoxide. Analogous adducts of potassium alkoxides have previously been described and identified for phenylpotassium[10] and benzylpotassium.[5] The metalation reaction is completed within a few minutes and reaction times longer than 30 min do not appreciably increase the degree of metalation.

Functionalization of Metalated Polystyrene by Reaction with Electrophiles. The "polymetalated" polystyrene is then allowed to react *in situ* with various electrophiles to afford a randomly functionalized polystyrene within a few minutes of reaction at room temperature. Our initial experiments have used a variety of test electrophiles including the following: deuterium oxide, chlorotrimethylsilane (TMSCl), dodecyl bromide, carbon dioxide, and a small dendritic[11] aldehyde [G-1]-CHO. In view of the very high reactivity of the organopotassium derivative, it is possible to anticipate favorable functionalization reactions with a broad spectrum of other electrophiles.

The reaction of polymetalated polystyrene with a first-generation dendritic aldehyde [G-1]-CHO is not only an example for its reaction with carbonyl compounds, but it also demonstrates the applicability of this grafting process for the preparation of highly branched dendritic structures. An alternative synthesis of this type of copolymers using the direct copolymerization of dendritic macromonomers has been described recently by Hawker and Fréchet.[12] A copolymer of dendrimer and polystyrene with a reversed architecture may also be prepared in a similar way; *i.e.*, a polyether dendrimer is first metalated by superbase and the metalated dendrimer is then used as a multisite initiator for the anionic polymerization of styrene to finally afford a dendrimer with pendant polystyrene chains.[13]

The yields and properties of multisite functionalized polystyrene prepared by the method mentioned above using a variety of electrophiles are summarized in Table 1. The yields are generally quite high. The degree of polystyrene metalation is controlled by the molar ratio of styrene repeat units in the polymer to superbase (PS/SB ratio) and may be varied almost at will within a broad range, such as from 10 to 1 styrene units per equivalent of superbase. The effectiveness of superbase, *i.e.*, the number of functional groups introduced as a function of the amount of superbase used in the metalation, varies from moderate to good (Table 1). Lower superbase effectiveness may be caused by the occurrence of side reactions either during the metalation (*e.g.*,

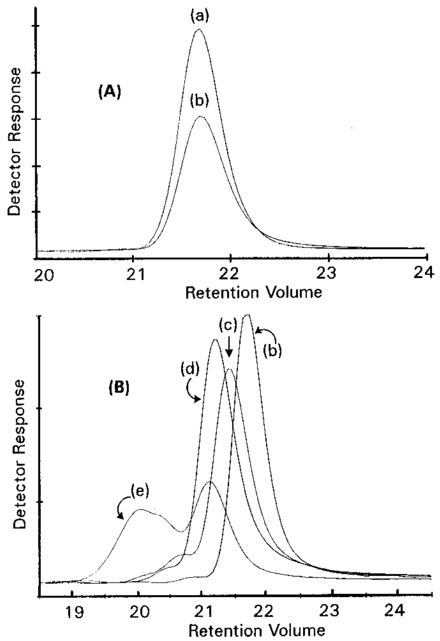


Figure 1. SEC eluograms of functionalized polystyrenes. Upper part A: (a) unsubstituted PS, (b) deuterated PS (ratio of styrene units per ^{2}H atom < 2). Lower part B: (b) deuterated PS (ratio of styrene units per ^{2}H atom < 2); (c) methoxycarbonyl-substituted PS (ratio of styrene units per methoxycarbonyl group = 1.2); (d) trimethylsilyl-substituted PS (ratio of styrene units per TMS group = 1.5); (e) dodecyl-substituted PS (ratio of styrene units per C_{12} group = 1.6).

superbase decomposition with time) or during the subsequent reaction with electrophiles. In the case of the reaction with the aldehydic dendron [G-1]-CHO, the low effectiveness may be due to the fact only 1 equiv of the aldehyde was used instead of the normal 5-fold excess of electrophile used in other experiments. The results shown in Table 1. document that vastly improved results are obtained in the metalation of polystyrene with superbase when compared to results obtained with the other reagents previously used for the same purpose.[7-9] In particular, the kinetics of the metalation reaction appear to be much improved, with more effective metalation occurring within a shorter time at room temperature. In addition, and as expected, potassium-substituted polystyrene appears to be significantly more reactive toward electrophiles than its lithium-substituted counterpart.

Effect of Metalation/Functionalization on Molecular Weight and Polydispersity. In general, the molecular weights of polystyrene functionalized by this method are quite close to the calculated values (Table 1, Figure 1). The molecular weight distribution data obtained by SEC show that some slight broadening occurs during functionalization, and this tendency is more pronounced if functionalization is carried out to a higher extent. The dodecyl-substituted polystyrene is an exception and its behavior is quite unusual (Table 1, Figure 1B, curve e). The mean molecular weight of the dodecyl-substituted polystyrene is much higher than the calculated value, and it exhibits a broad, polymodal molecular weight distribution curve. This behavior may be explained by the following side reactions:

$$\mathrm{PS(K)}_n + \mathrm{C_{12}H_{25}Br} \rightleftarrows \mathrm{PS(K)}_{n-1}\mathrm{Br} + \mathrm{C_{12}H_{25}K} \qquad (1)$$

$$\mathrm{PS(K)}_{n-1}\mathrm{Br} + \mathrm{PS(K)}_n \rightleftarrows \mathrm{PS(K)}_{n-1}\mathrm{-PS(K)}_{n-1} + \mathrm{KBr} \qquad (2)$$

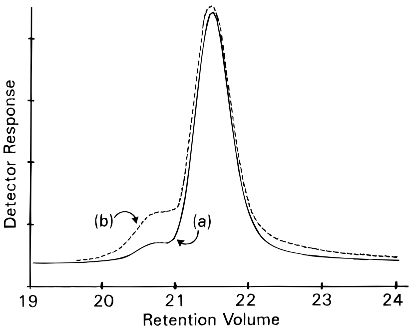


Figure 2. SEC eluograms of polystyrenes after metalation by various superbases (24 h) and protolysis: (a) superbase = (2-ethylhexyl)lithium + 3 equiv of potassium *tert*-pentoxide; (b) superbase = (2-ethylhexyl)lithium + 1 equiv of potassium *tert*-pentoxide.

As a result of such metal–halogen exchange side reactions that lead to the coupling of polymer chains, molecules with multiples of the original molecular weight are obtained. Thus, even if only a few of these coupling reactions actually occur, they cause a large molecular weight increase while still leaving a significant portion of the metalated sites in polystyrene available for the normal nucleophilic displacement reaction on dodecyl bromide. Although the equilibrium in reaction 1 is shifted to the left, even a small amount of metal–halogen exchange has a great effect on the molecular weight distribution of the product because reaction 2 cannot be avoided. As expected, the extent of these side reactions is more pronounced for highly metalated polystyrene. Interestingly, no cross-linked polystyrene has been obtained in this process, obviously because only a very limited number of such coupling reactions occurs.

In contrast to the results obtained with longer metalation times, the polydispersity of substituted polystyrene is only slightly higher than that of the starting polymer if the metalation time is kept below 2 h. For example, the metalation of a narrow-dispersity polystyrene ($M_w/M_n = 1.04$) for 30 min followed by protolysis leads to a product with an essentially unchanged polydispersity index ($M_w/M_n = 1.06$). However, if the metalation time is increased to 24 h, the polydispersity index increases to 1.1 (Figure 2, curve a). In metalations with no excess of potassium *tert*-pentoxide (*i.e.*, using a superbase prepared from equimolar amounts of the two components), the increase in polydispersity is significantly higher, reaching a value of 1.2 (Figure 2, curve b). This further confirms that it is more advantageous to use modified superbase containing an excess of the potassium alkoxide.

The polymetalated polystyrene is best handled in nonpolar hydrocarbon solvents because significant decomposition and other side reactions occur in the presence of aprotic donor solvents. For example, the polydispersity index of a trimethylsilyl-substituted polystyrene, prepared by metalation in cyclohexane for 300 min followed by reaction with chlorotrimethylsilane, is still near 1.09 (Figure 3, curve a). However, if the metalation mixture is diluted with THF and TMEDA (each 20% by volume) just 10 min before quenching with TMSCl, the polydispersity index in the final product exceeds 1.6 and a polymodal molecular weight distribution is observed for the reaction product (Figure 3, curve b). In addition, the number of organometallic bonds capable of reaction with TMSCl after this treatment decreases and only 0.04 TMS groups per styrene unit

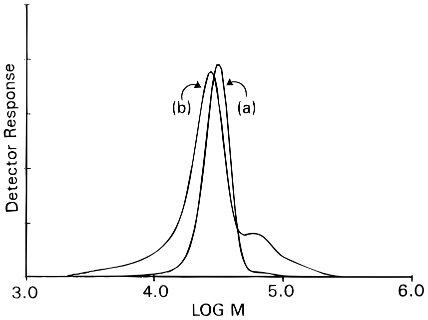


Figure 3. Transformation of multisite metalated polystyrene in the absence or presence of aprotic donor solvents: (a) metalation of polystyrene in cyclohexane quenched with trimethylsilyl chloride after 300 min; (b) the same metalation mixture quenched with trimethylsilyl chloride 10 min after addition of THF and TMEDA.

are found instead of 0.2 as is the case in the absence of THF/TMEDA. Thus, donor solvents, especially TMEDA, substantially accelerate the occurrence of decomposition and unfavorable side reactions for potassium multisite-metalated polystyrene.

Attempts to metalate polystyrene under conditions other than those mentioned above were unsuccessful. The rate of polystyrene metalation by a superbase prepared from butyllithium and potassium *tert*-pentoxide in THF at −80 °C was too slow. At room temperature, the reaction of the powerful organometallic reagents with THF predominates. Superbase prepared from butyllithium in cyclohexane is considered to be less suitable for the metalation of polystyrene because both the superbase and the metalated polystyrene are insoluble in cyclohexane and therefore a slow reaction can be anticipated.

Determination of the Site of Metalation. The site of potassium substitution in polystyrene was investigated by means of proton NMR spectroscopy using samples quenched with electrophiles and model compounds prepared for comparison purposes. Cumene, used as a simple model for polystyrene, was metalated by superbase using conditions identical to those used for polystyrene, and the cumylpotassium was then transformed by reaction with TMSCl. Three components were detected by GC/MS analysis in the isolated trimethylsilylated cumene. Two of these (73% by weight) had almost the same mass spectrum and are thought to be isomers of ring-substituted cumene. Analysis of the third component (27% by weight) reveals that it is a cumene moiety containing a trimethylsilyl group in its benzylic position. This isomer distribution obtained in this reaction is different from that obtained in the metalation of cumene using the butyllithium−TMEDA complex, where 97% of ring-substituted and only 3% of benzyl-substituted products were formed.[14] The benzylic position in cumene, although thermodynamically preferred, is obviously sterically hindered by the adjacent methyl groups and therefore, side chain metalation is only achieved using the much more reactive superbase. The ^{1}H NMR spectrum of the mixture of trimethylsilylated cumenes exhibits three resonances of CH_3−(Si) protons in the range of −0.5 to +0.5 ppm: at 0.26 and 0.25 ppm (for a total of 87%) and at −0.11 ppm (13%). Although the percentages of substitution determined by the two methods are not in close agreement, the more important finding for subsequent comparisons with substituted polystyrene is that TMS groups bound to aromatic rings absorb around 0.26 ppm, while those bound in the benzylic position absorb upfield at −0.11 ppm.

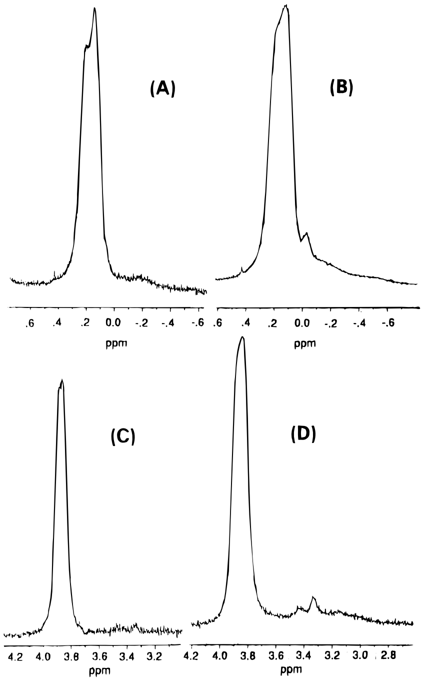


Figure 4. Proton NMR spectra of trimethylsilyl- and methoxycarbonyl-substituted polystyrenes: (A) 5.3 styrene units per trimethylsilyl group; (B) 1.5 styrene units per trimethylsilyl group; (C) 4.1 styrene units per methoxycarbonyl group; (D) 1.2 styrene units per methoxycarbonyl group.

In another experiment, the polymerization of styrene was initiated by benzylpotassium and then termination of the resulting polystyrene was accomplished using TMSCl, giving rise to a polystyrene in which each chain has a single TMS group attached at its terminal secondary benzylic position. The proton NMR spectrum of this polymer exhibits a multiplet between −0.12 and −0.27 ppm. In comparison, the proton NMR spectra of phenyltrimethylsilane[15a] and benzyltrimethylsilane[15b] show CH_3−(Si) signals at 0.29 and −0.01 ppm, respectively. Thus, it may be concluded that the proton signals for trimethylsilyl groups bound in the benzylic position of polystyrene should be located upfield of 0 ppm.

Two or three signals were detected in the proton NMR spectra of our trimethylsilylated polystyrene in the range between +0.5 and −0.5 ppm, depending on the degree of polystyrene substitution. In the "medium"-substituted polystyrene—with about 5 styrene units/TMS group—only two major signals at 0.23 and 0.16 ppm are found, corresponding to the ring-bound TMS groups (probably *m* and *p* derivatives) (Figure 4A). In addition to the two major signals at 0.2 and 0.16 ppm (representing 85% of the total TMS substitution), the "highly" substituted polystyrene—with about 1.5 styrene units/TMS group—also shows a new signal at −0.07 ppm (15%), which can be assigned to TMS groups bound to the backbone benzylic positions (Figure 4B). It therefore appears that the distribution of regioisomers in the metalation of polystyrene depends on the concentration of superbase used for the modification. At higher superbase concentration, some benzylic positions of polystyrene can also be metalated in addition to the aromatic rings, while at low superbase concentrations only the aromatic rings are metalated.

Similar findings are also made for polystyrene substituted with the methoxycarbonyl group. In a "medium"-substituted polystyrene (about 4 styrene units/ester group), only two signals near 3.86 ppm were detected (Figure 4C), while in the "highly" substituted polystyrene (about 1.2 styrene units/ester group) signals at 3.86 ppm (80% weight) and near 3.4 ppm (20% weight) were found (Figure 4D). In comparison, the proton NMR spectra of methyl benzoate[15c] and methyl phenylacetate[15d] show $CH_3-(O)$ signals at 3.92 and 3.49 ppm, respectively. Thus, the proton NMR spectra of polystyrene substituted with methoxycarbonyl groups are in full agreement with the spectra of the trimethylsilylated polystyrene and confirm a substitution pattern where aromatic substitution predominates over backbone (benzylic) substitution. It is nevertheless interesting to note that the benzylic position, despite its well-known lack of reactivity,[16] can actually be accessed.

Overall, these results indicate that the metalation of polystyrene by superbase, and consequently the functionalization by electrophiles, occurs primarily on the aromatic rings of the polymer. The proportion of substituents bound in the benzylic positions of polystyrene is low, although it may be increased by using a higher SB/PS ratio. Accordingly, our earlier preliminary results on the distribution of substituents[4] appear to have overestimated benzylic substitution.

Conclusion

Superbase appears to be the reagent of choice for the side-chain functionalization of polystyrene. Randomly substituted polystyrenes containing a variety of side-chain pendant groups are obtained in a simple one-pot process involving the introduction of potassium atoms, followed by quenching with electrophilic species. The use of potassium superbases leads to polymers with highly reactive organopotassium sites that are capable of rapid reaction with a broad spectrum of electrophiles. The average degree of substitution of polystyrene may be varied within a broad range and may even reach almost one substituent for each styrene unit. When compared to other metalation procedures, the use of potassium superbases is advantageous for its effectiveness, experimental ease, and applicability to room temperature modifications. Overall, this efficient one-pot procedure, which obviates the need for specialty monomers or demanding polymerization techniques, is likely to be of great interest for the preparation of specialty polymers and copolymers that may have outstanding interfacial properties or high chemical reactivity. The solubility of the superbase in hydrocarbon solvents is also extremely advantageous for the chemical modification of commodity hydrocarbon polymers such as the newly commercialized high-performance elastomers[17] derived from poly(isobutylene-*co*-4-methylstyrene).

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