REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE June 30, 1996	3. REPORT TYPE AND DATES COVERED Technical Report # 29

4. TITLE AND SUBTITLE

Functionalization of Reactive Polymers by Metalation with Superbases followed by Reaction with Electrophiles

5. FUNDING NUMBERS

C N00014-91-1338

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8. PERFORMING ORGANIZATION REPORT NUMBER

C N00014-91-1338

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Department of the Navy
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

19960711 002

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

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12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

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14. SUBJECT TERMS

Superbase, rubber, functionalization, surface, metalation

15. NUMBER OF PAGES

14

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL

OFFICE OF NAVAL RESEARCH

Grant # N00014-91-J-1338

R&T Code 313t003---07

Dr. Kenneth J. Wynne

Technical Report #29

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ABSTRACT:

In order to test novel routes for the functionalization of polyolefins, hydrocarbon-soluble superbases have been used for the selective metalation of a copolymer of isobutylene and p-methylstyrene. The metalation reaction directed at the benzylic p-methyl position is followed by ^{1}H NMR spectrometry after quenching with an electrophile. Superbases obtained by the procedure of Lochmann involving the reaction of butyl lithium with a heavier alkali alkoxide have a reactivity that increases with the size of the metal cation. Best results are obtained using a superbase derived from s-BuLi and cesium l-(-)-menthoxide in the ratio of 1:3. Complete metalation of all the benzylic p-methyl groups is possible if an excess of superbase is used. This method of functionalization developed for solutions of the poly(isobutylene-co-p-methylstyrene) rubbers may also be applicable to introduce functional groups onto surfaces.

Introduction

Superbases (SB) have not only been used widely as highly reactive and selective reagents in organic chemistry[1-8], but they also have recently found applications in polymer synthesis.[9,10] Because of their high reactivity and solubility in a variety of reaction media the SB's are attractive reagents for the introduction of functional groups into polymers that are normally considered to have low reactivity. For example, we have been interested in the functionalization of a novel ozone-resistant elastomer obtained by the copolymerization of isobutylene with a small amount of p-methystyrene. The poly(isobutylene-*co*-p-methylstyrene) [poly(IB-PMS)] elastomer is prepared by cationic polymerization at low temperature in the presence of Lewis acid catalysts.[11] Typically this copolymer only contains a very small percentage of p-methylstyrene (PMS) units (2.3 mol%). Since the copolymer is largely poly(isobutylene) its properties are essentially those of butyl rubber, but the absence of the small percentage of olefinic unsaturation normally derived from the incorporation of some isoprene[12] in butyl rubber renders the material more chemically inert, in particular to the action of ozone. Conversely, this lack of olefinic unsaturation also means that novel chemistry based on the functionalization of the p-methyl styrene moieties must be developed for the curing of this elastomer. Free-radical bromination of the primary benzylic positions on the copolymer[11] has been used to afford a slightly halogenated rubber that can be cured by electrophilic aromatic substitution processes[13,14]. For some practical applications, it is desirable to develop a reactive polyisobutylene elastomer that is halogen-free. Since it is preferable to maintain the very low percentage of PMS incorporated into the final copolymer in order to preserve its outstanding elastomeric properties, this is a demanding process that requires very effective functionalization chemistry. For example a copolymer with M_n=250,000 has an average of only ~98 PMS units for well over 4000 isobutylene units per chain.

In earlier work with poly(IB-PMS) copolymers containing high percentages of PMS, Sharkey and Harris[15] have used a large excess of s-BuLi and N,N,N',N'-tetramethylethylene diamine (TMEDA) to effect a slow metalation of the aromatic PMS units in the copolymer. After quenching with CO_2 the degree of functionalization (percentage of PMS units carrying carboxylic acid groups) did not exceed 55-60%. Since the reaction is neither quantitative nor chemoselective and requires relatively harsh conditions with a large excess of reagents, it is not well suited for the chemical modification of the poly(IB-PMS) elastomer. In contrast, SB's have shown high selectivity with faster kinetics and have afforded high yields in the preparation of functionalized arylalkyl compounds.[1,7,16-22]

Probably the easiest and most versatile route to SB's is via metal exchange reaction between an alkyl lithium compound and a heavier alkali alkoxide (Scheme 1). Formation of the exceptionally strong oxygen-lithium bond provides the driving force to obtain the alkyl heavier alkali product. This method pioneered independently about thirty years ago by Lochmann and Schlosser has since found widespread application in organic synthesis. The procedure is not only useful for the "*in situ*" preparation of SB's but it also allows the isolation of the newly formed metal-alkyl in high purity.[7]

The most useful and striking feature of SB's prepared via metal exchange is their reactivity in solution. It is believed that the reactive species is a complex in which the newly formed lithium alkoxide and alkyl alkali are both present.[6,17] SB's of this type have been shown to exhibit higher stability when compared to the alkyl heavier alkali on its own. In addition, their composition (ratio of alkyl lithium and heavier alkali alkoxide) and the nature of the alkyl moieties present have been shown to alter both the reactivity and the selectivity of the metalation reaction.[3,6,7] In the case of the modification of the poly(IB-PMS) elastomer, the SB's prepared via a metal exchange reaction are particularly advantageous because of their solubility in the hydrocarbons that are the solvents of choice for both the starting elastomer and its metalated derivative. The solubility of the SB is easily optimized through appropriate selection of the alkyl moieties for both the metal alkoxide and alkyl.[6,7,23] This also alleviates the problem of having to use SB's that can only be obtained as finely suspended materials, since the latter are much more difficult to prepare and use in a reproducible manner. Furthermore the preparation of SB's containing metals with higher electropositivity, such as Cesium, is also facile and offers the possibility to increase reactivity if needed.[24,25] An additional advantage of the SB's obtained by metal exchange reactions is their selectivity. The metalation of p-cymene, a model compound for the PMS units of the elastomer, occurs primarily (92%) at the primary benzylic position if a four-fold excess of n-BuLi/t-PeOK (1/1) is used.[18] In contrast, cumene is only metalated to an extent of 50% under identical reaction conditions, while the mono-metalation of p-diisopropyl benzene only occurs in 20% yield. Ring metalation was negligible in all of these cases, although the SB mixture is also known to metalate aromatic rings quite effectively as demonstrated in our recent work with polystyrene.[10] The use of n-amyl sodium isopropoxide (1:1) with p-cymene only afforded a 52% overall yield of metalated material with approximately half of the metalation occurring at the primary benzylic-carbon while the rest was a mixture of di-metalated (ring and benzylic-carbon) product.[22]

Results and Discussion

Although a number of different SB's were investigated for the functionalization of the poly(IB-PMS) elastomer, the Lochmann[7] SB's obtained by metal exchange between alkali alkoxide and alkyl lithium, showed the best combination of solubility, reactivity, and selectivity.

In order to achieve the most effective metalation - including high selectivity towards the primary benzylic position, high degree of metalation, and high effectiveness of the SB - the effects of a number of reaction variables, such as composition of SB, metal counter ion, size of the alkoxide, time, temperature, and solvent have been investigated.

A typical reaction sequence involved the metalation of the copolymer using SB, followed by quenching with an excess of chlorotrimethylsilane (TMSCl). TMSCl was chosen as the probe electrophile because of its high reactivity and the ease with which the metalation-silylation process could be quantified by ^{1}H-NMR measurements. The resonances of the trimethylsilyl (TMS) groups appear as intense and sharp signals at about 0.5-0.0 ppm in the ^{1}H-NMR spectrum of the substituted copolymer. This range of chemical shifts is not occupied by any other species present in the reaction mixture, a feature that is important since the low concentration of reactive benzylic moieties in the copolymer makes complex analyses difficult to carry out. In some cases, the use of other electrophiles such as CO_2 or formaldehyde led to slightly (up to 5%) higher degrees of functionalization.

Effect of the Metal Ion.

The most significant factor that controls the reactivity and selectivity of the SB is the choice of the metal selected to prepare the metal alkoxide used in combination with s-BuLi for the *in situ* formation of the SB. This is readily demonstrated in a series of experiments in which only the metal used to form the metal alkoxide component of the SB was varied (Table I). Because of the low solubility of many other cesium alkoxides in cyclohexane, l-(-)-menthol was selected to prepare the metal menthoxides of Na, K, or Cs in cyclohexane. It should be noted that Cs menthoxide is less soluble in hexane or cyclohexane than t-PeONa or t-PeOK, but since t-PeOCs could not be prepared successfully, the menthoxides were deemed to be suitable alternatives. Samples of poly(IB-PMS) were then metalated for 15 min. at room temperature (RT) using the various SB's derived from the desired metal menthoxide and s-BuLi in cyclohexane. In all cases, metal alkoxides and s-BuLi were used in slight excess relative to the available PMS units present in the copolymer, and the reaction mixtures were quenched with a 2-3-fold excess of TMSCl prior to NMR analysis. As is shown in Table I, the degree of silylation at the primary benzylic position increases with the electropositivity of the metal counter ion. The use of sodium l-(-)-menthoxide afforded a product with only 5% silylation, whereas the equivalent SB's obtained from the potassium and cesium alkoxides afforded 36% and 71% silylation, respectively. These experimental observations match the expectation that a more electropositive metal counter ion increases the basicity of the s-butyl carbanion through an increase in bond ionicity[26,27] that, in turn, translates into higher reactivity. A similar trend has been observed by Finnegan[20] who found that t-butyl potassium is powerful enough to metalate pentane, while the corresponding sodium derivative is only able to deprotonate benzene. The reactivity of the equivalent lithium and Grignard reagents is even lower as they fail to metalate toluene unless special activation (e.g. TMEDA) is provided.

While basicity is certainly an important factor, it is likely that other factors, such as complex formation involving the metal alkoxide, also contribute to the outcome of the reaction. Differences in basicity cannot explain the observation that, in the case of the more reactive Cs SB, the amount of ring metalation is less than when K is the counter ion. At present, however, not enough data is available to attempt an explanation on the molecular level.

Also summarized in Table I are results in which s-BuLi was used in two-fold excess over PMS units in the presence of varying amounts of metal alkoxide. It appears that as the excess of alkoxide over s-BuLi increases, the degree of silylation at the benzylic position also increases, and ring metalation decreases. These results are in accordance with earlier observations by Lochmann et al.[23] who showed that using 3 equiv of t-PeOK in the presence of 1 equiv of alkyl lithium significantly increases the selectivity for the metalation of an aromatic side chain. Using these conditions, 93% of toluene was metalated in the side chain, 1% in the ring and the remaining 6% were unidentified products. However, to obtain essentially quantitative metalation, a two-fold excess of SB with a ratio of s-BuLi to Cs l-(-)-menthoxide of 1:3 had to be used, indicating that, given their extremely non-polar environment, the PMS units in poly(IB-PMS) are significantly less reactive compared to their low molecular weight analogs.

Effect of Temperature. An almost instantaneous color change was observed upon addition of s-BuLi to a solution containing both poly(IB-PMS) and K or Cs alkoxides at RT. A series of experiments was carried out to determine the effect of temperature on the metalation reaction. The results of these experiments using t-PeOK and s-BuLi are summarized in Table II. Metalation of the polymer was carried out in cyclohexane at RT and at 65°C, as well as in n-hexane at -48°C and -78°C. In all cases, the reactions were quenched after 15 min using TMSCl. While the degrees of metalation obtained at RT and at 65°C are comparable, ring metalation of the poly(IB-PMS) occurs to a lesser extent at 65°C despite the fact that decomposition of the organo potassium species should be considerably accelerated with increasing temperature. These findings suggest again that the reactive metalated species is actually a stabilized complex of the alkoxide and the K salt of the polymer. Metalations carried out at -48°C and -78°C afford lower degrees of functionalization while the ratio of ring vs benzylic metalation is increased. The metalation reaction done at -78^{O}C had to be carried out in twice the volume of n-hexane because of the reduced solubility of the SB, while the solubility of the polymer itself is not a factor. In practice, the reaction required staged cooling, with t-PeOK and s-BuLi pre-cooled to about -60^{O}C added first to a n-hexane solution of poly(IB-PMS), followed by immediate cooling of the resulting dark red/brown colored solution to -78^{O}C, a process that can be carried out without the formation of any precipitate. In contrast, the same procedure carried out entirely at -78^{O}C only afforded a yellow suspension that slowly turned to orange within several hours. This observation is independent of the sequence of addition of the reagents. We believe that, at this low temperature, the metal exchange is strongly retarded due to the presence of s-BuLi aggregates that remain stable because the solvation power of t-PeOK is low at that temperature. As the temperature is increased to -48^{O}C, sufficient entropy is gained to break some of the s-BuLi aggregates that exist prior to the addition of the alkoxide. Overall, we speculate that the decrease in extent of metalation at lower temperatures is a reflection of the lower concentration of monomeric s-BuLi that is available to undergo metal exchange. The change in selectivity observed at lower temperatures may be explained by variations in the structure of the aggregate surrounding the reactive benzylic center, a process that allows for higher selectivities at higher temperatures.

If one compares the degree of metalation obtained after 2 min with the results obtained after 15 min, it becomes apparent that most of the metalation takes place within the first 2 min and that a slight increase in the extent of reaction *vs.* time is only found for reactions run at RT or at 65^{O}C. Here again, the aggregation phenomena that are most prevalent at lower temperatures restrict the motions of the metalated polymer complexes preventing the adoption of more favorable conformations that would lead to higher degrees of metalation over time.

Effect of Solvent. Because SB's are extremely effective at proton removal, they can only be used with a very limited number of solvents. Figure 1 compares the evolution of the degree of silylation *vs.* time for two different solvents, cyclohexane at 65^{O}C and THF at -78^{O}C. As can be seen very clearly, cyclohexane is an inert solvent that may be used even at elevated temperatures since little side-reaction occurs. After one hour of reaction in cyclohexane at 65°C the yield of product obtained after silylation is more than 80%, and after 500 min at the same temperature it still exceeds 60%. In contrast, THF is readily attacked by SB. A maximum degree of silylation of 14% is reached after about 15 minutes but degradation continuously destroys anionic sites and the degree of silylation becomes essentially zero after 500 min.

It is a well known fact that solutions of s-BuLi in THF are only stable below -50°C[28] and the half-life of s-BuLi in THF at -50°C is about 100h[1]. If one replaces the lithium counter ion with sodium, the temperature for a 100h half-life drops to -100°C and for potassium the drop is even more significant to -150°C. The SB's involving complexes with stabilizing alkoxides are more tolerant of higher temperatures. For example a 1:1 mixture of n-BuLi and t-BuOK in THF was found to be stable at -50°C[29] while SB's derived from Na, K, Rb or Cs alkoxides via metal exchange with s-BuLi are stable in cyclohexane well above RT as a result of complex formation between the alkoxide and the s-BuK obtained by metal exchange.

Effect of alkyl lithium. Table III summarizes the effect of different alkyl lithium compounds in the presence of t-PeOK (R-Li/t-PeOK 1:3) on the degree of silylation at room temperature in cyclohexane. Although all three lithium reagents ensure a high degree of silylation, s-BuLi appears to be the best both in terms of selectivity and reactivity.

Effect of Additives. Numerous previous studies have shown that TMEDA is a useful activating reagent for BuLi, BuNa, BuK and other organometallic compounds.[15,29-31] The first successful direct metalation of ethene[32] was achieved using n-BuNa/TMEDA (1:1) or n-BuK/TMEDA (1:1). When used alone, n-BuLi adds to the double bond while n-BuNa or n-BuK prepared via metal exchange are not reactive enough to deprotonate ethene, although both reagents attack benzene readily despite the fact its pK_a value is similar to that of ethene. However, the addition of TMEDA to either n-BuNa or n-BuK increases their kinetic basicity sufficiently to allow their use in the metalation of ethene at -40°C. Addition of one molar equivalent of TMEDA to n-BuNa and n-BuK prepared in situ via metal exchange between s-BuLi and t-BuONa(K) yields a product that is highly reactive towards ethene.[32]

The use of TMEDA to activate the SB's was tested in a metalation/silylation using a ratio of 1:2:6:8 for PMS:t-BuLi:t-PeOK:TMEDA and the reaction product was compared to that obtained in an identical reaction without TMEDA. As can be seen in Figure 2. TMEDA has essentially no effect on the total amount of silylation and may only have a very slight effect on the ratio of ring *vs.* benzylic metalation, favoring the latter. Similarly, another complexing agent, proton sponge (1,8-bis(dimethylamino)naphthalene) is ineffective in promoting reaction.

A different picture emerges if t-BuLi is replaced with s-BuLi (Figure 3). In this case, the addition of TMEDA increases not only the total amount of silylation by about 15%, but also the percentage of ring metalation from 7% to 25%. It is likely that the difference in reactivity between s-BuLi and t-BuLi in the presence of TMEDA is due to steric effects, which, in turn, are assumed to originate from a strongly aggregated reactive species.

Effect of Molar Ratio of s-BuLi:t-PeOK. At present it is believed[6,7] that a ratio of 1:3 of alkyl lithium to metal alkoxide is the optimum combination to enhance both the reactivity and the selectivity of SB's. However these results have been obtained with low molecular weight compounds and it is possible that the combination of reagents for the metalation of a non-polar polymer may be quite different. Some data lending support to this hypothesis have already been presented in the previous paragraphs. In this section we will discuss the effect of varying the molar equivalents of alkyl lithium (from 0.88 to 6.0 with respect to PMS units in the copolymer) and metal alkoxide (from 1.0 to 10.0) on both the total amount of silylation, and on the selectivity of the metalation (ring vs benzylic position).

The first series of experiment was designed to uncover a possible critical composition between s-BuLi and t-PeOK that might induce a sudden increase in the amount of silylated polymer. Table IV reports the results obtained in an experiment started with less than a stoichiometric amount of s-BuLi with respect to PMS groups in the copolymer, and an equimolar ratio of PMS to t-PeOK (ratio s-BuLi/PMS/t-PeOK = 0.88:1:1). After withdrawal of a small aliquot of the metalated polymer, followed by its silylation for subsequent analysis, additional t-PeOK was added to the remaining reaction mixture, allowing 5 min. equilibration time before withdrawal of the next aliquot and addition of the next portion of the t-PeOK. Surprisingly, this series of experiments, eventually involving additions of both s-BuLi and t-PeOK to reach a final molar ratio of 1.14 : 1 : 3.9, led to a constant composition of the product that appeared to have been determined by the original formulation of the reaction mixture.

Table V summarizes results of parallel experiments in which the concentration of s-BuLi was varied from equimolar to a two- or three-fold excess with respect to the PMS units in the copolymer. At the same time the ratio of s-BuLi to t-PeOK was set at 1:1, 1:2 , 1:3 and 1:10. Two general observations can be made. The amount of silylation at the benzylic position increases with increasing amount of t-PeOK (with the exception of a ratio s-BuLi:t-PeOK = 2:4), whereas the relative amount of ring silylation to substitution at the benzylic position decreases at the same time. These results are in good agreement with observations by Lochmann et al. who found that both selectivity and the amount of silylation in similar metalation reactions increased with an increasing amount of the alkoxide component.[7,23] For experiments in which the ratio of s-BuLi to PMS unit is increased from 1:1 to 3:1, the total amount of silylation increases but the selectivity decreases as more s-BuLi is used (see also first column in Table VI). The use of a 10-fold excess of t-PeOK has a remarkable effect increasing the degree of metalation to about the same extent as the addition of another equivalent s-BuLi. However the use of a large excess of t-PeOK is advantageous since it leads to a more selective metalation of the polymer.

The discrepancy in the amount of metalation reported in Tables IV and V for a molar ratio of s-BuLi to t-PeOK of about 1:3 and the fact that the metalation reactions generally take less than 2 minutes to complete suggest that the intrinsic stability of the complexes formed during the <u>initial</u> metalation of the polymer is determinant.

The data shown in columns 2 and 3 of Table VI confirm that increasing the amount of s-Buli alone, while keeping the amount of alkoxide constant, has little or no effect on the degree of metalation at benzylic positions regardless of the counterion used (Na or K). This confirms the importance of the alkoxide component in the formation of the actual reactive species that are organometallic/alkoxide aggregates.[8]

Effect of Reaction Time. The metalation reaction of poly(IB-PMS) in the presence of Na, K, and Cs l-(-)-menthoxide was monitored over a period of more than 1000 min by withdrawing aliquots at given time intervals, quenching them with an excess of TMSCl, and analyzing them by ^{1}H NMR spectrometry. As can be seen in Fig 4, the maximum degree of metalation is reached within 2 min of the addition of the second component of the SB (s-BuLi) in the metal exchange reaction. No further metalation is observed in the next 200-300 min, regardless of the nature of the metal ion used in the alkoxide component of the SB. In the following 700 min a degradation process leading to a significant decrease in the number of available anionic sites on the polymer is seen to take place. Although decomposition of the highly reactive anionic sites, possibly leading to alkali hydrides, does occur over extended periods of time, the stability of the metalated polymer species is remarkable. It allows the polymer to be used in reactions with other electrophiles in a convenient way.

Chiral Induction using Superbase. While our initial motivation for the use of menthol for the preparation of metal alkoxides was the higher solubility of cesium menthoxide, the use of a chiral component in the SB offers the possibility of chiral induction if a suitable electrophile can be chosen. Such chiral induction will of course only occur if the alkoxide remains in close vicinity to the metalated center, implying the presence of a complexed carbanionic species. For a first glimpse into this matter we chose to monitor the reaction of trimethylacetaldehyde with poly(IB-PMS) using Cs l-(-)-menthoxide as the chiral component in the formation of the chiral SB (Scheme 2). We used a 1:1 and a 1:3 ratio of s-BuLi to Cs l-(-)-menthoxide. After precipitation to remove the chiral alcohol, the functionalized polymer was characterized by ^{1}H-NMR, which indicated a degree of functionalization of 85%. Residual l-(-)-menthoxide resonances were not detected. Measurements of the optical rotation of the polymer revealed a small but significant positive rotation when a ratio of 1:1 (s-BuLi to Cs l-(-)-menthoxide) was used and a small negative rotation for a ratio of 1:3. It must be recalled here that since the polymer contains only very few reactive p-methylstyrene sites, only a small rotation can be expected.

^{6}Li NMR Evidence for the Reactive Species. ^{6}Li-NMR proved useful to gain some insight into the structure and composition of the reactive metalated center on the polymer. Although ^{6}Li is considerably less abundant than its ^{7}Li isotope, it possesses a number of favorable properties that make its use more attractive than ^{7}Li. Due to its very small quadrupole moment, ^{6}Li behaves almost like a spin I=1/2. It also shows fairly long spin lattice relaxation times, T_1, and therefore exhibits reasonably narrow NMR lines.[33] Other alkali metal nuclei would, in theory, have been more useful, but neither ^{23}Na, nor ^{39}K or ^{41}K are of any particular benefit for NMR investigations due to their large quadrupole moments. In addition, these nuclei usually exhibit quite short spin lattice relaxation times, T_1, leading to broad NMR lines.[34] Therefore we chose to analyze metalated polymer samples using labeled Et^{6}Li and t-PeOK in n-hexane. We also metalated poly(IB-PMS) in the absence of a higher metal by activating Et^{6}Li with TMEDA, and prepared several other comparative samples that were identical but did not contain the polymer. The ^{6}Li-NMR spectra obtained at room temperature are shown in Figure 5. Spectra a and b show the resonances of the lithium species without and in the presence of poly(IB-PMS) using Et^{6}Li and t-PeOK as metalating reagent. Both spectra show only one sharp signal, indicating that, in each case, only one lithium species is present. The difference in chemical shift between the two spectra is very small suggesting that the lithium species being formed via metal exchange is essentially the same regardless of the presence of the polymer. The value of the chemical shift falls in the range where aliphatic lithium alkoxides are expected to absorb. Once the NMR experiment was completed, the samples were quenched using an excess of TMSCl and ^{1}H-NMR analysis of the product confirmed that a high degree of silylation (73% benzylic / 9% ring) had been achieved. The situation is totally different when NMR spectra c, d and e are examined. Spectrum c confirms the presence of one lithium species which can safely be assumed to be the complex between TMEDA and Et^{6}Li. Spectrum d shows resonances obtained from an identical solution of TMEDA and Et^{6}Li, but this time poly(IB-PMS) is present. The spectrum was recorded after the reaction mixture had been heated to 55°C for 40 min. As can be seen clearly, the formerly sharp resonance has broadened considerably and also shifted to higher field. This result is in good agreement with prior observations that resonances of benzyl lithium species occur at higher field than is the case of aliphatic lithium compounds.[34] The considerable line broadening is attributed to lithium ion exchange which is too fast for the NMR time scale at RT, so that only the weighed average of the chemical shifts is observed. Therefore the NMR spectrum of this solution was also recorded at -75°C after heating the sample for an additional 5 h at 55°C (spectrum e). Even at this temperature the broad resonance could not be resolved but the additional heating had caused the resonance to move even further to higher field. A possible explanation, taking into account the slow nature of lithiation with RLi/TMEDA, is that the reaction between Et^6Li/TMEDA and poly(IB-PMS) was actually not complete after the initial heating period (40 min to 55°C) and further heating drives the reaction closer to completion, with more benzyl lithium species being formed. As mentioned earlier, these absorb at higher field when compared to the Et^6Li/TMEDA complex initially present (spectrum c).

Although indirect, this evidence supports the formation of a metalated polymer species in which the counter ion is potassium and not lithium when the metalation involves a SB derived from Et^6Li and t-PeOK. This finding is based on the following observations:

i) Regardless of the presence or absence of poly(IB-PMS), metal exchange between Et^6Li/t-PeOK leads to a single lithium species, which is believed to be an aggregate that contains lithium t-pentoxide. The numerous successful and high yield preparations of alkyl potassium compounds by Lochmann et al.[6,7] also support the contention that metal exchange is almost quantitative.

ii) The lithium species formed by using TMEDA (not t-PeOK) in the presence of Et^6Li is a single species but different from the latter as can be seen by the difference in chemical shift.

iii) The NMR of poly(IB-PMS) metalated using Et^6Li/TMEDA indicates the presence of at least two different lithium species, one of which is believed to be the benzylic lithiated structure derived from the PMS units present in the polymer, while the other is the original complex between TMEDA and Et^6Li. The shift towards higher field upon further heating is consistent with the assumption that more benzyl lithium centers are formed slowly upon heating.

iv) The chemical shifts of the lithium species formed using both metalating reagents are different when reactions are done in the absence or in the presence of the polymer.

v) The dark red color found for the polymer metalated with Et^{6}Li/t-PeOK is consistent with the color previously reported for benzyl potassium.[32, 35]

Other Superbases. A number of other SB's were also tested in the metalation of poly(IB-PMS); these included $NaNH_2$, KNH_2, $NaNH_2$/2-methoxyethanol, KNH_2/2-methoxyethanol, BuLi/12-crown-4, BuLi/15-crown-5, Cumyl potassium and trimethylsilylmethyl potassium. In all cases, little reaction was observed despite the presence of a large excess of metalating agent.

It is not surprising that some difficulties are encountered in the metalation of a non-polar polymer such as poly(IB-PMS). As a result of the low degree of PMS incorporation and the very low polarity of the copolymer, truly *quantitative* metalation is only achieved using an excess of the very powerful Lochmann base consisting of the s-BuCs reagent in the presence of lithium l-(-)-menthoxide. The interplay between the deprotonation of poly(IB-PMS), during which a highly polar species is formed, and its hydrophobicity, is certainly a cause for this relatively sluggish reaction. It is likely that the metalated centers that are created have a strong tendency to aggregate making it increasingly more difficult for the SB to deprotonate other positions on the polymer. This would explain why the use of a larger and larger excess of SB causes the amount of metalation to reach a maximum value which, only in the case where cesium is the counter ion, reaches 100%.

Experimental Section

Chemicals. Poly(IB-PMS), designated as XP-50, (Exxon Chemical Company) was purified by precipitation from concentrated cyclohexane into isopropanol. The clear and colorless product was dried under vacuum at 60°C for at least 24h prior to use both a commercial grade P(IB-PMS) with M_n = 250,000 and a low molecular weight analog with M_n = 10,000 were tested in the reaction [M_n= 10000, M_w/M_n= 3.5 by GPC (polystyrene standards)]. Composition of the copolymer: isobutylene content = 97.7 mol%, PMS content = 2.3 mol% (by ^{1}H-NMR). THF and cyclohexane were dried over Na/benzophenone and distilled when a dark purple color had developed. n-Hexane dried, deoxygenated and purified using activated alumina and a supported copper catalyst was stored over activated molecular sieve (4Å). Alkyl lithium compounds received as solutions in hydrocarbon solvents (Aldrich) were titrated using 1,10-Phenanthroline as indicator.[37] Ethyl ^{6}Li was prepared as described in the literature[38,39] and purified by vacuum sublimation before use. t-Amyl alcohol and 2-methoxyethanol (Aldrich 99%) were purified by fractional distillation over sodium. TMEDA (Aldrich 99%) was dried over $LiAlH_4$ and fractionally distilled under vacuum. TMSCl (Aldrich 99%) was dried over CaH_2 then fractionally distilled from CaH_2 under argon. Bis(trimethylsilylethyl) mercury[40], trimethylsilylmethyl potassium[36] and cumyl potassium[41] were prepared according to the literature.

Metalation. Metalation reactions were carried out in an atmosphere of purified argon (Oxisorb®, Matheson; $O_2 < 0.1$ ppm).

General Procedure. Poly(IB-PMS) was dissolved in either cyclohexane (room temperature and above), n-hexane (low temperature) or THF, and the homogeneous 5% (w/v) solution was stirred. After addition of the metal alkoxide (~1 molar solution for t-PeONa and t-PeOK in hexane or cyclohexane, or ~0.1 molar solution for Na, K, and Cs l-(-)-menthoxide in cyclohexane) at the appropriate temperature the alkyl lithium component (~1.3 molar solution of s-BuLi in hexane) was then added. The color of the solution changed rapidly from colorless to yellow, orange, red or deep dark red depending on the alkoxide and the molar quantities of reagents (metal alkoxide and alkyl lithium) used. Metalations were allowed to proceed for a given time interval (usually 15 minutes). Addition of a 2-3 fold excess of TMSCl (neat or in solution), yielded a slightly turbid and almost colorless solution. Stirring was continued for at least one hour before work-up. Reactions with trimethylacetaldehyde were carried out in the same way.

Work-up. The organic phase, containing the functionalized polymer, was extracted with 10% aqueous HCl (twice), 1N aqueous NaOH (twice), saturated aqueous sodium bicarbonate solution (twice), and finally distilled water. Pouring the organic layer into isopropanol yielded a sticky white precipitate. The recovered polymer was washed with methanol several times then dried at

60°C for at least 24h under vacuum to afford either a viscous, clear and colorless liquid or a rubbery material depending on the Mw of this starting polymer.

For time-dependent studies aliquots of the metalated polymer solution were drawn at given time intervals and added to a 4-8-fold (based on alkyl lithium) excess of stirred neat TMSCl. After 1h the reaction mixture was precipitated into 5-10 times its volume of isopropanol and the product was worked-up as above.

Characterization.

Optical Rotation. Optical rotation measurements were run on a Perkin Elmer polarimeter.

^{1}H-NMR spectroscopy. Spectra were recorded on a Bruker AF 300 spectrometer at RT in $CDCl_3$ (used as internal standard). The degree of silylation was calculated from the integral of the resonances of the unsubstituted benzylic positions ($Ar\underline{CH_3}$ 2.31 ppm) in relation to the resonances of the benzylic position substituted with TMS groups ($Ar\underline{CH_2}TMS$ 2.03 ppm). The total amount of silylation at the benzylic positions was calculated from the integral of the resonances of the TMS groups (0.15 to -0.05) ppm). The degree of ring metalation was calculated by integration of resonances in the region between 0.40-0.15 ppm ($Ar(\underline{TMS})$. The absence of side reactions or polymer degradation during metalation could be confirmed in at least two ways: (i) By comparing the integral of aromatic resonances to the sum of integrals of all benzylic resonances, (ii) By comparing the integral of the resonances of the TMS substituted benzylic position with the integral of the TMS group itself.

^{6}Li-NMR spectroscopy. Spectra were recorded on a Varian Unity 500 spectrometer equipped with a custom built 3-channel probe designed to accommodate lithium pulses. The spectrometer operates at 73.56 MHz. Data were processed in a phase sensitive mode. NMR samples were prepared as described under "General Procedure". All samples were prepared in n-hexane and were allowed to react for about 15 minutes at room temperature. If not otherwise stated, spectra were recorded at room temperature with the exception of (e), which was recorded at -75°C. Their compositions were as follows: (a) Et^6Li (2 equiv.)/t-PeOK (6 equiv.), (b) poly(IB-PMS) (1 equiv.)/Et^6Li (2 equiv.)/t-PeOK (6 equiv.), (c) Et^6Li (4 equiv.)/TMEDA (7.3 equiv.), (d) poly(IB-PMS) (1 equiv.)/Et^{6}Li (4 equiv.)/TMEDA (7.3 equiv.), (e) sample d heated for 6h at 55°C. ^{6}Li-NMR data (external standard LiCl) : (a) 1.45 ppm (bs); (b) 1.43ppm (bs); (c) 2.50 ppm (bs); (d) 1.8 ppm (vbs); (e) 0.8 ppm (vbs).

Size Exclusion Chromatography. SEC analysis was performed on a liquid chromatograph consisting of a Waters 510 pump, a U6K injector (Waters), a Viscotek 110 differential viscometer, and a differential refractometer (refractoMonitor (Milton Roy)), the detectors being connected in parallel. THF at 40°C with nominal flow rate of 1 ml/min was used as the mobile phase. The separations were achieved across banks of four 5-μm PL Gel columns (Polymer Laboratories) with porosities 100 Å, 500 Å, 1000 Å, and Mixed C (200 Å-1000000 Å) in THF. The system was calibrated with 16 monodisperse polystyrene (PSt) standards. The molecular weight characteristics were calculated using universal calibration.

Crosslinking is absent in the reactions studied. This was proven by reacting metalated poly(IB-PMS) with D_2O (see "General Procedure" and "Work-up"). The GPC traces before and after the reaction were essentially identical. However, a slight decrease in the concentration chromatogram towards lower molecular weight was observed and was attributed to the loss of some lower molecular weight material during precipitation.

Conclusion

Given the highly non-polar nature of the poly(IB-PMS) copolymer used in this study, it is remarkable that clean, and even quantitative functionalization could be achieved with very short reaction times and relatively moderate amounts of the SB's. Notable findings include the following:

- SB's prepared via a metal exchange reaction between alkyl lithium and metal alkoxide showed a pronounced increase in reactivity and selectivity with increasing size of the metal counter ion (Cs>K>Na>Li).
- A two-fold excess of the SB, s-BuLi/Cs l-(-)-menthoxide (1:3), allowed essentially quantitative metalation of poly(IB-PMS) at the p-methyl position. Ring metalation was less than 2%. This SB

is far better than any previously studied SB in terms of its selectivity and the degree of metalation it affords.

- It is possible to achieve a degree of metalation of more than 70% by using only a very small excess of the most reactive SB (s-BuLi/Cs l-(-)-menthoxide (1.1:1.25)). Replacing the cesium counter ion by potassium lowers the degree of metalation to about 40%, a finding that highlights the exceptionally high reactivity of SB's prepared from heavier alkali metal alkoxides and alkyl lithium.
- Within the temperature range studied (-78°C to 65°C), the temperature has little effect on the metalation, provided the solvent is compatible with the process. THF is rapidly decomposed by the SB's employed in this study, even at low temperatures (-78°C).
- The stability of the metalated polymer is sufficient to allow further reactions with electrophiles, even at 65°C.
- Reactions of poly(IB-PMS), metalated with s-BuLi and Cs l-(-)-menthoxide, with trimethylacetaldehyde suggest that it may be possible to design SB's capable of chiral induction.
- A comparison of the ^{6}Li NMR spectra of poly(IB-PMS) metalated by using Et^{6}Li/TMEDA or by using Et^{6}Li/t-PeOK suggests strongly that the reactive intermediate in the case of the Et^{6}Li/t-PeOK system is the aggregated potassium salt of poly(IB-PMS) and not the lithium salt.

All of these results contribute to our understanding of the underlying mechanism of metalation via metal exchange reactions. Not only is the potassium salt of the polymer the reactive species but, at least for the substrate studied here, the metal alkoxide also plays an important role stabilizing the reactive species so that the metalated polymers is fairly stable even at elevated temperatures. We are currently exploiting this interesting metalation reaction for the direct functionalization of commercial samples poly(IB-PMS) copolymers.

Acknowledgments.

Financial support of this research by the Office of Naval Research and Exxon Chemical Corporation is acknowledged with thanks. Helpful discussions with Dr. L. Lochmann and the assistance of J. Remenar in running the ^{6}Li-NMR experiments are also gratefully acknowledged.

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Table I. Comparison of the degree of silylation[a] (metalation) of poly(IB-PMS) by superbase derived from s-BuLi and different alkoxide

s-BuLi:menthoxide	Na l-(-)-menthoxide $ArCH_2TMS/ArTMS$	K l-(-)-menthoxide $ArCH_2TMS/ArTMS$	Cs l-(-)-menthoxide $ArCH_2TMS/ArTMS$
1.10:1.25	5% / 0%	36% / 4%	71% / 1%

s-BuLi:alkoxide	t-PeONa $ArCH_2TMS$ / ArTMS	t-PeOK $ArCH_2TMS$ / ArTMS	Cs l-(-)-menthoxide $ArCH_2TMS$ / ArTMS
2.0:2.0	38% / 0%	74% / 12%	94% / 5%
2.0:4.0	-	68/10	90/3
2.0:6.0	-	84/7	99/2

[a] Degree of silylation expressed in %. Metalation reactions were carried out for 15 minutes at room temperature in cyclohexane. Excess TMSCl was used for quenching.

Table II. Effect of temperature on the degree of silylation[a] (metalation) in hydrocarbon solvents.

Temp. (^{o}C)	after 2 minutes % $ArCH_2TMS$ / % ArTMS	after 15 minutes % $ArCH_2TMS$ / % ArTMS
-78	58/9	55/9
-48	76/9	76/10
20	72/8	84/7
65	76/6	81/3

[a] Degree of silylation expressed in %. s-BuLi/t-PeOK (2:6) was used in two-fold excess in the metalation of poly(IB-PMS). The reactions were carried out for 2 and 15 minutes at each temperature in cyclohexane or n-hexane respectively. Excess TMSCl was used for quenching.

Table III. Effect of the alkyl lithium compound used in the silylation reaction[a] (metalation) of poly(IB-PMS).

Alkyl Li	% $ArCH_2TMS$ / % ArTMS
Et^6Li	73/9
s-BuLi	84/7
t-BuLi	68/10

[a] Alkyl Li/t-PeOK (2:6). The reaction was allowed to proceed for 15 minutes in cyclohexane, before TMSCl was introduced as quencher.

Table IV. Effect of sequential adjustments in the composition of s-BuLi/t-PeOK on selectivity and the degree of silylation[a] of poly(IB-PMS) in a single experiment.

s-BuLi:t-PeOK	% $ArCH_2TMS$ / % ArTMS
0.88:1.0	37/4
0.88:1.3	36/5
0.88:2.0	34/5
0.88:3.0	34/5
0.97:3.3	37/3
1.06:3.6	35/6
1.14:3.9	37/3

[a] The reaction mixture was allowed to equilibrate for 5 minutes after each addition before aliquots were taken and quenched using an excess of TMSCl.

Table V. Effect of the composition of s-BuLi/t-PeOK on selectivity and the degree of silylation[a] of poly(IB-PMS) in a series of parallel experiments.

Ratio of s-BuLi / t-PeOK	%$ArCH_2TMS$ / % ArTMS	Ratio of s-BuLi / t-PeOK	%$ArCH_2TMS$ / % ArTMS	Ratio of s-BuLi / t-PeOK	%$ArCH_2TMS$ / % ArTMS
1.0:1.0	37/4	2.0:2.5	74/12	3.0:3.0	73/17
1.0:2.0	41/4	2.0:4.0	68/10	3.0:6.0	77/15
1.0:3.0	54/3	2.0:6.0	84/7	3.0:9.0	87/10
1.0:10.0	73/5	---	---	---	---

[a] Degree of silylation expressed in %. Metalation reactions were allowed to proceed for 15 minutes at room temperature before TMSCl was introduced in excess as quencher.

Table VI. Effect of the composition of s-BuLi/t-PeOM (M=K or Na) on selectivity and the degree of silylation[a] of poly(IB-PMS).

s-BuLi/ t-PeOK	$ArCH_2TMS$ / ArTMS	s-BuLi/ t-PeONa	$ArCH_2TMS$ / ArTMS[b]	s-BuLi/ t-PeOK	$ArCH_2TMS$ / ArTMS
1.0:2.0	41/4	2.0:2.0	38/--	1.1:1.25	52/7
2.0:4.0	68/10	4.0:2.0	36/--	2.1:1.25	56/7
3.0:6.0	77/15	6.0:2.0	35/--	3.1:1.25	53/16

[a] Degree of silylation expressed in %. Metalation reactions were allowed to proceed for 15 minutes at room temperature before TMSCl was introduced in excess as quencher.

[b] The amount of ring metalation was not determined.

FIGURE CAPTIONS.

Fig. 1. Comparison of the solvents c-hexane (at 65°C) and THF (at -78°C) used in the metalation of poly(IB-PMS). The Superbase s-BuLi/t-PeOK was used in two-fold excess and the reaction was quenched by addition of aliquots of the reaction mixture to neat TMSCl at given time intervals.

Fig. 2. Effect of complexing agents on the reactivity of t-BuLi/t-PeOK (1:3). Metalation reactions were carried out for 15 minutes at each temperature in cyclohexane or hexane. TMSCl was used as quencher.

Fig. 3. Effect of TMEDA on the reactivity of s- and t-BuLi/t-PeOK (1:3). Metalation reactions were carried out for 15 minutes at each temperature in cyclohexane or hexane. TMSCl was used as quencher.

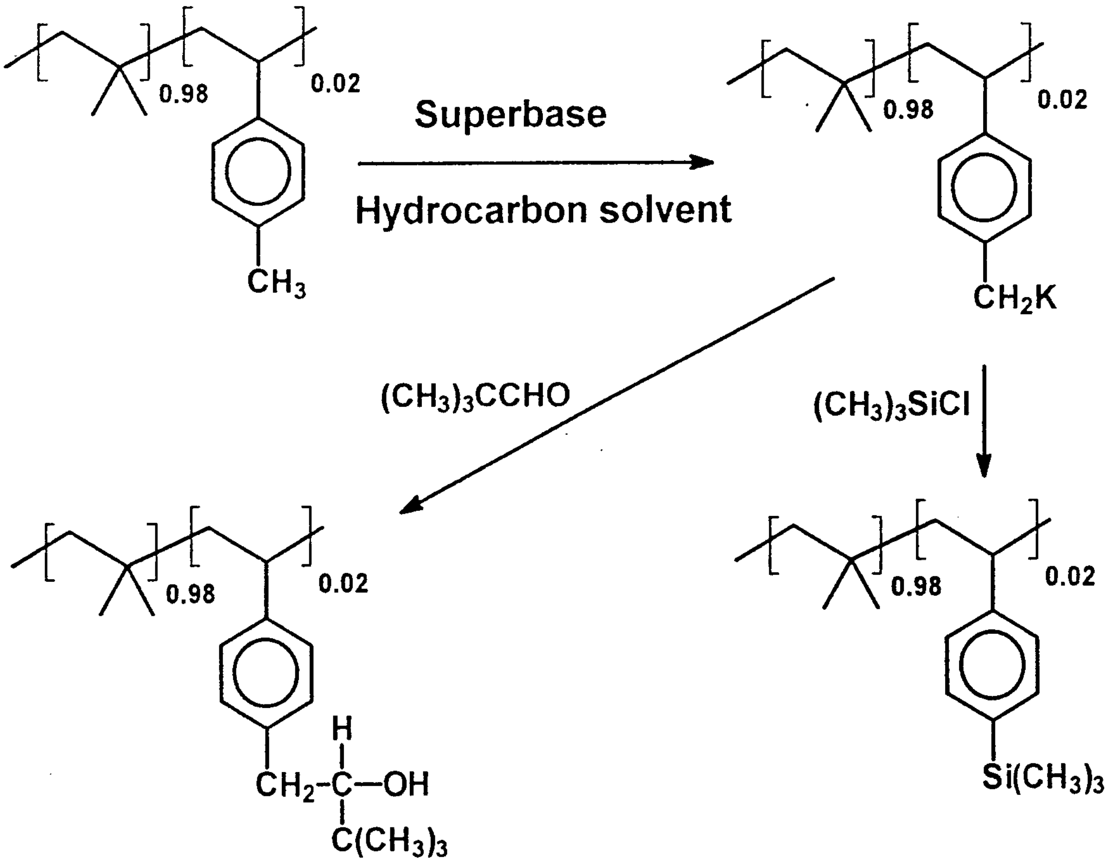
Fig. 4. Effect of reaction time on the metalation of poly(IB-PMS) at room temperature using s-BuLi/M^+ l-(-)-menthoxide (M^+=Na, K, Cs) carried out in cyclohexane. TMSCl was used as quenching agent. Aliquots of the reaction mixtures were taken at time intervals and added to neat TMSCl.

Fig. 5. ^{6}Li NMR spectra. (a) Et^{6}Li/t-PeOK (2:6) at room temperature after 20 minutes (b) poly(IB-PMS)/Et^{6}Li/t-PeOK (1:2:6) after 20 minutes at room temperature (c) Et^{6}Li/TMEDA (4:7.3) at room temperature after 20 min. (d) poly(IB-PMS)/Et^{6}Li/TMEDA (1:4:7.3) at room temperature after heating the reaction mixture for 40 min. at 55°C (e) poly(IB-PMS)/Et^{6}Li/TMEDA (1:4:7.3) at room temperature after heating the reaction mixture for 6h at 55°C .

$$\mathrm{R\text{-}Li} + \mathrm{R'OM} \rightleftharpoons \mathrm{R\text{-}M} + \mathrm{R'OLi}$$

$M = Li, Na, K, Rb, Cs$

SCHEME 1



SCHEME 2

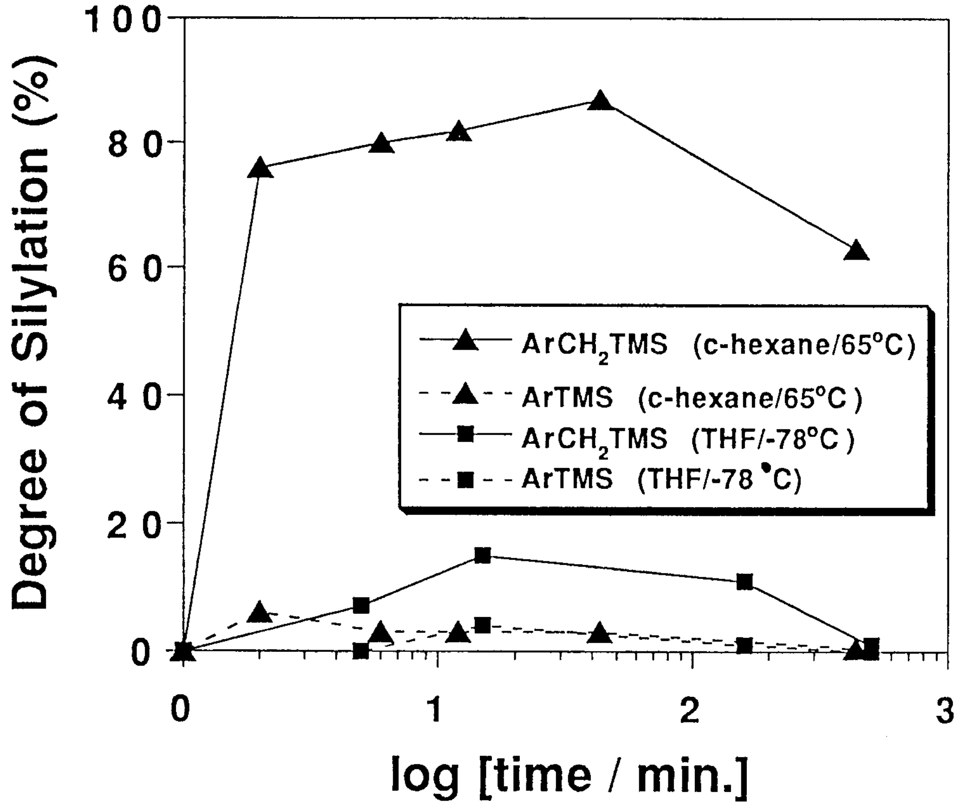

Degree of Silylation (%)
100
80
60
40
20
0
0
1
2
3
log [time / min.]
ArCH$_2$TMS (c-hexane/65°C)
ArTMS (c-hexane/65°C)
ArCH$_2$TMS (THF/-78°C)
ArTMS (THF/-78°C)

FIGURE 1

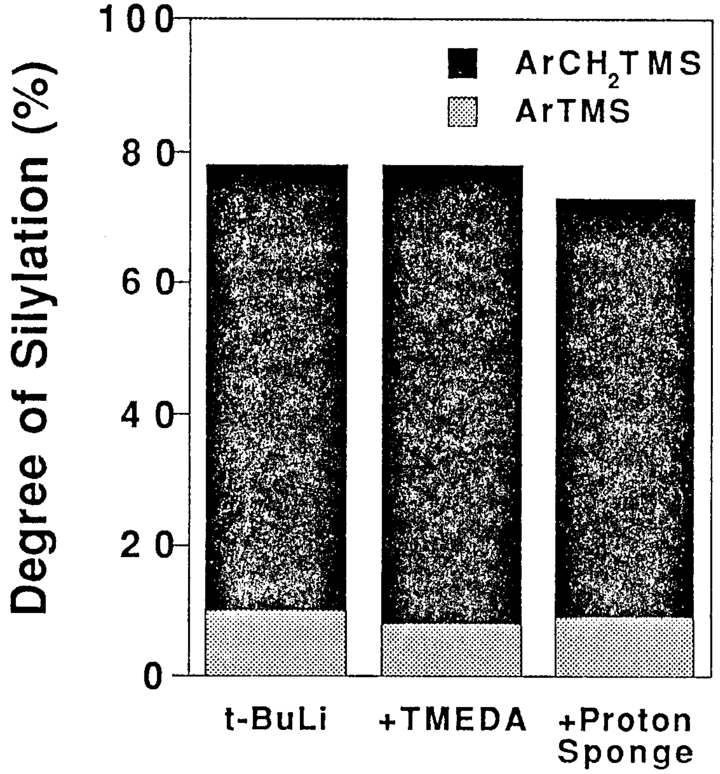

Degree of Silylation (%)
100
80
60
40
20
0
■ $ArCH_2TMS$
▨ ArTMS
t-BuLi
+TMEDA
+Proton Sponge

FIGURE 2

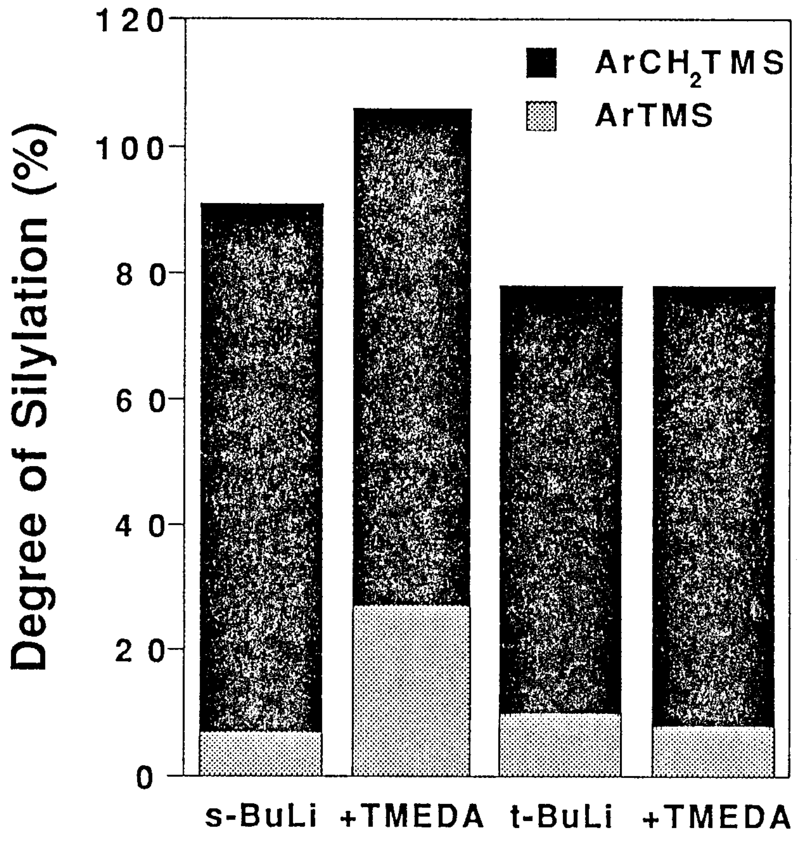

Degree of Silylation (%)
120
100
80
60
40
20
0
ArCH$_2$TMS
ArTMS
s-BuLi
+TMEDA
t-BuLi
+TMEDA

FIGURE 3

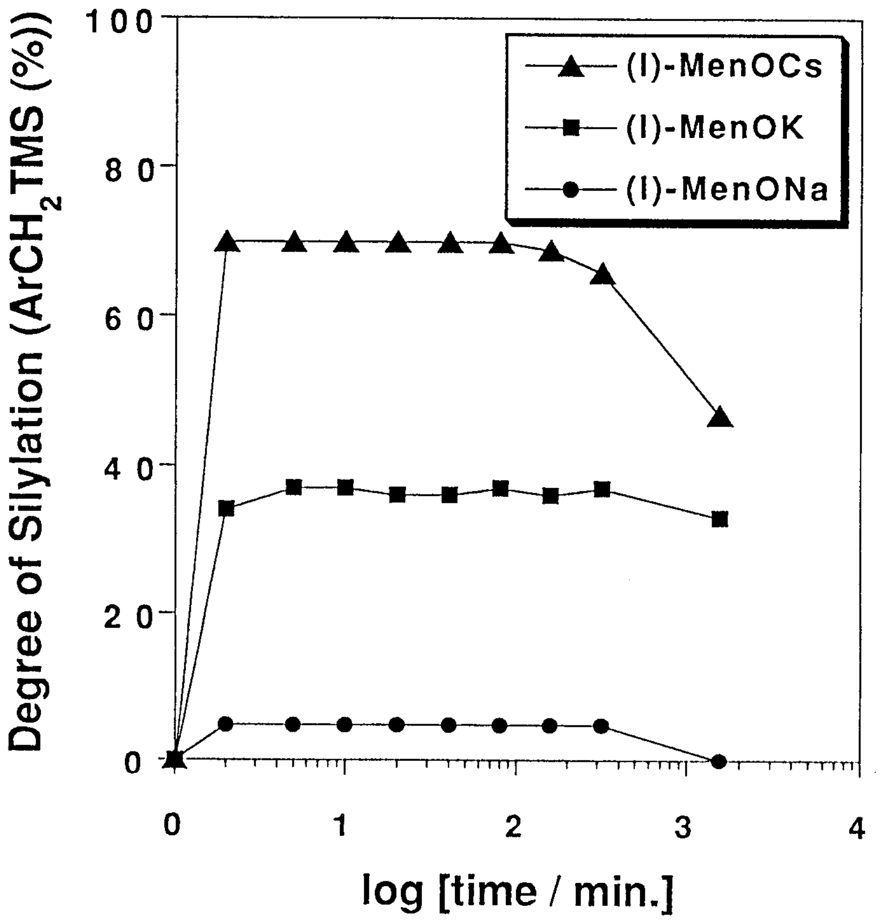

Degree of Silylation (ArCH$_2$TMS (%))
100
80
60
40
20
0
0
1
2
3
4
log [time / min.]
(l)-MenOCs
(l)-MenOK
(l)-MenONa

FIGURE 4

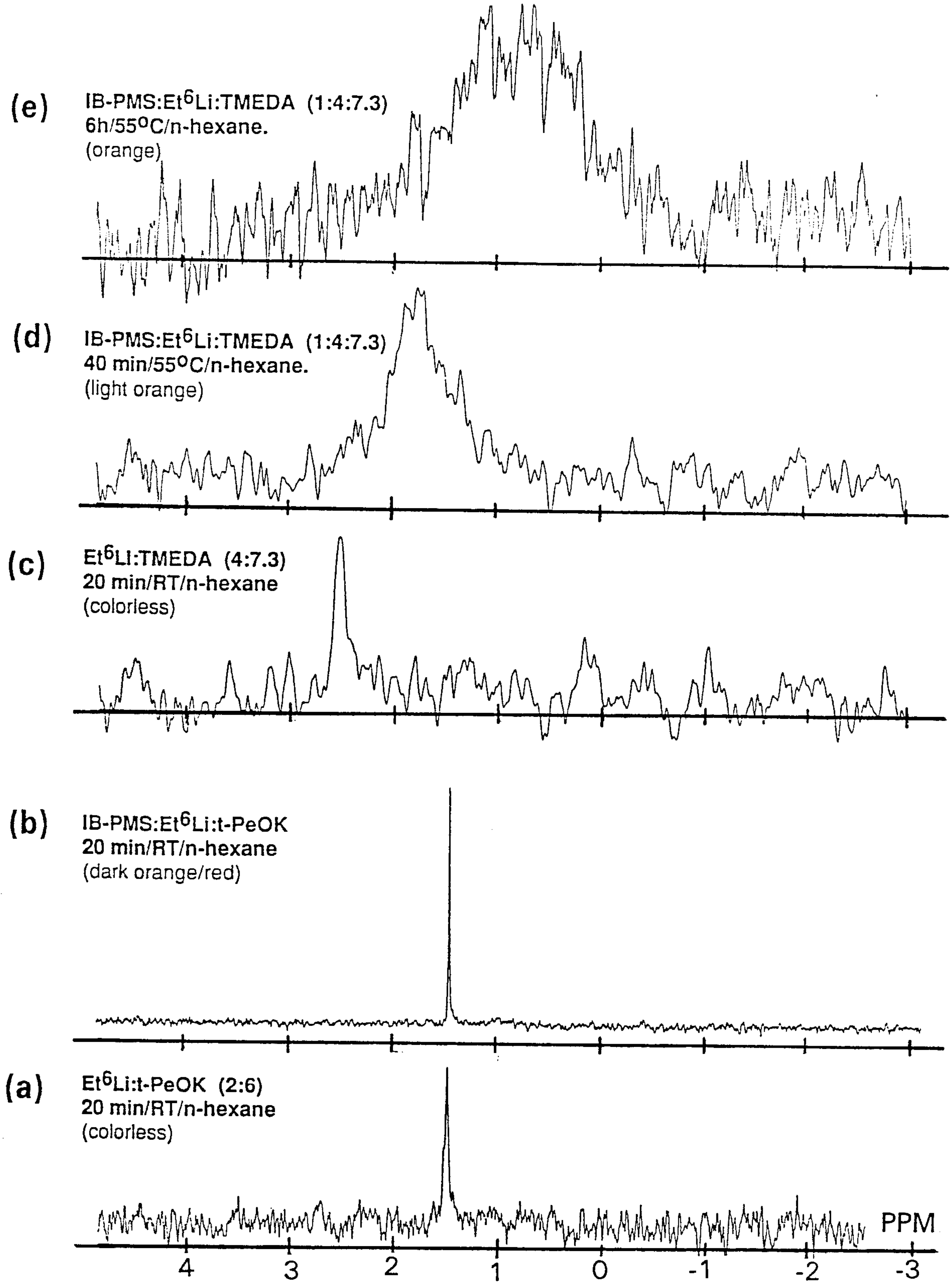

(e)
IB-PMS:Et6Li:TMEDA (1:4:7.3)
6h/55°C/n-hexane.
(orange)
(d)
IB-PMS:Et6Li:TMEDA (1:4:7.3)
40 min/55°C/n-hexane.
(light orange)
(c)
Et6Li:TMEDA (4:7.3)
20 min/RT/n-hexane
(colorless)
(b)
IB-PMS:Et6Li:t-PeOK
20 min/RT/n-hexane
(dark orange/red)
(a)
Et6Li:t-PeOK (2:6)
20 min/RT/n-hexane
(colorless)
PPM
4
3
2
1
0
-1
-2
-3

FIGURE 5