ANIONIC SYNTHESIS OF WELL-DEFINED POLYMERS WITH AMINE END GROUPS

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SUMMARY: The results for efficient tertiary and primary amine functionalization of polymeric organolithium compounds in hydrocarbon solution at room temperature are described for termination reactions with N-trimethylsilylbenzophenone imine, 3-dimethylaminopropyl chloride and 2,2,5,5-tetramethyl-1-(3-chloropropyl)-1-aza-2,5-disilacyclopentane. Functionalizations with the functionalized initiator, 2,2,5,5-tetramethyl-1-(3-lithiopropyl)-1-aza-2,5-disilacyclopentane are presented. Conditions for quantitative amine functionalization were observed for all of these reactions and reagents.

Introduction

One of the unique and useful aspects of alkyllithium-initiated, living anionic polymerization is the ability to prepare well-defined, ω-functionalized polymers by post-polymerization reactions with electrophilic reagents [1-3]. A particular challenge has been to develop methods that work in hydrocarbon solution at room temperature or at higher temperatures, i.e. under conditions in which polydienes with high 1,4 microstructure are obtained[2]. Although a variety of functionalization reactions have been reported, many of these specific functionalization reactions are either inefficient or have not been adequately characterized. A particular challenge has been to prepare primary amine-functionalized polymers[1-9], while avoiding complex, multistep processes[10].

In general, it is necessary to protect the primary amine group because of the acidity of the amine protons; for example, the pK_a of cyclohexylamine has been estimated to be 41.6 [11]. Herein, the scope and limitations of living anionic functionalization methods for synthesis of amine-functionalized polymers are delineated with emphasis on new, efficient procedures. All polymerization and functionalization reactions have been carried out in all glass, sealed reactors using breakseals and standard high vacuum techniques [12].

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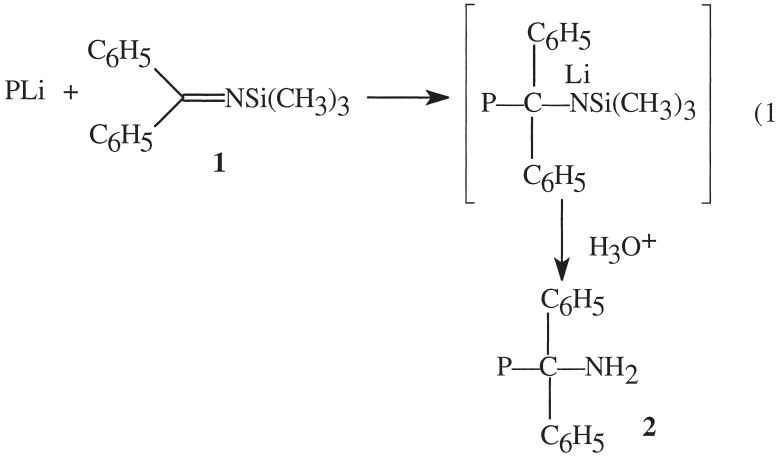
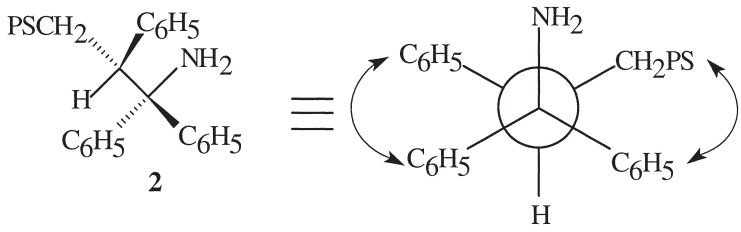
Reactions of polymeric organolithium compounds with N-trimethylsilyl-protected benzophenone imine



One approach for the anionic synthesis of primary amine-functionalized polymers is based on the reaction of polymeric organolithium compounds with N-trimethylsilyl-protected imines [4,5,7]. In order to effect efficient functionalization, the protected imine should not contain acidic alpha hydrogens (enolization-like side reactions) [4,5], nor should they be derivatives of aldehydes (Cannizzarro-like side reactions) [7]. Following this rationale, the N-trimethylsilyimine derivative of benzophenone (**1**) was prepared [13] and investigated as a functionalization agent for preparation of primary amine functionalized polymers (**2**) by reaction with polymeric organolithium compounds as shown in Eq. (1). The reaction of poly(styryl)lithium with **1** was effected in benzene solution at room temperasture using both normal (addition of **1** to PSLi) and inverse addition procedures. The amine functionalization of PSLi by reaction with **1** required 8 hours in benzene solution using the inverse addition (PSLi added to **1**). In the presence of 5 vol % THF (added after the polymerization) the functionalization reaction was competed in 2 hours. For both of these functionalization reactions, no non-functional polymer was observed by TLC analysis, the functionalized polymer was isolated in > 99 % yield by silica gel column chromatography and the functionalities determined by end-group titration were 93 % and 97 % in benzene and in the presence of THF, respectively. It is noteworthy that no dimer formation was observed, since dimer formation was observed for functionalizations with N-(benzylidene)-trimethylsilylamine [7]. The relatively slow rate of addition of PSLi to **1** is presumably due to the steric congestion

which develops in the transition state for the reaction. A Newman projection[14] of the product **2** illustrating the unfavorable gauche-gauche interactions is shown below.



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Reactions of polymeric organolithium compounds with amine-substituted alkyl chlorides

The reaction of polymeric organolithium compounds with substituted alkyl chlorides has been investigated as a general functionalization reaction as shown in Eq. (2) [15]. Although high functionalization yields have been reported

$$PLi + Cl{-}CH_2CH_2CH_2{-}Z \longrightarrow P{-}CH_2CH_2CH_2{-}Z \qquad (2)$$

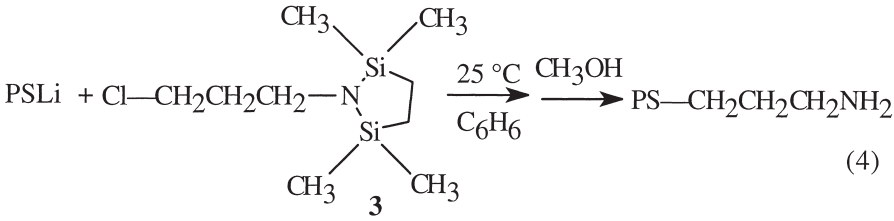
Z = -OR, NR_2, -SR, etc.

for such functionalization reactions at low temperatures in THF [8,16,17], a systematic study of this reaction showed that at room temperature and above in hydrocarbon solution, the reaction is complicated by lithium-halogen exchange leading to polymer-polymer coupling reactions (dimer formation) and by hydrogen abstraction from the β-hydrogen of the alkyl chloride (formation of unfunctionalized polymer) [15]. The results for functionalization of poly(styryl)lithium are shown in Eq. (3). In conjunction with a comprehensive

$$\text{PSLi} + \text{Cl—CH}_2\text{CH}_2\,\text{CH}_2\text{N(CH}_3)_2 \xrightarrow[25\ ^\circ\text{C}]{\text{C}_6\text{H}_6} \underset{67\ \%}{\text{PS—CH}_2\text{CH}_2\text{CH}_2\text{N(CH}_3)_2} + \underset{23\ \%}{\text{PS—PS}} + \underset{10\ \%}{\text{PS—H}} \qquad (3)$$

study of experimental variables which could increase the efficiency of this and other functionalization reactions of polymeric organolithiums with substituted alkyl chlorides, the effect of the addition of lithium halides has been investigated. Previous work has indicated that cross-associated aggregates of alkyllithium compounds and lithium halides [18] generally have decreased reactivity, and presumably higher selectivity compared with the uncomplexed alkyllithiums [19-22]. Therefore, it was of interest to determine if added lithium chloride would promote the functionalization reactions of polymeric organolithium compounds with 3-dimethylaminopropyl chloride in hydrocarbon solution. Quite unexpectedly, it was found that ω-dimethylamino-polystyrene was obtained in quantitative yield from the functionalization of poly(styryl)lithium with 3-dimethylaminopropyl chloride in the presence of one equivalent of lithium chloride. No dimer formation was observed by SEC and amine end-group titration was consistent with quantitative functionalization. No unfunctionalized polystyrene was detected by TLC analysis and the amine-functionalized polystyrene was isolated in quantitative yield by silica gel column chromatography.

In order to determine the generality of the effect of lithium chloride on functionalization reactions with substituted alkyl chlorides, the reaction of poly(styryl)lithium with 2,2,5,5-tetramethyl-1-(3-chloropropyl)-1-aza-2,5-disilacyclopentane (**3**) has been investigated at room temperature in hydrocarbon solution as shown in Eq. (4). In the absence of lithium chloride, SEC analysis showed the presence of dimer (10 %) and the amine functionality of the product was only 77 % as determined by end-group titration. However, in the presence of 1.5 equivalents of lithium chloride, no dimer formation was observed by SEC and the functionality was 99 % as determined by end-group titration. No non-functionalized polymer was detected by TLC analysis. With respect to the sensitivity of the TLC method for detection of non-funcitonalized polymer, previous studies have shown that this technique is capable of detecting 1-2 wt. % levels of non-functionalized polymers [9]. These results indicate



(4)

that lithium chloride is effective in promoting the coupling of polymeric organolithiums with substituted alkyl chlorides. Since these reactions are efficient in hydrocarbon solution at room temperature and above and since a variety of substituted alkyl chlorides are readily available, this methodology for chain-end functionalization has the potential to be the most general and useful method for chain-end functionalization of polymeric organolithium compounds.

Functionalization with functionalized initiators.

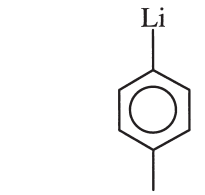
A simpler, quantitative functionalization methodology utilizes functionalized alkyllithium initiators [1,23]. There are several distinct advantages in the use of a functionalized initiator. For alkyllithium-initiated polymerization, each functionalized initiator molecule will produce one macromolecule with a functional group from the initiator residue at the initiating (α) chain end and with the active carbanionic propagating species at the terminal (ω) chain end regardless of molecular weight as shown in Eq. (5).

$$\textbf{prot-N-}RLi + n\ \text{monomer} \xrightarrow[\geq 25\ ^\circ C]{RH} \textbf{prot-N-}PLi \qquad (5)$$

Because most functional groups of interest (e.g., hydroxyl, carboxyl, amino) are not stable in the presence of either simple or polymeric organolithium reagents, it is generally necessary to use suitable protecting groups in the initiator [1]. A suitable protecting group is one that is not only stable to the anionic chain ends but is easily removed upon completion of the polymerization to generate the desired functional group.

The utility of alkyllithium initiators with protected hydroxyl groups (*t*-alkoxy and *t*-butyldimethylsiloxy) has been investigated for preparation of functionalized polymers (monofunctional, telechelic, heterotelechelic and functionalized, star-branched) in hydrocarbon

solution [24,25]. Like hydroxyl groups, primary and secondary amine groups are not stable in the presence of organolithium chain ends; they undergo proton transfer reactions with the active chain ends [26]. As discussed previously, a suitable protecting group for a primary amine is the corresponding *bis*(trialkylsilyl) derivative [8,16] . Schulz and Halasa [27] prepared *p*-lithio-N,N-*bis*(trimethylsilyl)aniline (**4**) and investigated its use as a protected amine initiator for the anionic polymerization of butadiene and isoprene. Unfortunately, like many other functionalized alkyllithium initiators, **4** is not soluble in hydrocarbon solvents. Therefore,



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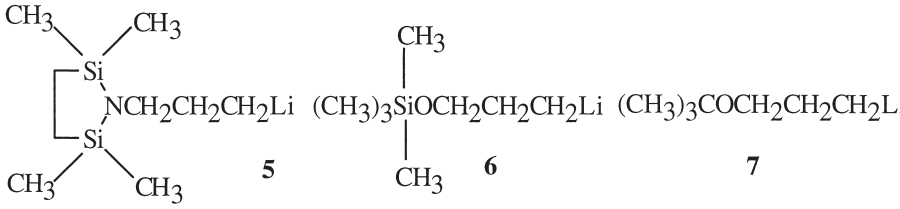
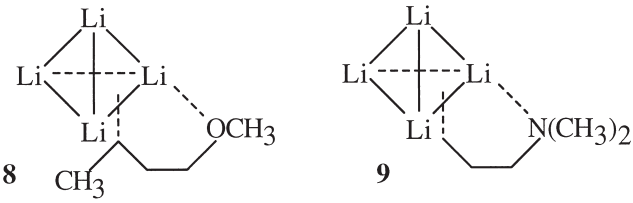
it was necessary to prepare the initiator in diethyl ether and to effect polymerizations in mixtures of hexane and diethyl ether. Polybutadienes with relatively narrow molecular weight distributions and functionalities of 0.69-1.0 were obtained using this initiator; however, the vinyl microstructures of these polydienes ranged from 39-50 %. A hydrocarbon-soluble amine-functionalized initiator is required to prepare amine-functionalized polydienes with high 1,4-microstructure [2].

A potentially useful protected amine-functionalized initiator is 2,2,5,5-tetramethyl-1-(3-lithiopropyl)-1-aza-2,5-disilacyclopentane (**5**). This initiator is soluble in cyclohexane, a necessary but not sufficient condition for a useful alkyllithium initiator [24] . However, unlike previous studies with protected hydroxyl-functionalized initiators such as 3-(*t*-butyldimethylsiloxy)propyl-lithium (**6**) and 3-(*t*-butoxy)propyllithium (**7**) [24,25], this initiator did not initiate polymerization of isoprene in either cyclohexane or benzene, at room

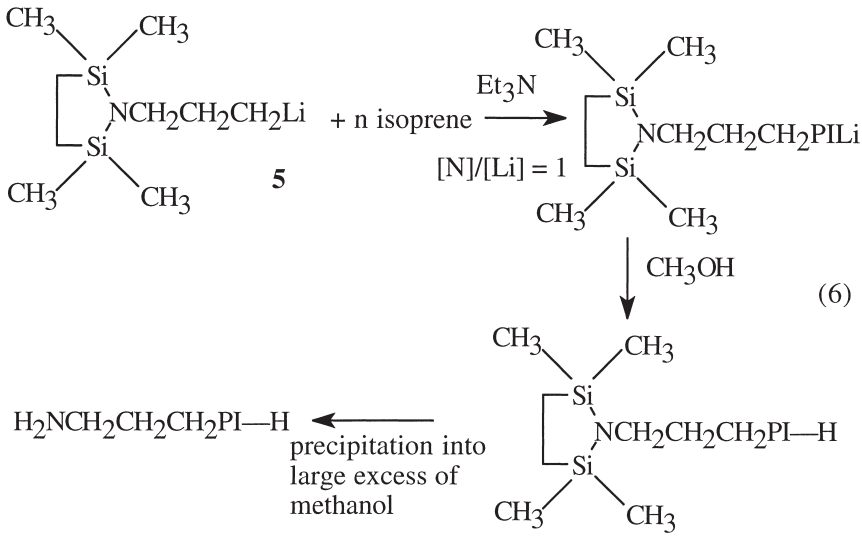


temperature or at 60 °C. These results suggest that there are some specific interactions of the lithium centers in the corresponding aggregated species which stabilize the initiator, making it less reactive. The x-ray crystal structures of both 3-lithio-1-methoxybutane (**8**) [28] and 3-dimethylamino-1-lithiopropane (**9**) [29] show tetrameric structures for both of these organolithiums with intramolecular coordination of the heteroatom to lithium as indicated schematically below. It is interesting to note that 3-dimethylamino-1-lithiopropane is also tetrameric in benzene solution [30], whereas most primary alkyllithiums such as *n*-butyllithium and ethyllithium are hexameric in hydrocarbon solution [2]. These results suggest that intramolecular stabilizing interactions can occur when there are heteroatoms available for coordination as substituents on the 3-carbon of the organolithium. Thus, such interactions may be responsible for the reduced reactivity of **5** as an initiator for isoprene polymerization.



Another factor that may contribute to the reduced reactivity of initiator **5** is the ability of silicon to inteeract with nucleophiles by expanding it octet to form a pentacoordinated siliconate intermediate [31]. To the extent that coordination of the carbanionic chain end to a silicon atom in the protecting group, the chain end could be stabilized and thus be less reactive.

Fortunately, it was possible to active this initiator towards isoprene polymerization by addition of one equivalent of triethylamine at 60 °C as shown in Eq. (6).



Under these conditions, the observed molecular weight (M_n = 8,300 g/mol) was higher than the calculated value (M_n = 7,000 g/mol) and the molecular weight distribution was narrow (M_w/M_n = 1.08). The observed molecular weight corresponds to an initiator efficiency of only 84 %. The polyisoprene microstructure was 85 % 1,4. Only one spot was observed by TLC analysis of the product. Furthermore, and most importantly, the amine functionality was determined to be 1.06 by amine end group titration. It is noteworthy that no polymerization was observed at room temperature in the presence of only one equivalent of triethylamine. Further work is in progress to evaluate the usefulness and applications of this protected amine-functionalized initiator.

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