Macromol. Symp. **132**, *281-291 (1998)*

POLYMER SYNTHESIS USING FUNCTIONALIZED ALKYLLITHIUM INITIATORS: TELECHELIC, HETEROTELECHELIC AND FUNCTIONALIZED STAR-BRANCHED POLYMERS.

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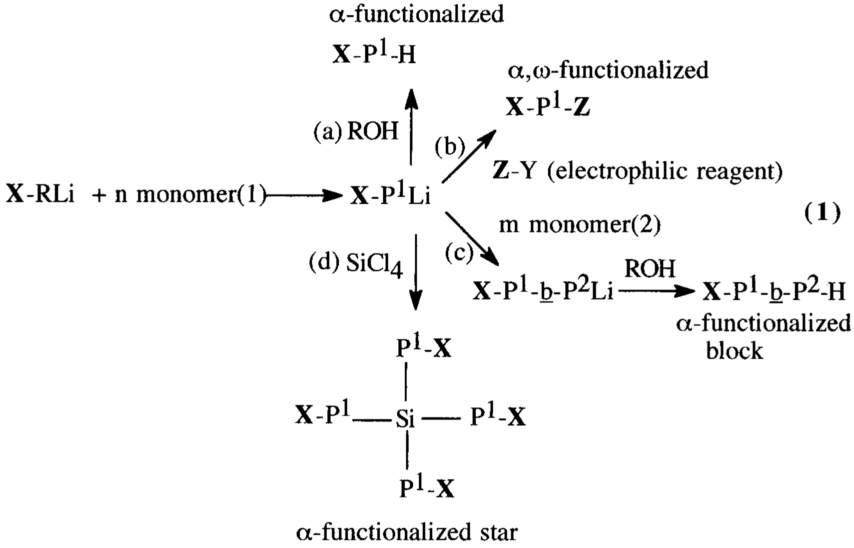
Abstract. Alkyllithium initiators with hydroxyl groups protected with either t-butoxy or t-butyldimethylsiloxy groups have been used to prepare α-functionalized polymers, α,ω-telechelic, α,ω-heterotelechelic and multifunctional star-branched polymers.

INTRODUCTION

Alkyllithium-initiated anionic polymerization is a useful method for synthesis of polymers with well-defined structures for academic and commercial purposes (Refs. 1-3). Polystyrenes, polydienes and poly(meth)acrylates can be prepared with control of molar mass, molar mass distribution, copolymer composition and microstructure, architecture and chain-end functional groups. The most general anionic methods for preparation of chain-end functionalized polymers utilize post-polymerization reactions with a variety of electrophilic reagents (Refs. 1,4,5). Unfortunately, many of these functionalization reactions are not quantitative and produce polymeric side-products in addition to unfunctionalized polymer chains (Refs. 1,4,6). A simpler, quantitative functionalization methodology utilizes functionalized alkyllithium initiators as illustrated in the following scheme, where P represents a polymer chain and -X ,-Z are functional groups (Refs. 7-9). 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 (Refs. 10-12). A suitable protecting group is one that is not only stable to the anionic chain ends but is also readily removed upon completion of the polymerization to generate the desired functional group.

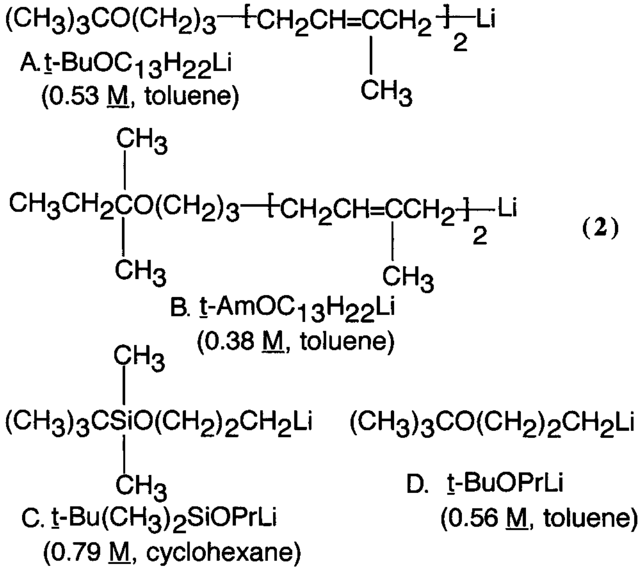
CCC 1022-1360/98/$ 17.50



(1)

There are several unique advantages of using functionalized alkyllithium initiators to prepare chain-end functionalized polymers (Ref. 7). For living 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 [see (a) in scheme (1)] regardless of molar mass. Advantages relative to functionalization by electrophilic termination are that it is not necessary to be concerned about efficient and rapid mixing of reagents with viscous polymers or with the stability of the anionic chain end that is of concern at the elevated temperature conditions often employed in anionic polymerization (Ref. 1). The use of functional alkyllithium initiators provides the added advantage of the ability to prepare telechelic [(b), scheme (1), X = Z] and heterotelechelic [(b, scheme (1), X ≠ Z)] polymers, functionalized block copolymers [see (c) in scheme (1)] and star-branched polymers with functional groups at the initiating ends of each branch [see (d) in scheme (1)].

A recent paper has presented experimental criteria with which to judge if a functionalized alkyllithium initiator is generally useful for preparation of well-defined, α-functionalized polymers (Ref. 13). The following protected hydroxyl-functionalized alkyllithium initiators shown in scheme (2) were evaluated using these criteria for the polymerization of styrene,



$(CH_3)_3CO(CH_2)_3-\!\!\left[CH_2CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}CH_2\right]_2\!\!-Li$

A. t-BuOC$_{13}$H$_{22}$Li
(0.53 M, toluene)

$CH_3CH_2\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}O(CH_2)_3-\!\!\left[CH_2CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}CH_2\right]_2\!\!-Li$ (2)

B. t-AmOC$_{13}$H$_{22}$Li
(0.38 M, toluene)

$(CH_3)_3C\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{Si}}}}O(CH_2)_2CH_2Li$

C. t-Bu(CH$_3$)$_2$SiOPrLi
(0.79 M, cyclohexane)

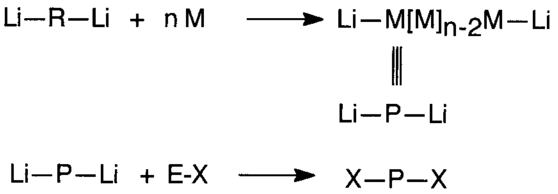
$(CH_3)_3CO(CH_2)_2CH_2Li$

D. t-BuOPrLi
(0.56 M, toluene)

isoprene and butadiene. In this paper, the use of these hydrocarbon-soluble, organolithium initiators for the preparation of a variety of functional polymers will be described.

RESULTS AND DISCUSSION

Telechelic polymers. The synthesis of α,ω-difunctional (telechelic) (X-P-X) polymers has traditionally utilized soluble dilithium initiators (LiRLi) to prepare α,ω-dilithiumpolymers (LiPLi) which can be reacted with electrophilic functionalizing agents (E-X) as shown in scheme (3), where M is an anionically polymerizable monomer (Ref. 2). Although aromatic radical anions are efficient anionic initiators for preparation of α,ω-dicarbanionic polymers, they generally require the use of a polar solvent such as THF for their preparation (Ref. 3). Unfortunately, the use of a polar solvent results in the formation of polydienes with high side-chain vinyl enchainment which leads to a higher T_g material (Ref. 14). In order to prepare elastomeric polydienes with high 1,4-microstructure and low T_g values, it is necessary to utilize lithium as counterion in a hydrocarbon solvent (Refs. 1,2,14). However, the requisite dilithium initiators have proven to be difficult to prepare and use in hydrocarbon media because chain end association generally leads to insoluble or inefficient initiators (Ref. 9). In addition, any adventitious impurities present initially in the



$$\mathrm{Li{-}R{-}Li} + n\,\mathrm{M} \longrightarrow \mathrm{Li{-}M[M]_{n\text{-}2}M{-}Li} \equiv \mathrm{Li{-}P{-}Li}$$

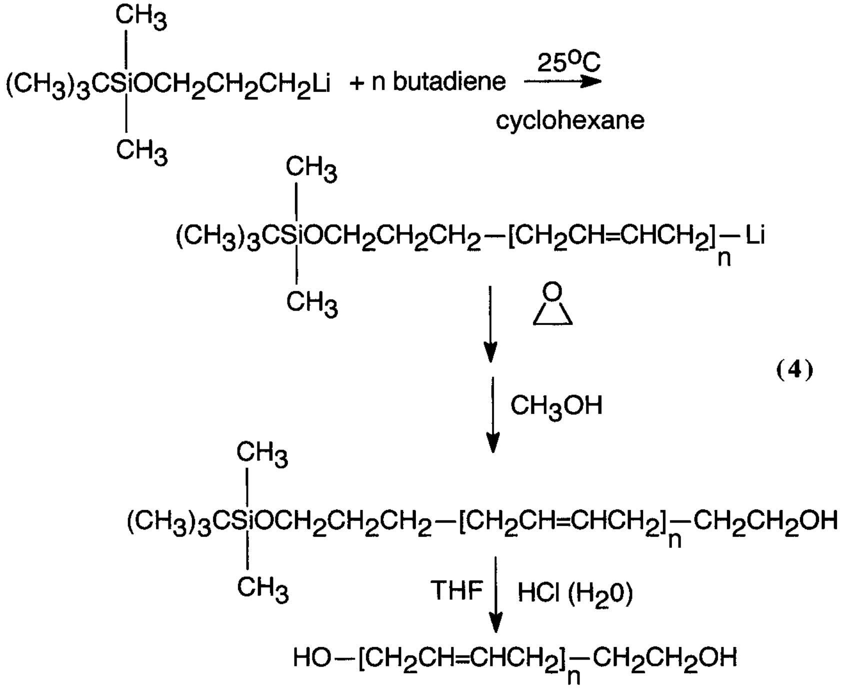
$$\mathrm{Li{-}P{-}Li} + \mathrm{E\text{-}X} \longrightarrow \mathrm{X{-}P{-}X}$$

(3)

solvent or monomer can lead to partial termination which will form some monofunctional chains. Even when all of these limitations can be overcome, the efficient preparation of α,ω-difunctional (telechelic) polymers by chain-end functionalization is problematic because the polar end groups of the functional chain ends are highly associated and this causes gel formation during the functionalization reaction (Refs. 1,8,15).

The use of functionalized alkyllithium initiators provides a simple, general methodology for the synthesis of telechelic and heterotelechelic polymers, with linear and branched structures [see scheme (1)]. If a functionalized alkyllithium initiator is to be generally useful, it must satisfy the following criteria, i.e., (a) it is soluble in hydrocarbon media; (b) it efficiently initiates chain growth such that observed number average molar masses are in good agreement with calculated values; (c) it initiates chain grow rapidly or competitively with the rate of propagation such that narrow molar mass distribution polymers can be obtained; (d) the protecting group is stable to the anionic polymerization conditions; and (e) the protecting group can be readily removed upon completion of the polymerization (Ref. 13). All of the protected, functional initiators shown in Scheme 2 satisfy the above criteria and their use for the preparation of functionalized polymers has been investigated in detail.

The preparation of α,ω-dihydroxypolybutadiene is outlined in scheme (4). Even at room temperature in cyclohexane the siloxy-protected initiator initiates butadiene polymerization to efficiently form the corresponding well-defined [M_n (obs) $\approx$ M_n (calc)] poly(butadienyl)-lithium. Removal of a small sample and termination with methanol for base polymer characterization showed that a narrow molar mass distribution polydiene is formed ($M_w/M_n \leq 1.1$). In addition, ^{1}H NMR analysis shows the presence of two peaks characteristic of the protecting group at δ 0.05 and 0.90 ppm corresponding to the $\text{-Si(C}\underline{\text{H}}_3)_2\text{C(CH}_3)$ and $\text{-Si(CH}_3)_2\text{C(C}\underline{\text{H}}_3)_3$ protons, respectively. Removal of the $\underline{\text{t}}$-butyldimethylsiloxy group [see Scheme (4)] results in formation of an α-hydroxy-functionalized polybutadiene with a functionality of 1.0 as determined by standard end-group titration (Ref. 16). The microstructure of this polybutadiene was 90 % 1,4-enchainment as determined by ^{1}H



(4)

$$(CH_3)_3C\overset{CH_3}{\underset{CH_3}{Si}}OCH_2CH_2CH_2Li + n\ \text{butadiene} \xrightarrow[\text{cyclohexane}]{25^oC}$$

$$(CH_3)_3C\overset{CH_3}{\underset{CH_3}{Si}}OCH_2CH_2CH_2-[CH_2CH{=}CHCH_2]_n-Li$$

$$\downarrow \overset{O}{\triangle}$$

$$\downarrow CH_3OH$$

$$(CH_3)_3C\overset{CH_3}{\underset{CH_3}{Si}}OCH_2CH_2CH_2-[CH_2CH{=}CHCH_2]_n-CH_2CH_2OH$$

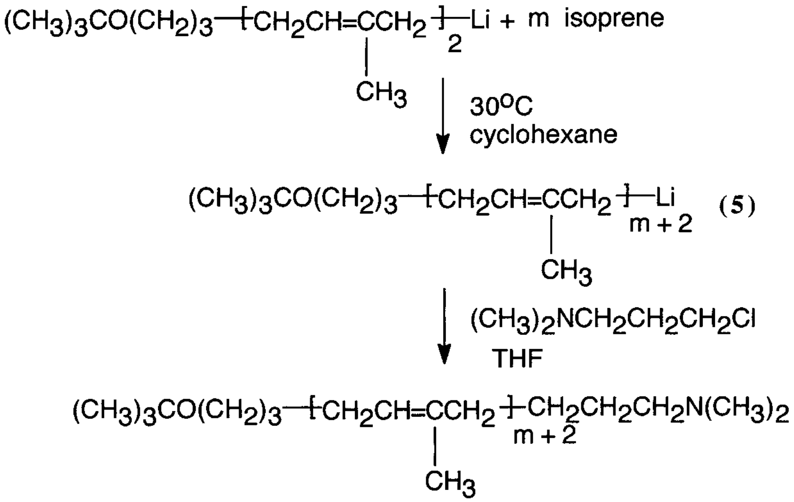
$$\text{THF} \downarrow \text{HCl } (H_2O)$$

$$HO-[CH_2CH{=}CHCH_2]_n-CH_2CH_2OH$$

NMR analysis using standard peak assignments and integration methods (Refs. 1,17).

Termination with ethylene oxide to form the corresponding ω-hydroxyethylated polymer is a simple, quantitative functionalization reaction (Ref. 18). The t-butyldimethylsiloxy-protecting group is readily removed using a variety of reagents. For example, in the seminal patents of Shepherd and Stewart (Ref. 19), this protecting group was facilely removed by stirring the α-t-butyl-dimethylsiloxy-protected polybutadienes in tetrahydrofuran at room temperature with tetra(n-butyl)ammonium fluoride for 2 hours. Handlin, Benning and Willis (Ref. 20) removed this siloxy protecting group by treatment of a cyclohexane solution of the polymer with methanesulfonic acid in isopropanol with a small amount of water. As described previously, the t-butyldimethylsiloxy-protecting group can also be removed by stirring a THF solution of the polymer with one equivalent of aqueous HCl and heating under reflux for 1 hour (Ref. 13,21). The protecting group was completely removed after this relatively mild procedure as shown by the ^{1}H NMR analysis of the resulting polymer. The functionality of the resulting α,ω-dihydroxyl-functionalized polybutadiene was 2.0 as determined by end-group titration (Ref. 16). Thus, the use of t-butyldimethylsiloxy-protected alkyllithium initiator provides a simple, quantitative method for the preparation of telechelic α,ω-dihydroxyl-functionalized polybutadienes with high 1,4-microstructure, controlled molar mass and narrow molar mass distribution.

Heterotelechelic polymers. The use of protected, functionalized alkyllithium initiators also provides a versatile methodology for the preparation of heterotelechelic α,ω-difunctional polymers that have different functional end groups [X ≠ Y, scheme (1)] (Ref. 7). As previously shown in path (b) in scheme (1), the living α-functionalized, ω-lithio polymer can be reacted with electrophilic reagents (Z-Y) to form a wide variety of heterotelechelic polymers (X-P-Z). The functionalization reaction with 3-dimethylaminopropyl chloride [see scheme (5)] has been investigated to evaluate the scope and limitations of this method.



$$(CH_3)_3CO(CH_2)_3\text{—}[CH_2CH{=}\underset{\substack{|\\CH_3}}{C}CH_2]_2\text{—}Li + m\ \text{isoprene}$$

$$\Big\downarrow \begin{array}{l}30^{o}C\\ \text{cyclohexane}\end{array}$$

$$(CH_3)_3CO(CH_2)_3\text{—}[CH_2CH{=}\underset{\substack{|\\CH_3}}{C}CH_2]_{m+2}\text{—}Li \qquad (5)$$

$$\Big\downarrow \begin{array}{l}(CH_3)_2NCH_2CH_2CH_2Cl\\ THF\end{array}$$

$$(CH_3)_3CO(CH_2)_3\text{—}[CH_2CH{=}\underset{\substack{|\\CH_3}}{C}CH_2]_{m+2}CH_2CH_2CH_2N(CH_3)_2$$

The SEC chromatogram of the products of this functionalization reaction is shown in Fig. 1. A base polymer sample was removed for comparison and it exhibited a narrow, monomodal molar mass distribution (M_w/M_n = 1.06), controlled molar mass (M_n = 3,200 g/mol) and 89 % 1,4-microstructure. The product mixture from the functionalization contained some dimer product, presumably resulting from lithium-chlorine exchange followed by Wurtz coupling. After silica gel column chromatography, the pure α-t-butoxy-ω-dimethylamino-functionalized

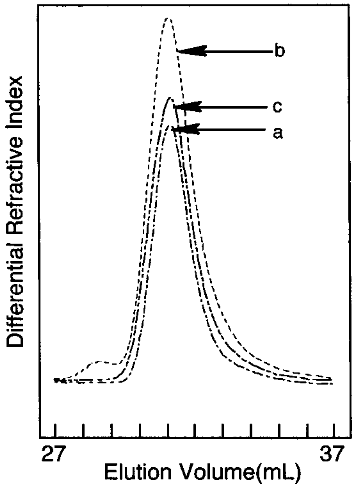
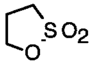


Fig. 1. SEC chromatograms of (a) base polyisoprene, (b) crude 3-dimethylaminopropyl chloride functionalization reaction mixture, and (c) purified ω-dimethylaminopolyisoprene.

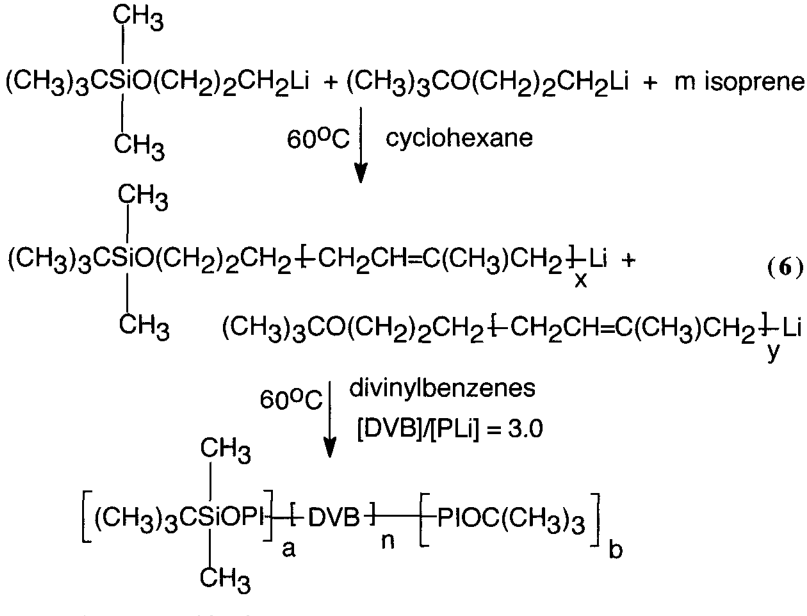
polyisoprene was isolated in 85 % yield. For the corresponding poly(butadienyl)lithium, the amination reaction proceeds with 90 % efficiency even in cyclohexane in the absence of THF. For poly(styryl)-lithium, this functionalization reaction is not as efficient; the ω-dimethyl-amino-functionalized polystyrene is obtained in only 67 % yield. A variety of other heterotelechelic polymers have been prepared and are listed in Tab. 1. These procedures are only limited by the efficiencies of the terminal end-functionalization reactions with electrophiles (Refs. 1,4). Unfortunately, many of these functionalization reactions are considerably

Tab. 1. Synthesis of α,ω-heterotelechelic polystyrenes.

Initiator	Terminating Agent	ω-Functionality	Efficiency (%)
$\underline{t}$-BuOC$_{13}$H$_{22}$Li		-SO$_3$H	93
	C$_6$H$_5$CH=NSi(CH$_3$)$_3$	-NH$_2$	90
	CO$_2$	-CO$_2$H	95
	(CH$_3$)$_2$NCH$_2$CH$_2$CH$_2$Cl	-N(CH$_3$)$_2$	93

less than quantitative (Refs. 1,4,6), although specific procedures have often been developed to optimize the yields of these functionalizations. Functionalized, star-branched polymers. Another unique type of functionalized polymer which can be prepared with functionalized alkyllithium initiators is the functionalized star-branched polymer as shown by path (d) in scheme (1). Using a functionalized alkyllithium initiator produces a star-branched polymer with uniform arms and with a functional group at every branch chain end (Ref. 7). In addition to the use of multichlorosilanes, a useful linking agent is divinylbenzene (DVB), which is usually obtained as a complex mixture containing different isomers as well as ethylstyrenes (Refs. 1,22,23).

The synthesis of a functionalized star-branched polyisoprene is shown in scheme (6). Using an equimolar mixture of the t-butoxy- and siloxyalkyllithium initiators, it was possible to prepare a heteroarm, star-branched polymer in which the polymer chain ends had two different



$$\mathrm{(CH_3)_3C\overset{CH_3}{\underset{CH_3}{Si}}O(CH_2)_2CH_2Li + (CH_3)_3CO(CH_2)_2CH_2Li} + m\ \mathrm{isoprene}$$

$$\xrightarrow[\text{cyclohexane}]{60^oC}$$

$$\mathrm{(CH_3)_3C\overset{CH_3}{\underset{CH_3}{Si}}O(CH_2)_2CH_2{+}CH_2CH{=}C(CH_3)CH_2{+}_x Li} + \mathrm{(CH_3)_3CO(CH_2)_2CH_2{+}CH_2CH{=}C(CH_3)CH_2{+}_y Li} \qquad (6)$$

$$\xrightarrow[{[DVB]/[PLi] = 3.0}]{60^oC,\ \text{divinylbenzenes}}$$

$$\left[\mathrm{(CH_3)_3C\overset{CH_3}{\underset{CH_3}{Si}}OPI}\right]_a \!\!{+}\mathrm{DVB}{+}_n \left[\mathrm{PIOC(CH_3)_3}\right]_b$$

kinds of protected hydroxyl groups. Isoprene was polymerized with the mixture of initiators and then the resulting mixture of functionalized poly(isoprenyl)lithiums [M_n (arm; SEC) = 44,000 g/mol] was linked at 60°C with 3 equivalents of DVB. The resulting star-branched polyisoprene was obtained in 89 % yield in admixture with 11 % of the unlinked arms as shown by SEC in Fig. 2. The M_n of the star was estimated to be 390,000 g/mol by the universal calibration method; this

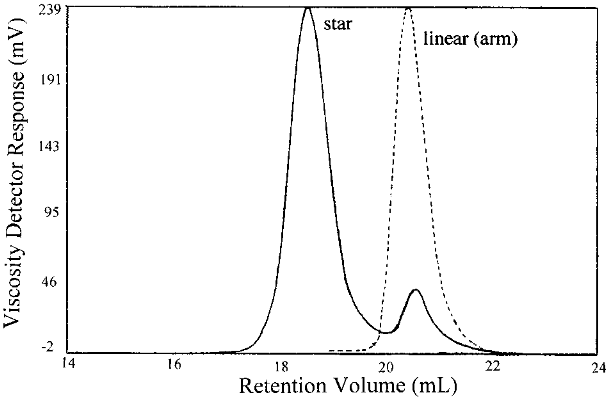


Fig. 2. SEC chromatograms of base arm polyisoprene prepared with mixed protected initiators and corresponding functionalized polyisoprene star polymer prepared by linking with divinylbenzenes.

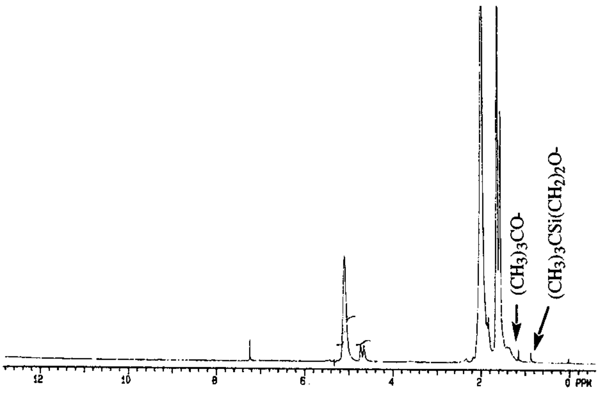


Fig. 3. ^{1}H NMR of functionalized polyisoprene star polymer prepared with mixed protected initiators and linking with DVB.

result corresponds to 8.7 arms per star. The apparent molar mass distribution was $M_w/M_n = 1.12$. It was interesting to note that for these high molar mass polymer arms and stars, ^{1}H NMR resonances corresponding to the t-butyl groups in the t-butoxy group and the t-butyldimethylsiloxy group were observed at $\delta = 1.17$ and 0.90 ppm, respectively [see Fig. (3)] . This type of star polymer is of interest since the t-butyl-dimethylsiloxy group can be selectively removed by hydrolysis with aqueous HCl in THF as indicated previously (Refs. 13,21) . Thus, use of these hydroxyl groups for chain-extension, linking or initiation of polymerization could be accomplished in the presence of the protected t-butoxy end groups. These polyisoprene stars have also been efficiently hydrogenated using the Falk catalyst (Ref. 24), provided that the protecting groups are not removed prior to hydrogenation.

CONCLUSIONS

Alkyllithium initiators with hydroxyl groups protected by either t-butoxy groups or t-butyldimethylsiloxy groups are efficient, reactive and useful for the polymerization of styrene and diene monomers on hydrocarbon solution to form monofunctional, difunctional telechelic, difunctional heterotelechelic and multifunctional star-branched polymers.

ACKNOWLEDGEMENTS

The authors are grateful to FMC, Lithium Division, for generous support of this research and for providing samples of functional initiators and sec-butyllithium.

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