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ANIONIC SYNTHESIS OF HYDROXY-FUNCTIONALIZED POLYMERS USING FUNCTIONALIZED INITIATORS AND ELECTROPHILIC TERMINATION

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SUMMARY: The results for efficient hydroxy-functionalization of polymeric organolithium compounds in hydrocarbon solution at room temperature are described using oxirane, methyloxirane, ethyloxirane, phenyloxirane and oxetane. Conditions for quantitative hydroxy-functionalization were observed for all oxiranes except methyloxirane, which undergoes significant proton transfer from the methyl group. The use of protected hydroxy-functionalized alkyllithium initiators to prepare α,ω-heterotelechelic polymers with ω-amino and ω-carboxy groups is described.

Introduction

There has been growing interest, research and progress on the development of new synthetic methods for the preparation of well-defined polymers with reactive functional groups1). Living polymerizations in general and alkyllithium-initiated polymerization in particular provide versatile methods for the preparation of chain-end and in-chain functionalized polymers2). The absence of chain termination and chain transfer reactions in living anionic polymerization provides several methodologies for the preparation of well-defined, functionalized polymers2,3). Herein, the scope and limitations of living anionic functionalization methods for synthesis of hydroxy-functionalized polymers are delineated with specific examples. Recent advances in the synthesis of hydroxy-functionalized polymers are presented.

Basic attributes of living anionic polymerization for preparation of functionalized polymers

Living anionic polymerization is particularly suitable for the synthesis of polymers with well-defined structures2,3). Because of the absence of termination and transfer reactions, each initiator molecule produces one living polymer chain. This factor results in the ability to predict and control the number-average molecular weight of the polymer (M_n = g of

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monomer/moles of initiator). If the initiator contains a functional group, each polymer chain will have the functional group incorporated into the polymer chain at the initiating (α) chain end. If the initiator is suitably reactive, then the rate of initiation will be competitive with or faster than the rate of propagation; as a consequence, polymers with narrow molecular weight distributions can be obtained[4) ($X_w/X_n = 1 + [X_n/(X_n + 1)^2]$). Living anionic polymerizations generate polymer chains with stable carbanionic chain ends that, in principle, can be converted into a diverse array of functional end groups by reaction with a variety of electrophilic reagents[1-3). Other unique features of living anionic polymerization which can be coupled with functionalization chemistry include: (a) formation of block copolymers by sequential addition of monomers and (b) formation of star-branched polymers by using multifunctional initiators or by post-polymerization addition of electrophilic linking agents[2). Thus, living anionic polymerization and functionalization chemistry can be combined to prepare well-defined, functionalized polymers with varied compositions and molecular architectures.

Limitations of living anionic polymerization chemistry

Alkyllithium-initiated anionic polymerization can provide well-defined polymers with low degrees of compositional heterogeneity provided that careful experimental procedures are employed. The most rigorous procedures involve careful purification, storage and handling of monomers, solvents, initiators and other reagents using all-glass, sealed reactors, breakseals and standard high-vacuum techniques[5). The use of less rigorous procedures introduces compromises that may or may not affect the compositional homogeneity of the polymer product. For example, procedures for anionic polymerizations under a positive pressure of a purified, inert gas have been described; such procedures are utilized for large-scale industrial anionic polymerization processes[6). The success of these systems often relies on the ability to add an additional amount of alkyllithium initiator to react with oxygen, water and other reactive impurities rapidly at the beginning of the polymerization. In general, the products of these reactions are lithium alkoxide salts whose presence in the polymerization system is often ignored. However, lithium salts can cross-aggregate with the initiator and with the propagating polymeric organolithium chain ends to change their degree of aggregation, the rates of initiation and propagation, and the chemistry of post-polymerization functionalization reactions[2). The ability to critically evaluate experimental results requires that experimental descriptions be detailed enough to determine the impurity levels for these species in the system. The relationship between initiator stoichiometry and number-average molecular weight is helpful in this regard. This self-cleansing aspect of alkyllithium-initiated polymerizations is limited to the initial monomer and solvent charge. Subsequent addition of monomers, linking or functionalization agents containing impurities will result in termination of active chains. Therefore, careful termination with high-purity reagents is essential for preparation of well-defined, functionalized polymers by anionic polymerization. For example, molecular oxygen is an ubiquitous impurity that is difficult to remove or prevent from ingress into the reactor. If oxygen (air) is introduced during termination, small amounts of dimeric impurities can be formed2,7,8).

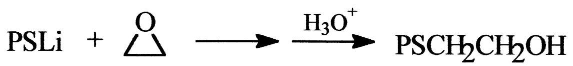
A final caveat is that the use of alkyllithium-initiated polymerization of styrene and diene monomers does not necessarily provide a well-defined polymer. This situation arises from a variety of sources including too much reliance on the presumed elegance and control of living anionic polymerization without adequate structural characterization9), the overdependence on the precedents provided by the results from reactions of low-molecular-weight analogs, or because of poor experimental techniques.

In order to critically evaluate a given functionalization reaction, it is important to utilize a number of characterization methods to determine the course of the reaction and the purity of the functionalized polymer. In general, no one method can be relied upon to provide unambiguous, quantitative information on the course of a given functionalization reaction because of the experimental errors inherent in most analytical methods3).

Functionalization by electrophilic termination

One of the unique aspects of alkyllithium-initiated, living anionic polymerization is the ability to prepare ω-functionalized polymers by post-polymerization reactions with electrophilic reagents. A particular challenge has been to develop methods that work in hydrocarbon solution at room temperature or higher temperatures, i.e., under conditions in which polydienes with high 1,4 microstructure can be obtained2). Although a variety of functionalization reactions have been reported, many of these specific functionalization reactions are either inefficient or have not been adequately characterized3). Fortunately, a variety of efficient methods have been developed for preparation of ω-hydroxy-functionalized polymers including ring-opening reactions of epoxides and oxetane. These methods will be described in the following sections.

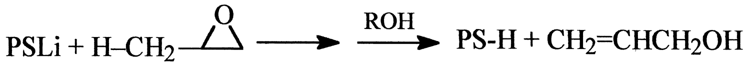
(a) *Oxirane*. The preparation of hydroxy-terminated polymers from polymeric organolithium compounds by reaction with oxirane in hydrocarbon solution is one of the few simple, efficient functionalization reactions. It also serves to emphasize the uniqueness of organolithium-initiated polymerizations. The direct reaction of polystyrene-lithium with excess oxirane in benzene solution produces the corresponding 2-hydroxyethylated polymer in quantitative yield without formation of detectable amounts of oligomeric ethylene oxide blocks (Eq. 1)[10].



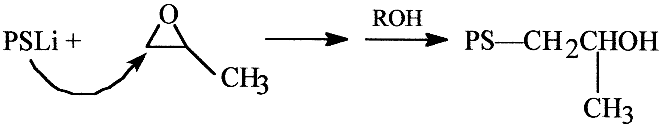
(1)

Apparently, the high degree of aggregation of lithium alkoxides and the strength of this association even in polar solvents renders them unreactive[11].

(b) *Methyloxirane*. The functionalization of polystyrene-lithium ($M_n = 2.1 \times 10^3$, $M_w/M_n = 1.04$) with an excess of methyloxirane in hydrocarbon solution forms the corresponding hydroxypropylated product in 93 % yield; 7 % of unfunctionalized polystyrene is also formed (see Eq. 2)[12]. The unfunctionalized polymer product presumably arises from a hydrogen transfer reaction (Eq. 3) which is analogous to a chain transfer reaction to monomer which is observed in methyloxirane polymerization and which limits[13] the molecular weight to lower than 6000. ^1H and ^{13}C NMR analyses of the pure ω-hydroxy-functionalized polymer were consistent with predominant reaction at the primary carbon of the oxirane ring to form the secondary alcohol product (Eq. 2); less than 3 % of the reaction occurs at the secondary carbon to form the corresponding primary alcohol product. No evidence for oligomerization of methyloxirane was observed by ^{13}C NMR analysis.



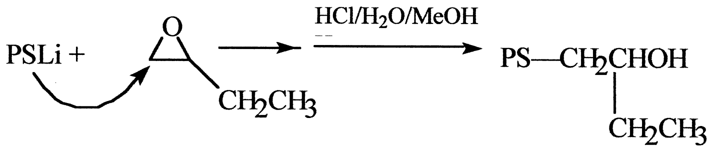
(2)



(3)

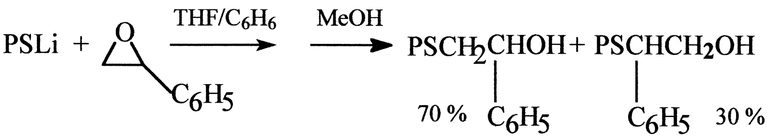
(c) *Ethyloxirane*. The functionalization of polystyrene-lithium with excess ethyloxirane was examined in benzene solution at room temperature[14]. The functionalization efficiency was determined to be higher than 99 % by end-group titration and product separation by column chromatography. ^1H and ^{13}C NMR analyses indicated that the exclusive mode of reaction was attack at the less-substituted methylene carbon of ethyloxirane to form the corresponding secondary alcohol as shown in Eq. 4. As observed previously for methyloxirane functionalization[12], both the chain-end methine protons (^1H NMR) and the terminal carbon

(^{13}C NMR) in the hydroxy-functionalized polymer exhibit multiple resonances because of the formation of meso and racemo diastereomeric chain ends.



(4)

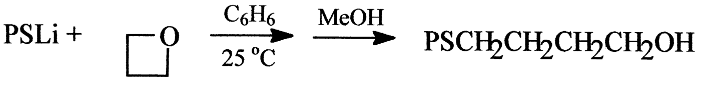
(d) *Phenyloxirane*. The reaction of polystyrene-lithium with phenyloxirane in benzene forms the corresponding ω-hydroxy-functionalized polystyrene in only 76 % yield[15,16]. The other products correspond to unfunctionalized polystyrene (9 %), styrene dimer (5.6 %) and a small amount of styrene trimer (0.1 %). The formation of the non-functionalized products has been ascribed to electron transfer reactions. In toluene solution at -78 °C, the functionalized polymer was obtained in 94 % yield. When this functionalization was carried out in the presence of THF ([THF]/[PSLi] ≥ 15), the corresponding hydroxy-functionalized polymer was obtained in quantitative yield (Eq. 5). The regiochemistry of the addition was determined by ^{1}H NMR analysis and this indicated that 70 % of the product corresponds to addition to the oxirane methylene carbon to form the secondary alcohol end group and 30 % addition occurs at the oxirane methine carbon to form the primary alcohol end group.



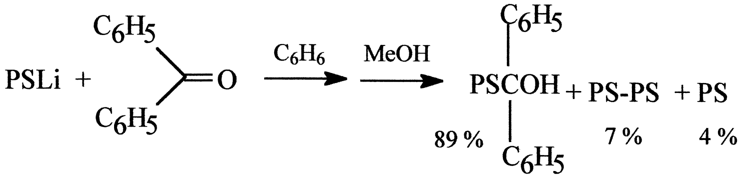
(5)

(e) *Oxetane*. Polystyrene-lithium undergoes a very facile functionalization reaction with oxetane[17] as shown in Eq. 6. The functionalized polymer was obtained in essentially quantitative yield (> 98 %) as determined by thin-layer chromatography (< 1 % of non-functionalized polymer) and silica gel column chromatography (functionalized polymer isolated in 98 % yield). Similar results were obtained for functionalization of polybutadiene-lithium.

(6)



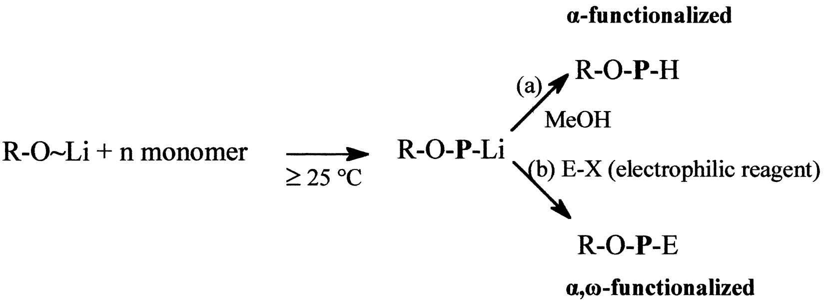
(f) *Carbonyl compounds.* Previous studies have shown that the functionalization reactions of polymeric organolithium compounds with carbonyl compounds are not generally useful. Proton transfer reactions occur for carbonyl compounds with enolizable hydrogens. For aldehydes, the alkoxide products can undergo Cannizzarro reactions by hydride transfer to unreacted aldehyde[18)]. For benzophenones, the incursion of electron transfer reactions would be expected to result in formation of polymeric dimers and unfunctionalized polymer from the intermediate polystyryl radicals[19,20)]. However, reasonable functionalization yields (89 %) were obtained from the reaction of benzophenone with polystyrene-lithium[21)] (Eq. 7). With a 0.2 molar excess of benzophenone at 50 °C, the yield of hydroxy-functionalized polymer was 94 % (4 % of styrene dimer, 2 % PS).



(7)

Functionalization by using functionalized initiators

A simpler, quantitative functionalization methodology utilizes functionalized alkyllithium initiators[22)]. The utility of alkyllithium initiators with protected hydroxy groups has been investigated for preparation of functionalized polymers (monofunctional, telechelic, heterotelechelic and functionalized, star-branched) in hydrocarbon solution[23,24)]. Because most functional groups of interest (e.g., hydroxy, carboxy, 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 also readily removed upon completion of the polymerization to generate the desired functional group. 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 as shown in Scheme 1. This methodology of producing α-functionalized living polymers can be used to prepare telechelic and α,ω-heterotelechelic polymers as shown in Scheme 1. For example, using 3-(*tert*-butyldimethylsilyloxy)propyllithium as initiator to polymerize butadiene in cyclohexane followed by termination with oxirane and deprotection with acid, the corresponding α,ω-dihydroxypolybutadiene was obtained with a hydroxy functionality of two[24)]. Analogous polymerization of isoprene followed by termination with 3-(dimethylamino)propyl chloride[25] and deprotection provided the corresponding well-defined, α-hydroxy-ω-[3-(dimethylamino)propyl]polyisoprene in 85 % yield after column chromatography.



Scheme 1
Synthesis of α-functionalized and α,ω-difunctionalized polymers using functionalized alkyllithium initiator. (R – protecting group, **P** – polymer chain)

Using an isoprene chain-extended analog of 3-(1,1-dimethylpropyloxy)propyllithium[23,24] to polymerize styrene in benzene followed by freeze-drying and carbonation with gaseous carbon dioxide provided the corresponding α-hydroxy-ω-carboxypolystyrene in 97 % yield after column chromatography. The use of functionalized initiators to prepare a wide variety of α,ω-heterotelechelic polymers and their applications is currently under investigation.

Acknowledgements

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