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Recent Advances in the Anionic Synthesis of Chain-End Functionalized Polymers

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Summary: Recent results for the preparation of chain-end functionalized polymers using alkyllithium-initiated anionic polymerization are described. Termination with 4-chloro-1,1,1-trimethoxybutane has been used to prepare trimethoxy ortho ester (carboxyl)-functionalized polymers. Functionalization with the oxiranes, glycidoxypropyltrimethoxysilane, 3,4-epoxy-1-butene and 1,1,1-trifluoro-2,3-epoxypropane, has been investigated to prepare trimethoxysilyl-functionalized polymers, 1,3-diene-functionalized macromonomers and trifluoromethyl-functionalized polymers, respectively. Secondary amine-functionalized polymers have been prepared by termination with N-(benzylidene)methylamine and also using an N-benzyl tertiary amine-functionalized alkyllithium initiator followed by hydrogenolysis of the benzyl group.

Keywords: anionic polymerization; chain

Introduction

Living alkyllithium-initiated polymerizations provide versatile methods for the preparation of chain-end functionalized polymers.[1-4] The methodologies available for the anionic synthesis of well-defined, functional polymers include termination with electrophilic reagents and the use of functionalized initiators.[4] Herein, recent results using these methods for the anionic synthesis of ortho ester, trimethoxysilyl, hydroxyl, diene and amine chain end functionalized polymers are described.

Functionalization with 4-Chloro-1,1,1-trimethoxybutane

Ortho ester (carboxyl) functionalization Because the direct carboxylation of polymeric organolithiums with carbon dioxide in hydrocarbon solution is an inefficient functionalization reaction, [1,3,7] it was of interest to investigate the use of an ortho ester-functionalized alkyl chloride, 4-chloro-1,1,1-trimethoxybutane (CTB), to prepare ortho-ester functionalized polymers as shown in Equation 1. The ortho ester functionalized polymers can be hydrolyzed to the corresponding carboxyl-functionalized polymers. [7] This type of functionalization

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reaction has been investigated by Nakahama and coworkers; [7] however, their procedures

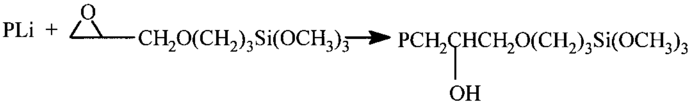
$$\mathrm{PLi} + \mathrm{Cl{-}CH_2CH_2CH_2C(OCH_3)_3} \longrightarrow \mathrm{P{-}CH_2CH_2CH_2C(OCH_3)_3} \quad (1)$$

utilized tetrahydrofuran as solvent, the corresponding alkyl bromides, and temperatures of –78 °C. The direct reaction of CTB in benzene solution with poly(styryl)lithium (PSLi; M_n = 1400) at room temperature formed the corresponding ortho ester-functionalized polymer in only 84-88 % yield. The other products corresponded to unfunctionalized polystyrene (<1 %) and polystyrene dimer (12 %). Using neat CTB (1.25 equivalents), the ortho ester-functionalized polystyrene was obtained in > 93 % yield. The highest functionalization yield (97 %) was obtained using 5 molar equivalents of lithium chloride as additive. The ortho ester-functionalized polymers were quantitatively converted to the corresponding methyl esters and then to the carboxyl-functionalized polymers by treatment first with HCl in dioxane/H_2O followed by hydrolysis with LiOH in THF and then neutralization with dilute aqueous HCl. The ^1H NMR spectrum of the crude product mixture after termination with methanol exhibited a peak at δ 3.20 ppm corresponding the the methoxy protons of the ortho ester group and an additional small peak at δ 3.62 ppm corresponding to the methyl ester group. The ^{13}C NMR spectrum of the methyl ester exhibited peaks at δ 174 ppm (carbonyl carbon) and at δ 53 ppm (methoxy carbon). The yields of functionalized polymers were determined by ^1H NMR, quantitative column chromatography and carboxyl end group titration with alcoholic KOH.

Functionalizations with Epoxides

Glycidoxypropyltrimethoxysilane. Trialkyoxysilane functionalization One of the most useful functionalization methods in anionic polymerization is the reaction of PLi compounds with epoxides.[1,8] For example, the reaction of PSLi with excess ethylene oxide (3-5 equivalents) yields the corresponding hydroxethylated product in quantitative yield without the formation of detectable amounts of oligomerization products.[9] Therefore, it was of interest to investigate the use of substituted oxiranes for the introduction of other functional groups at the chain end.

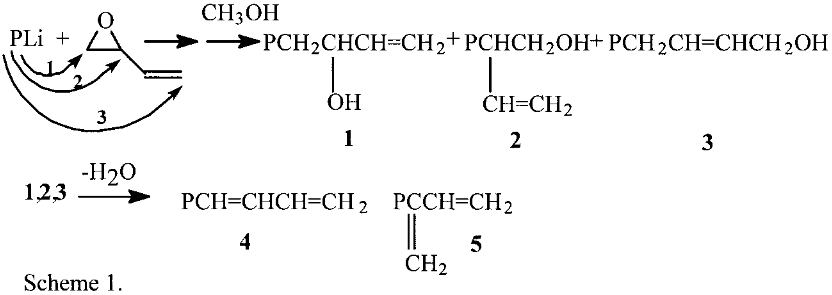
The renewed interest in the use of silica as a reinforcing filler for elastomers[10] has generated a need for functionalized elastomers that can aid in the dispersion of silica and promote polymer-filler interactions. Trialkoxysilyl-functionalized elastomers should be excellent candidates for this purpose. The preparation of trialkoxysilyl-functionalized polymers has been investigated using the termination reaction of PLi compounds with glycidoxypropyltrimethoxysilane (GPTS) as shown in Eq. 2. The functionalization of poly(styryl)lithium (M_n = 2,000) with GPTS (1.5 equivalents) was effected in benzene



$$\mathrm{PLi} + \overset{O}{\triangle}\!\!-\!CH_2O(CH_2)_3Si(OCH_3)_3 \rightarrow PCH_2\underset{OH}{\underset{|}{C}}HCH_2O(CH_2)_3Si(OCH_3)_3 \quad (2)$$

at room temperature by inverse addition. The SEC chromatogram of the products showed significant amounts of dimer formation (48 wt %). PSLi was end-capped with 5 equivalents of butadiene to form poly(styrene-*b*-butadienyl)lithium (PS-*b*-PBDLi). When PS-*b*-PBDLi was functionalized with GPTS, 56 wt % dimer was formed. PSLi was also end-capped with a stoichiometric amount of 1,1-diphenylethylene to form the corresponding polymeric 1,1-diphenylalkyllithium (PS-DPELi). For the functionalization of PS-DPELi with GPTS, the amount of dimer formation was reduced to 20 wt %. Thus, in terms of the effect of chain end structure, the amount of dimer formation increased in the order: PD-DPELi < PSLi < PS-*b*-PBDLi. The effect of added lithium 2,3-dimethyl-3-pentoxide on the functionalization of PSLi with GPTS was also investigated in benzene solution at room temperature. Quite unexpectedly, the amount of dimer formation decreased to only 3 wt % in the presence of 5 molar equivalents of lithium 2,3-dimethyl-3-pentoxide. The products from this functionalization reaction were characterized by ^{1}H NMR, ^{13}C NMR and ^{29}Si NMR spectroscopy. The CH_3OSi protons were observed at 3.6 ppm by ^{1}H NMR and the corresponding methoxy carbon was observed at 50 ppm by ^{13}C NMR. A single, sharp peak corresponding to $Si(OCH_3)_3$ was observed at –41.5 ppm by ^{29}Si NMR spectroscopy. No resonance was observed in the region of 10 to –10 ppm, where $Si(OR)_2$ groups would be expected. [11] The trimethoxysilyl-functionalized polystyrene prepared in the presence of lithium 2,3-dimethyl-3-pentoxide was hydrolyzed with dilute aqueous HCl in tetrahydrofuran followed by heating under vacuum at 115 °C. The products of the hydrolysis-condensation cycle were a four-armed, star-branched polymer (92 %) with a narrow molecular weight distribution (M_w/M_n = 1.08) and unfunctionalized polymer (8 %). These results confirm the efficiency of the functionalization procedure using GPTS in the presence of lithium 2,3-dimethyl-3-pentoxide.

3,4-Epoxy-1-butene. Diene-functionalized macromonomers The known chemistry of the reactions of alkyllithium compounds with 3,4-epoxy-1-butene (EPB)[12] suggested a facile procedure for the synthesis of diene-functionalized macromonomers (Scheme 1). The addition of a benzene solution of EPB (1.2 molar equivalents) to a benzene solution of PSLi was effected at room temperature. No dimeric products were observed by SEC analysis of the product mixture. After purification by column chromatography, 95 wt % functional polymer and only 5 % unfunctionalized polymer were isolated, independent of the reaction conditions. Based on the known reactions of alkyllithium compounds with EPB, it was expected that three isomeric reaction products would be formed resulting from 4,3- (**1**), 3,4- (**2**) and 1-4-addition (**3**). It was not possible to distinguish among these possible products by ^{1}H NMR since only broad peaks were observed for the vinyl protons (δ = 4.8-5.6 ppm) and the hydrogens on the carbons bonded to the hydroxyl groups (broad multiplet at δ = 3.72 ppm). ^{13}C NMR provided definitive information on the product distribution. The expected carbon chemical shifts for structures **1-3** were calculated using the empirical additivity equations developed by Grant and Paul.[13] The carbons bonded to oxygen were observed at δ = 57.9 ppm (calc. 60.5 ppm, **3**), 63.4 ppm (calc 65.6 ppm, **2**) and 70.5 ppm (calc 72.5 ppm, **1**). Based on quantitative ^{13}C NMR measurements (d_1 = 6 sec) the product distribution for normal addition corresponded to almost equal amounts of each product (33 % **1**, 29 % **2**, 38 % **3**). The product distribution was altered by the addition of lithium salts, but no single product predominated. When triethylamine was added ([TEA]/[PSLi] = 20) and when poly(styryl)lithium was end-capped with butadiene ([BD]/[PSLi] = 3-5), only the 1,4-addition product (**3**) was obtained.

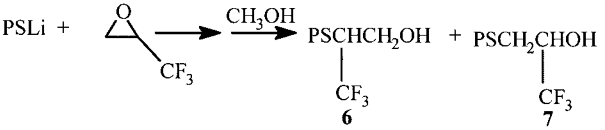


Scheme 1.

The product mixture (**1,2,3**) was dehydrated by heating under reflux in cyclohexane in the presence of either toluenesulfonic acid or Amberlyst® 15 ion-exchange resin (see Scheme 1). The diene-functionalized macromonomer product (**4,5**) was characterized by MALDI-TOF-mass spectrometry. The major peaks [e.g. (Ag)Bu-$(C_8H_8)_{21}C_4H_5$, *m/z* (obs) 2402.0, *m/z*(calc) 2402.4) corresponded to the expected molecular weights for polystyrenes with butyl and butadienyl end groups and differed in mass by 18.1 mass units compared to the mass spectrum for the EPB functionalized polymer.

<u>1,1,1-Trifluoro-2,3-epoxypropane</u> It was of interest to investigate the anionic

functionalization chemistry of 1,1,1-trifluoro-2,3-epoxypropane (TEP) to introduce trifluoromethyl and hydroxyl groups at chain ends. The reaction of PSLi with TEP (3.5 equivalents) proceeded for 12 hours before quenching with methanol. SEC analysis indicated the formatioon of dimer (10 wt %). The ^1H NMR spectrum of the products showed two peaks at δ 3.8 and 3.4 ppm, which could be assigned to the methylene hydrogens of the primary alcohol (**6**) or the methine hydrogen for the secondary alcohol (**7**) as shown in Eq. 3.



(3)

The ^{13}C NMR spectrum of the products exhibited a broad peak at δ 123.5 ppm corresponding to the trifluoromethyl group and four peaks in the region of δ 68.3-69.6 ppm. By ^{13}C NMR APT, these peaks were assigned to methine carbons indicative of the secondary alcohol product, **7**. No peak was observed in the region of δ 60-62 ppm where a primary hydroxyl group might be expected. These results suggest that the regiochemistry of addition involves predominant attack of PSLi at the least substituted carbon of TEP to form the secondary alcohol product, **7**. The observation of two peaks in the δ 3-4 ppm range of the ^1H NMR spectrum may, therefore, correspond to diastereomers. Another peak was observed at δ 33.6 ppm in the ^{13}C NMR spectrum that corresponds to significant amounts of functionalized polystyrene.[8] The products were further characterized by MALDI-TOF mass spectrometry. A significant series of peaks corresponding to unfunctionalized polystyrene was observed, consistent with the results of ^{13}C NMR analysis. The major series of peaks corresponded to the functionalized polymer (17-mer: calc m/z = 2046.1, observed m/z =2045.8). From the mass spectrum it was estimated that the product distribution corresponded to 46 % non-functional polymer and 54 % functionalized polymer. These results indicate that this is one of the least efficient functionalization reactions of polymeric organolithiums with oxiranes. For example, the functionalization efficiencies for ethylene oxide, propylene oxide, butene oxide and styrene oxide were determined to be >99 %,[8] 92 %,[15] 99 %[16] and 85%,[17] respectively.

Preparation of Secondary-Amine-Functionalized Polymers

Tertiary amine-functionalized initiators have been used to quantitatively prepare secondary amine-functionalized polymers by hydrogenolysis of the benzyl protecting group after polymerization and termination. Terminal secondary amine-functionalized polymers have also been prepared in high yield [99 % for poly(butadienyl)lithium] using the corresponding alkyl chloride (N-methyl-N-benzylaminopropyl chloride) as termination agent followed by hydrogenolysis of the benzyl group. The secondary amine-functionalized polymers have also been prepared in high yields (96 %) by termination reactions of polymeric organolithiums with N-(benzylidene)methylamine followed by quenching with methanol. The functionalization products were characterized by SEC, TLC, NMR (^{1}H, ^{13}C,), FTIR and MALDI-TOF mass spectrometry.

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