Macromol. Symp. **2005**, *226,* 69-77

Anionic Polymerization Chemistry of Epoxides: Electron-Transfer Processes

Roderic P. Quirk, Deanna L. Pickel, Hiroaki Hasegawa*

Maurice Morton Institute of Polymer Science, The University of Akron, Akron, Ohio 44325-3909, USA
Fax: (+1) 330-972-7510; E-mail: rpquirk@uakron.edu

Summary: The reaction of poly(styryl)lithium (PSLi) with styrene oxide (SO) in benzene solution has been investigated. In addition to the functionalized polymer (83.5 wt %) the product mixture consisted of unfunctionalized polymer (9 wt %) and a dimeric product (5.6 wt %). The structure of the dimeric product was determined to be the head-to-head dimer. The regiochemistry of the addition reaction was unselective: 53 mol % addition to the methylene carbon and 47 mol % corresponding to addition to the hindered, methine carbon. Based on the formation of the dimer and the lack of regioselectivity, a pathway involving electron transfer from PSLi to SO was proposed. To further investigate the propensity to react via this electron-transfer mechanism, the SO functionalization of the adduct of PSLi with 1,1-diphenylethylene was investigated as well as the functionalization of PSLi with 1,1-diphenylethylene oxide.

Keywords: anionic polymerization; 1,1-diphenylethylene oxide; electron-transfer; functionalization of polymers; poly(styryl)lithium; styrene oxide

Introduction

One of the unique features of living anionic polymerization is the ability to prepare a variety of ω-chain-end functionalized polymers by treatment of the living anionic chain ends with different electrophilic reagents. [1-3] Although there are many functionalization reactions described in the literature, many of these functionalization reactions have not been well characterized. A further limitation is the fact that many of the reported functionalization reactions do not proceed efficiently at room temperature or above in hydrocarbon solution, i.e. under conditions that 1,3-dienes are polymerized with high 1,4-enchainment. [1] A striking exception to this is the functionalization of polymeric organolithium compounds with epoxides such as ethylene oxide (EO). [4] For example, the functionalization of poly(styryl)lithium (PSLi) with excess ethylene oxide (4 mol equiv) in hydrocarbon solution produces the functional polymer in > 99 % yield without detectable amounts of oligomeric ethylene oxide segments. [5,6] The explanation for the unreactivity of lithium alkoxides compared to other alkali metal alkoxides with respect to ethylene oxide polymerization (or oligomerization) is that lithium alkoxides are more strongly

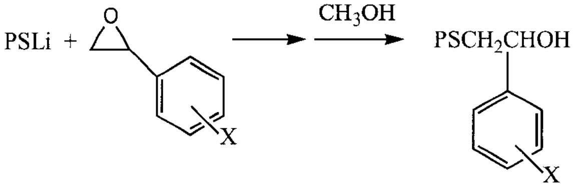
DOI: 10.1002/masy.200550807

aggregated in hydrocarbon solution[7] and that significant dissociation to form unassociated, reactive species does not occur. [4]

Recent careful re-examination of this reaction using MALDI-TOF mass spectrometric analysis has shown that detectable amounts of oligomerization do occur in the presence a larger excess of ethylene oxide (10 mol equiv) or with longer reaction times. [8,9] In contrast, poly(butadienyl)lithium undergoes more rapid oligomerization even in the presence of only 4 molar equivalents of EO. [9,10] The reasons for the differences in oligomerization reactivity for a polymeric lithium alkoxide with a polybutadiene backbone versus the analogous lithium alkoxide with a polystyrene backbone are currently under investigation.

Efficient functionalizations of PSLi with 1-butene oxide and propylene oxide without oligomerization have also been reported. [11,12] The functionalization of poly(styryl)lithium with a 2 molar excess of propylene oxide in hydrocarbon solution formed the corresponding hydroxypropylated polymer in 93 % yield accompanied by 7 % of the unfunctionalized polymer.[11] The reaction is regioselective resulting in predominantly (97 %) a secondary alcohol chain end, which corresponds to the product expected from attack of the organolithium on on the least hindered, methylene carbon of the propylene oxide ring. The reaction of 1-butene oxide with PSLi yielded less than 1 % of unfunctionalized polymer, while the functional product was isolated in > 99 % yield. [12] The reaction was also regioselective; only the secondary alcohol product resulting from attack at the least hindered methylene carbon was detected. The functionalization of polymeric organolithium compounds with 3,4-epoxy-1-butene, a functional epoxide, has also been investigated as a route to functional polymers. [13] High yields of enol-functionalized polymer (95 %) were obtained, but the reaction was not regioselective (38 % 1,4-, 29 % 2,4-, and 33 % 4,3-). A highly regioselective 1,4-addition product was obtained when either triethylamine, poly(dienyl)lithium chain ends, low temperatures or inverse addition was utilized.

These investigations suggested that epoxides may provide a facile route to a variety of functional polymers by attaching other substituents to the epoxide ring. Therefore, the functionalization of PSLi with styrene oxide was investigated. If this functionalization were quantitative, a variety of substituents and more than one substituent at a time could be placed on the benzene ring of styrene oxide to form a variety of functional polymers (see Eq. 1).



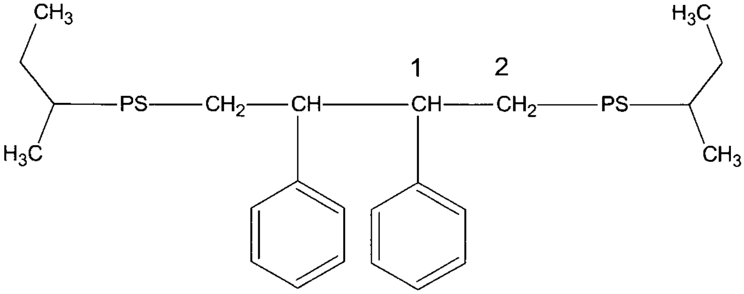
(1)

Experimental

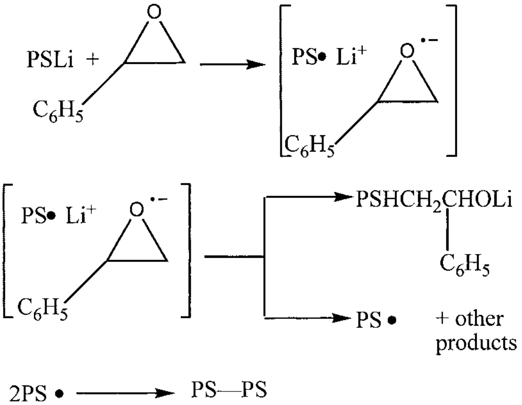
All polymerizations were carried out in all-glass reactors under standard high vacuum conditions. [14] Monomers and solvents were purified using standard procedures. [14,15] Mass spectra were acquired as described previously. [6,8,10,12,13]

Discussion

The functionalization of poly(styryl)lithium (M_n = 1900) with a 0.3 molar excess of styrene oxide in benzene at room temperature was investigated. SEC analysis of the resulting polymer showed an unexpected bimodal distribution, with the higher molecular weight species exhibiting a molecular weight twice that of the base polystyrene. Upon purification, the corresponding ω-hydroxyl-functionalized polymer was isolated in 85% yield with unfunctionalized polystyrene (9.0 %), polystyrene dimer (6 %), and polystyrene trimer (ca. 0.1 %). Fortunately, a quantitative yield of ω-hydroxy-functionalized polystyrene could be obtain in the presence of ≥15 equivalents of THF ([THF]/[Li]). The MALDI-TOF mass spectrum of the products showed that the high molecular weight product corresponded to an unfunctionalized dimer [e.g. C_4H_9-$(C_8H_8)_{24}$-$C_4H_9 \bullet Ag^+$, calc. monoisotopic mass = 2718.5 Da, obs. *m/z* = 2718.6]. The dimeric product was isolated by column chromatography followed by fractionation. The ^{13}C NMR spectrum of the dimer exhibited a peak at δ = 49.5 ppm. This peak was assigned to the methine carbon in a head-to-head dimer (see 1 in structure below) based on calculated chemical shifts using the additivity principles of Grant and Paul[16,17] and also the ^{13}C NMR assignments for the head-to-head dimer reported by Rinaldi and coworkers (δ = 48.1-51.1 ppm). [18,19]

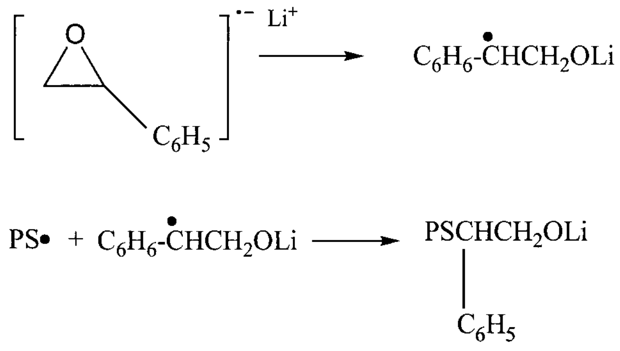


An electron transfer mechanism is proposed to explain the formation of unfunctionalized, head-to-head polystyrene dimer in this reaction as shown below.



Scheme 1.

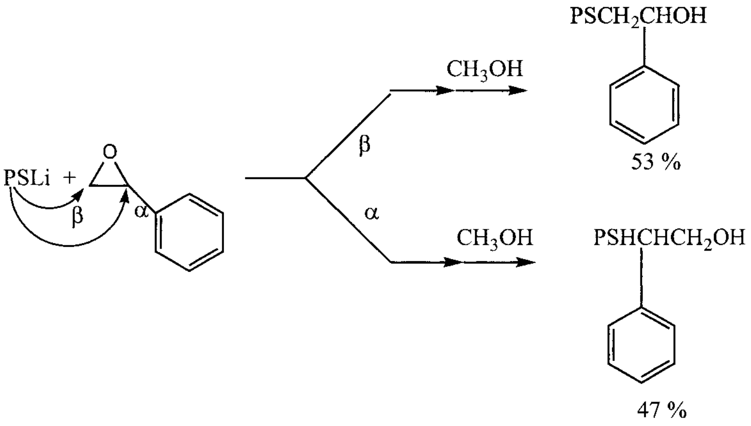
The formation of the radical anion of styrene oxide has been implicated in a variety of reduction reactions of SO. For example, the formation of the radical anion of styrene oxide (SO) can be inferred from the formation of 2-phenylethanol (83 %) in the reduction of SO with sodium in liquid ammonia. [20] The same product was formed in 87 % yield by reduction of SO with lithium naphthalene. [21] Recently Grobelny and coworkers[22] reported that the reduction of SO with K^-,K^+ (15-crown-5)$_2$ similarly led exclusively to products resulting from ring-opening of the oxirane ring and reactions at the more-substituted, α-position. The proposed mechanism for these reactions involves electron transfer to the epoxide, followed by ring cleavage of the radical anion to give a species containing an oxyanion and a radical. [23] The regiochemistry of the ring-opening of the radical anion (see Scheme 2) has been explained using *ab initio* molecular orbital calculations. [23] It is noteworthy that the calculated electron affinity of oxirane is −51 kcal/mol. These results suggest that the observed reaction of PSLi with SO could involve another step in addition to those shown in Scheme 1 (see Scheme 2).



Scheme 2.

However, it would be expected that if the reaction only proceeded as shown in Scheme 2, then the only product that would be observed would correspond to the primary alcohol product. Thus, it was important to establish the regiochemistry of the ring-opening of styrene oxide in the presence of poly(styryl)lithium.

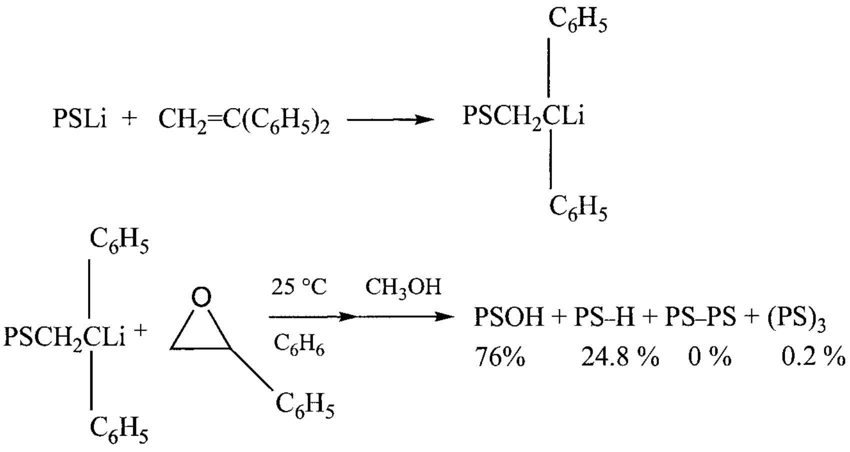
Previous studies of the ring opening of styrene oxide with nucleophiles have shown that the regiochemistry is very sensitive to the steric and electronic nature of the nucleophile as well as to the presence of coordinating Lewis acids. [24-32] The regiochemistry of the ring opening of styrene oxide by PSLi was determined by quantitative ^{13}C NMR spectroscopy after establishing peak assignments based on calculated carbon chemical shifts[16,17] in conjunction with the attached proton test. It was found that the product mixture consisted of 53 mole % of the secondary alcohol corresponding to addition to the least hindered oxirane carbon and 47 mol % of the primary alcohol corresponding to addition to the more hindered oxirane carbon (see Scheme 3). It is obvious that the formation of both substitution products in similar yields is not consistent with the dominance of steric effects



Scheme 3.

as expected based on the regiospecificity for the analogous reactions of PSLi with propylene oxide and 1-butene oxide. [11,12] It is also not consistent with the sole pathway proceeding via ring-opening of the styrene oxide radical anion as shown in Scheme 2, since this would predict only the formation of the primary alcohol product. [21-23] The regiochemical results suggest that there might be two competing mechanisms operating. The normal nucleophilic ring-opening occurs at the less sterically-hindered β-position to form the secondary alcohol product. Electron transfer leads to the formation of the primary alcohol product (Schemes 1,2). Another possibility is that an exothermic[33] radical-radical anion coupling reaction occurs in the solvent cage (Scheme 1) before ring-opening of the radical anion. This exothermic reaction would be expected to be unselective and could lead to the formation of approximately equal amounts of each product.

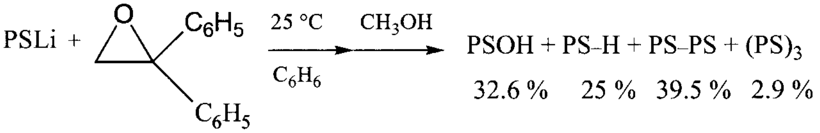
Effect of Chain-end Structure on Styrene Oxide Functionalization. The observation of the formation of significant amounts of the head-to-head dimer of polystyrene from the functionalization of PSLi with SO and the apparent lack of regiospecificity for the ring-opening is consistent with the incursion of an electron-transfer mechanism for the reaction of PSLi with SO. If electron transfer competes with nucleophilic addition, it would be expected that the electron-transfer pathway would be favored by using a polymeric organolithium chain end that would form a more stable radical. Thus, poly(styryl)lithium was end-capped with 1,1-diphenylethylene and the resulting polymeric 1,1-diphenylalkyllithium was functionalized with styrene oxide. The results are shown in Scheme 4. Quite surprisingly, compared to the reaction with PSLi, there is somewhat less



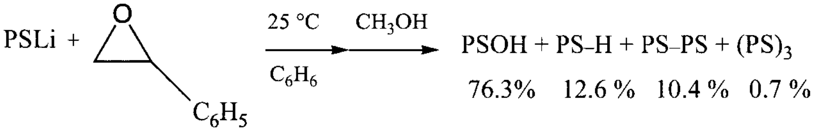
Scheme 4.

functionalized polymer formed (83.5 % for PSLi), no dimer and more unfunctionalized polymer formed (9 % non-functional and 5.6 % dimer for PSLi). The lack of dimer formation would be expected for the more hindered 1,1-diphenylalkyl radical. The regiochemistry of this addition, however, is quite surprising. The secondary alcohol product corresponding to addition to the less-hindered methylene carbon was only formed in 31 % yield, while the primary alcohol product corresponding to addition to the more-hindered methine carbon was formed in 45 % yield. These results are certainly not expected for a simple nucleophilic ring-opening mechanism and suggest that the electron-transfer mechanism may be involved.

<u>Functionalization of PSLi with 1,1-Diphenylethylene Oxide</u>. If electron transfer competes with nucleophilic addition for the reaction of PSLi with SO, it would also be expected that this pathway would be favored by using 1,1-diphenylethylene oxide which would be expected to form a more stable radical anion. The results for the reaction of 1,1-diphenylethylene oxide (DPEO) with PSLi are shown below in eq. 2. The analogous analytical data for the reaction with PSLi are listed for comparison in eq. 3.

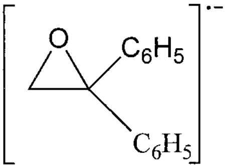


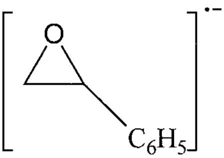
(2)



(3)

The results for functionalization of PSLi with DPEO show that there is much less functionalized polymer, significantly more dimer formation and more unfunctionalized polymer formed compared to the analogous reaction with SO. These results are consistent with a more favorable electron transfer mechanism for DPEO compared to SO as suggested by examination of the structures of the two radical anions shown below. It is noteworthy that the regiochemistry of this addition reaction is quite different from the reaction with styrene oxide. Only the secondary alcohol product corresponding to addition addition to the least hindered carbon was formed in the reaction of PSLi with DPEO. Regardless of the mechanism, it is clear that the alternative product containing a highly sterically hindered 1,1,2-triphenylethane-type unit was not formed, as expected. For the electron-transfer mechanism, the ring-opened radical (see Scheme 2 and structure below) would be both more stable and more sterically hindered with respect to coupling with the polystyryl radical. As a consequence, the main products, dimer and non-functional polymer, would result from diffusion of the polystyryl radical out of the solvent cage.





$$\left[\mathrm{PS}\bullet\ \ \mathrm{Li}^{\oplus}\qquad (\mathrm{C_6H_5})_2\dot{\mathrm{C}}\mathrm{CH_2O}^{\ominus}\right]$$

Conclusions

Evidence for an electron-transfer mechanism, perhaps in competition with normal nucleophilic ring-opening, has been obtained for the reaction of poly(styryl)lithium with styrene oxide. Significant amounts of head-to-head dimer and non-functional polymers, as well as the lack of regiospecificity provide evidence for the electron-transfer mechanism. Formation of less hydroxyl-functionalized polymer was found for the reaction of styrene oxide with the adduct of PSLi with 1,1-diphenylethylene and for the reaction of poly(styryl)lithium with 1,1-diphenylethylene oxide. These results suggest that the electron-transfer mechanism is more favorable when either the radical or the radical anion formed by electron transfer are more stable.

Acknowledgements

The authors are grateful to Nippon Shokubai Company, Ltd. (Japan), Sartomer and Dynasol Elastomeros for financial support of this research. We would also like to thank FMC, Lithium Division and Chemetall Foote Corporation for providing samples of *sec*-butyllithium and dibutylmagnesium.

[1] H. L. Hsieh, R. P. Quirk, “Anionic Polymerization: Principles and Practical Applications”, Marcel-Dekker, New York 1996.
[2] R. P. Quirk, "Anionic Synthesis of Polymers with Functional Groups", in: “Comprehensive Polymer Science, First Supplement,” S. L. Aggarwal, S. Russo, Eds., Pergamon Press, Oxford 1992, p. 83.
[3] A. Hirao and M. Hayashi, *Acta Polym.* 1999, *50*, 219.
[4] R. P. Quirk, D. L. Gomochak, *Rubber Chem. Technol.* **2003**, *76*, 812.
[5] R. P. Quirk, J.-J. Ma, *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 2031.
[6] R. P. Quirk, R. T. Mathers, J-J Ma, C. Wesdemiotis, M. A. Arnould, *Macromol. Symp.* **2002**, *183*, 17.
[7] V. Halaska, L. Lochmann, D. Lim, *Collect. Czech. Chem. Commun.* **1968**, *33*, 3245.
[8] R. P. Quirk, R. T. Mathers, C. Wesdemiotis, M. A. Arnould, *Macromolecules* **2002**, *35*, 2912.
[9] H. Ji, N. Sato, W. K. Nonidez, J. W. Mays, *Polymer* **2002**, *43*, 7119.
[10] R. P. Quirk, Y. Guo, C. Wesdemiotis, M. A. Arnould, *Polymer* **2004**, *45*, 3423.

[11] R. P. Quirk, G. M. Lizarraga, *Macromolecules* **1998**, *31*, 3424.

[12] R. P. Quirk, Q. Ge, M. A. Arnould, C. Wesdemiotis, *Macromol. Chem. Phys.* **2001**, *202*, 1761.
[13] R. P. Quirk, D. L. Gomochak, C. Wesdemiotis, M. A. Arnould, *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 947.
[14] M. Morton, L. J. Fetters, *Rubber Chem. Technol.* **1975**, *48*, 359.
[15] W. L. F. Armarega, C. L. L. Chai, “Purification of Laboratory Chemicals”, 5th ed., Elsevier, Oxford, 2003.
[16] E. G. Paul, D. M. Grant, *J. Am. Chem. Soc.* **1963**, *85*, 1701.
[17]] R. M. Silverstein, F. X. Webster, “Spectrometric Identification of Organic Compounds”, 6th ed. , John Wiley & Sons, Inc., New York, 1998.
[18] D. R. Hensley, S. D. Goodrich, H. J. Harwood, P. L. Rinaldi, *Macromolecules* **1994**, *27*, 2351.
[19] D. R. Hensley, S. D. Goodrich, A. Y. Huckstep, H. J. Harwood, P. L. Rinaldi, *Macromolecules* **1995**, *28*, 1586.
[20] E. M. Kaiser, C. G. Edmonds, S. D. Grubb, J. W. Smith, D. Tramp, *J. Org. Chem.* **1971**, *36*, 330.
[21] E. Bartmann, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 653.
[22] Z. Grobelny, A. Stolarzewicz, B. Morejko-Buz, A. Maercker, S. Krompiec, T. Bieg, *J. Organometal. Chem.* **2003**, *672*, 43.
[23] A. E. Dorigo, K. N. Houk, T. Cohen, *J. Am. Chem. Soc.* **1989**, *111*, 8976.
[24] C. H. DePuy, F. W. Breitbeil, K. L. Eilers, *J. Org. Chem.* **1964**, *29*, 2810.
[25] S. J. Cristol, R. F. Helmreich, *J. Am. Chem. Soc.* **1952**, *74*, 4083.
[26] M. M. Kayser, P. Morand, *Can. J. Chem.* **1980**, *58*, 302.
[27] H. Gilman, D. Aoki, D. Wittenberg, *J. Am. Chem. Soc.* **1959**, *81*, 1107.
[28] E. J. Corey, D. Seebach, *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 1075.
[29] M. Chini, P. Crotti, F. Macchia, *J. Org. Chem.* **1991**, *56*, 5939.
[30] L. D. Pachon, P. Gamez, J. J. M. van Brussel, J. Reedijk, *Tetrahedron Lett.* **2003**, *44*, 6025.
[31] M. Chini, P. Crotti, L. Favero, M. Pineschi, *Tetrahedron Lett.* **1991**, *51*, 7583.
[32] P. Crotti, V. D. Bussolo, L. Favero, F. Maccia, M. Pineschi, *Tetrahedron Lett.* **1994**, *35*, 6537.
[33] G. S. Hammond, *J. Am. Chem. Soc.* **1955**, *77*, 334.