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Living Ring-Opening Polymerization of *N*-Sulfonylaziridines: Synthesis of High Molecular Weight Linear Polyamines

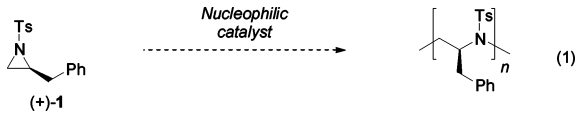
Ian C. Stewart, Cameron C. Lee, Robert G. Bergman,* and F. Dean Toste*

Department of Chemistry, University of California, Berkeley, California 94720

Received August 9, 2005; E-mail: rbergman@berkeley.edu; fdtoste@berkeley.edu

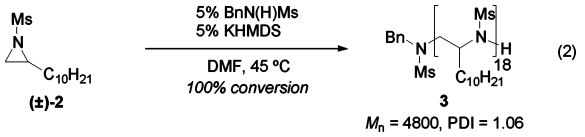
Polymerization of cyclic ethers, particularly epoxides, to generate low polydispersity, high molecular weight linear polyethers has been made possible by over a century of investigation.[1] In contrast, methods for the conversion of cyclic amines into linear polyamines are much more limited, despite the utility of such materials.[2] Low temperature polymerization of aziridine affords linear polyethyleneimine, which must be separated from branched isomers by precipitation.[3] The increasing availability of differently substituted aziridines,[4] including enantioresolved aziridines, during the past few years increases the potential utility of methods for the controlled polymerization of these monomers.[5] Herein we report the living polymerization of aziridines via an anionic ring-opening pathway using very simple initiator mixtures, leading to polyamines with very low polydispersities.

During investigations into the reactivity of a nucleophilic transition metal complex, we observed the ring-opening polymerization of *N*-tosylaziridine (+)-**1** (eq 1). A series of control experiments led us to discover that the addition of amide nucleophiles could also promote the polymerization. However, the polymer derived from (+)-**1** exhibited very low solubility in all organic solvents, which hindered characterization and likely limited chain growth.



(1)

To address this problematic insolubility, we prepared 2-*n*-decyl-*N*-mesylaziridine **2**[6] from the corresponding epoxide.[7] Addition of 5 mol % each of *N*-benzyl methanesulfonamide and KHMDS to a solution of **2** in DMF effected the polymerization of **2** within 18 h (eq 2). Most noteworthy was the very low polydispersity (1.06) observed for the resulting polymer.



(2)

While the decyl moiety likely does increase the solubility of the resulting polymer, we had modified both the substituent and the enantiopurity of the monomer in switching from (+)-**1** to (±)-**2**. We hypothesized that the increased solubility of the polymer formed from **2** could also be a consequence of its presumed atactic stereochemistry. To probe the effect of monomer stereochemistry on polymerization, we prepared both enantiopure and racemic samples of 2-methyl-*N*-tosylaziridine (**4**) from D-alaninol and DL-alaninol, respectively. Using conditions similar to those used in eq 2, enantiopure monomer (*R*)-**4** provided *sparingly soluble* polymer sample **5**, with $M_n = 2100$ and PDI = 1.10.[8] However, the racemic monomer (±)-**4** produced *highly soluble* polymer **6** with $M_n = 6300$ and PDI = 1.07 (eq 3).[9]

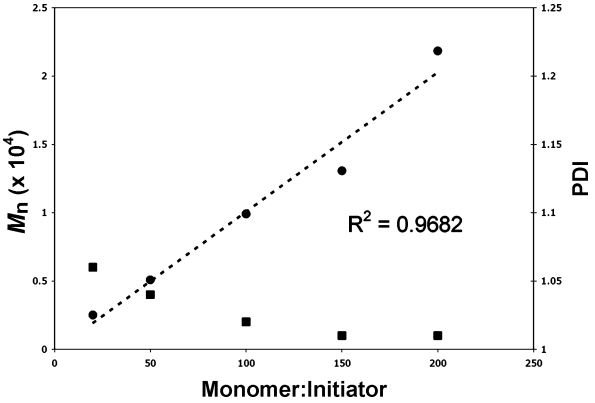
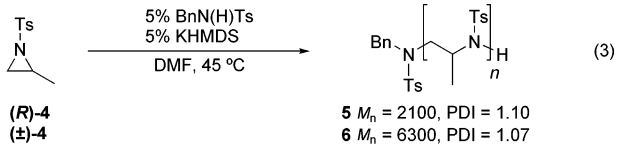


Figure 1. Relationship of number average molecular weight (●) (MALDI-TOF) to monomer:catalyst ratio at a fixed concentration of monomer, [(±)-**7**] = 1.0 M. Polydispersities (■) measured by SEC.



(3)

Although the narrow polydispersities of the products suggest that the polymerizations are living, we sought further experimental evidence for this conclusion. Due to its ease of preparation and purification on larger scale, we used the methanesulfonyl analogue (±)-**7** as our standard monomer for subsequent experiments. Samples of varying molecular weights were prepared by altering the monomer:initiator ratio from 20 to 200 (eq 4). As shown in Figure 1, number average molecular weight (M_n) is linearly proportional to the initiator loading up through molecular weights exceeding 20 000. The resulting poly(sulfonamides) can then be converted to the corresponding polyamines by an operationally simple lithium naphthalide reduction at ambient temperatures.[7]

(4)

With samples of varying chain lengths in hand, we sought to establish that the polymer chains were linear and not branched. The hydrodynamic diameters of polymers **8a**−**e** were measured by dynamic light scattering. The slope from a linear fit of a double logarithmic plot of diameter versus molecular weight (M_n) represents the exponent of a Mark−Houwink-type equation, where $D = kM^{\alpha}$. The α value of 0.54 that was derived from this preliminary analysis

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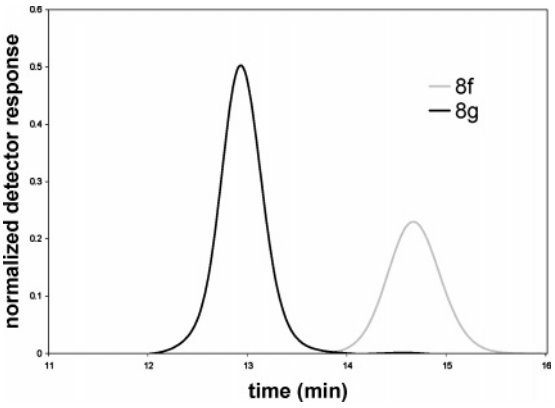
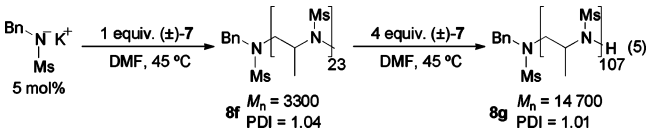


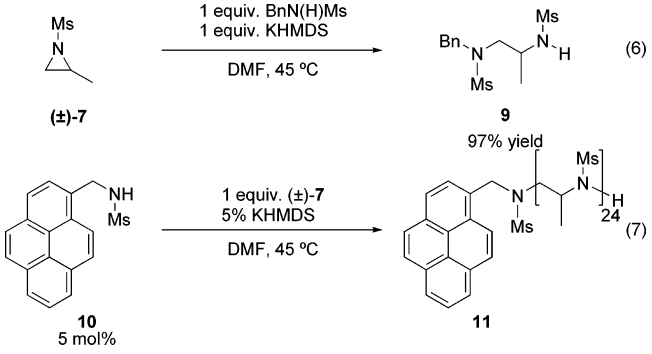
Figure 2. Normalized and overlaid SEC chromatograms showing chain extension of **8f** to **8g** (eq 5).

suggests that this polymer behaves like a flexible linear polymer in solution and is likely devoid of significant branching.[10]

In hopes of coupling this aziridine polymerization to other anionic polymerization reactions for the preparation of block copolymers, we first investigated the possibility of extending the living chains by the addition of (±)-**7** in two aliquots (eq 5). As shown by size exclusion chromatography (Figure 2), the polymer chains continue polymerization upon the addition of the second aliquot of (±)-**7**, further supporting that the polymerization is living.



We assume that the amide initiator, generated by the deprotonation of a primary sulfonamide by KHMDS, functions as a nucleophile to promote ring-opening of the aziridine.[11] In support of this hypothesis, addition of 1 equiv of the potassium amide of *N*-benzyl methanesulfonamide to a solution of (±)-**7** in DMF generated disulfonamide **9** in high yield (eq 6).[12] Furthermore, by replacing the *N*-benzyl methanesulfonamide initiator with *N*-methylpyrenyl methanesulfonamide **10**, the absolute concentration of pyrene-containing end groups in a purified polymer sample could be measured (eq 7). End group analysis of the resulting polymer by UV spectroscopy showed 92% incorporation of the pyrene moiety into the polymer chains.



The rate law for the polymerization of (±)-**7** initiated by isolated potassium *N*-methanesulfonylbenzylamide was determined by monitoring the disappearance of (±)-**7** by ^{1}H NMR spectroscopy (eq 8). As expected, a first-order dependence on (±)-**7** was observed. A first-order dependence on potassium amide suggests that the initiation event does not occur at initiator aggregates, which has been invoked to explain fractional kinetic orders in other anionic polymerization reactions.[13]

$$\text{rate} = k_{\text{obs}}[(\pm)\text{-}\mathbf{7}][\text{BnNMs}^{-}\text{K}^{+}] \qquad (8)$$

In summary, we have described the living ring-opening polymerization of sulfonylaziridines initiated by amide nucleophiles under mild conditions. The reaction exhibits fast induction and first-order propagation, yielding narrow molecular weight distributions of poly(sulfonamides), which can be deprotected under mild conditions. This reaction offers a new complementary method for the preparation of these interesting and useful linear polyamine structures, which until now were only easily accessible via the cationic polymerization of 2-oxazolines.[14] The anionic nature of this method should allow the use of functionalized monomers that are not compatible with cationic polymerization conditions and the formation of interesting copolymers by initiating aziridine polymerization with a living anionic polymer. The diversity of aziridines that are easily synthetically accessible makes this a promising new method in polymer synthesis.

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Supporting Information Available: Experimental procedures and characterization data for new compounds are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Formation of crystalline oligomers of enantiopure aziridines has been reported: Araki, T.; Nagata, K.; Tsukube, H. *J. Polym. Sci.: Polym. Chem. Ed.* **1979**, *17*, 731−746.
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