

Synthesis of α,α' -dipotassio-*m*-xylene and its use as a dianionic initiator

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Summary

α,α' -Dipotassio-*m*-xylene was prepared by di-metalation of *m*-xylene with a butyllithium/potassium *t*-butoxide mixed base system. Its functionality was determined by combining the dianion with chlorotrimethylsilane which resulted in the di-substituted carbosilane. GC and ^1H NMR analysis confirmed that the di-substituted carbosilane was synthesized in >90% yield. The effectiveness of this dianion as an initiator for living anionic polymerization was demonstrated by the polymerization of isoprene and the synthesis of the triblock copolymer of dimethylacrylamide-isoprene-dimethylacrylamide.

Introduction

Dianionic initiators are of primary interest in their ability to form telechelic polymers and block copolymers. By using difunctional initiators, the center of the polymer is first synthesized allowing the ends of the polymer to undergo additional reactions. The center-out approach permits the synthesis of symmetrical telechelic polymer or triblock copolymers with polar end segments.

Several methods have been established to prepare dianionic initiators; the earliest involves the use of an alkali metal to promote electron transfer reactions generating dimetal carbanions (1). More recent approaches involve addition of alkyllithium reagents to diolefins resulting in dilithium salts (2). Other methods include the deprotonation of acidic protons such as silanols (3) or alcohols (4).

Our approach has been to use mixed alkyllithium/potassium alkanoate bases as a means to generate initiators for anionic polymerization (5). These mixed bases, referred to as super bases (6), are known to metalate and multi-metalate benzylic and/or allylic stabilized hydrocarbons (i.e. toluene, xylene, butadiene, isobutylene) (7). Carbanions synthesized from these super bases can be isolated in high yields and characterized as organopotassium reagents. They have generally been used in the nucleophilic substitution/addition synthesis of low molecular weight compounds (6, 7). We have used these carbanions as anionic initiators for polymerization.

Herein, we describe the preparation of the difunctional initiator, α,α' -dipotassio-*m*-xylene, synthesized by di-metalation of *m*-xylene with butyllithium/potassium *t*-butoxide mixed base and the initiator's ability in synthesizing polyisoprene and poly(N,N-dimethylacrylamide-isoprene-N,N-dimethylacrylamide) (DMA-IP-DMA) block copolymers.

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Experimental

All polymerizations were performed in oven-baked (150 °C) glassware sealed with rubber septum under a purified nitrogen atmosphere. Reagent and solvent transfers were performed via syringe. Potassium *t*-butoxide, *n*-butyllithium, and *m*-xylene (gold label) were obtained from Aldrich and used without purification. All other materials were similarly obtained from Aldrich unless otherwise noted. Isoprene was distilled from sodium metal prior to use. N,N-dimethylacrylamide was vacuum distilled prior to use. Diphenylethylene was fractionally vacuum distilled from the red diphenylhexyl lithium, formed by the addition of *n*-butyllithium to 1,1-diphenylethylene. Tetrahydrofuran (THF) was freshly distilled from the deep blue potassium/benzophenone ketyl, made by combining benzophenone with potassium metal in the solvent. Hexane was washed with concentrated sulfuric acid, distilled water, saturated aqueous sodium bicarbonate, and finally distilled water. It was then dried over magnesium sulfate, filtered, and distilled from potassium onto molecular sieves where it was stored until needed.

α,α'-Dipotassio-*m*-xylene Initiator

A dry 100 mL three-neck round bottom flask equipped with a Teflon coated stir bar, a reflux condenser, and an addition funnel was sealed with rubber septa and flushed with N₂ gas for > 5 min. The vessel was charged with 50 mL of anhydrous hexane, 11.5 mL (28.8 mmol) of 2.5 M *n*-butyllithium, and 3.27 g (29.1 mmol) of potassium *t*-butoxide. To this cream-colored suspension was added 1.0 mL (8.2 mmol) of *m*-xylene in 5-10 mL of hexane through the addition funnel causing an immediate change to a light yellow color. After complete addition (typically within one minute), the yellow suspension was heated to reflux for ca. 12 hours changing it to a green/yellow color. The reaction mixture was transferred to a sealed vial by syringe and centrifuged. The top hexane layer was removed and fresh hexane added, and mixed with the solid. The washing process was repeated at least three times to remove residual butyllithium and lithium butoxide. Note: these organopotassium salts are pyrophoric. They are more reactive as powders and will blacken and/or ignite immediately upon exposure to air.

Polymerizations

A dry 250 mL three-neck round bottom flask equipped with an addition funnel and a stir bar was sealed with rubber septa and flushed with N₂ gas for > 5 min. THF (100 mL) was added by syringe to the reaction flask through the addition funnel, leaving 5 mL in the addition funnel in order to make an isoprene/THF solution. An initiator solution was made by suspending 0.5 g to 1.0 g of the dianion in 30 mL of THF (0.091-0.18 M) in a sealed centrifuge vial. A suspension was made in THF since the dianion was only sparingly soluble in this solvent. This solution was used to titrate THF (in the round bottom flask) to a faint pink, and usually required up to 1 mL. After titration, a measured amount of initiator was injected [usually 1.0 mL-5.0 mL (1.4×10^{-4} - 6.8×10^{-4} mol) depending on the desired molecular weight] causing the solution to turn a deep red. Five-to-ten mL (0.05-0.10 mol depending on the desired molecular weight) of isoprene was introduced into the addition funnel with the remaining THF. The isoprene solution was added to the round bottom flask in the course of minutes causing the color to change from red to a light yellow. The reagents were allowed to stir for 20 min. For the synthesis of polyisoprene, the reaction was terminated by adding methanol; otherwise, 1.0 mL (5.7×10^{-3} mol) of 1,1-diphenylethylene was added causing an immediate red solution. The flask was then submersed in a Dry Ice/acetone bath cooling the solution to ca. -78 °C. After equilibration, N,N-dimethylacrylamide (23 weight percent) was added causing the solution to revert back to a faint yellow. After an additional 20 minutes, 1.0 mL of methanol was added to terminate the polymerization. Yields of polymers were quantitative.

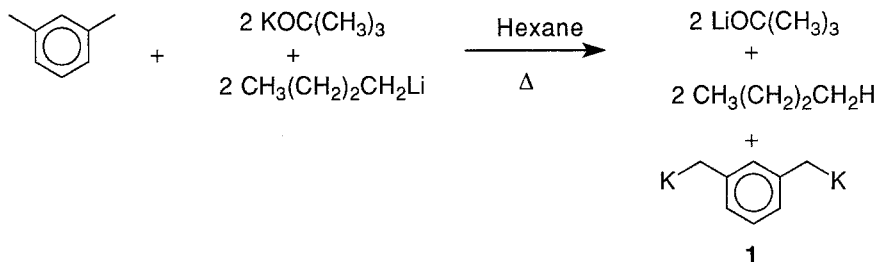
Characterization

^1H NMR spectra were performed on a Bruker wp-200 FT 200 MHz. Chemical shifts were reported relative to tetramethylsilane with CDCl_3 as the solvent. Gas Capillary Chromatography was performed on a Hewlett-Packard 5880A GC using an HP101 12 feet methylsilicone column. Data was collected on a NEC computer equipped with Waters PDA peak integration software. The molecular weight chromatography was performed on a Waters 150-C ALC/GPC using 5-styragel columns with pore sizes 500, 10^3 , 10^4 , 10^5 , and 10^6 Å with THF as the eluting solvent at a flow rate of 0.7 mL/min. Column calibration was performed using narrow molecular weight polystyrene standards ranging from 10^6 - 10^3 g/mol obtained from PolySciences. Data collection and reduction was performed on an Apple IIe computer running Interactive Microware Inc.'s Chromatochart software.

Results and Discussion

Synthesis and Characterization of Dianion

The dianion of *m*-xylene, **1**, was prepared from the mixed *n*-butyllithium/potassium *t*-butoxide base in hexane at reflux (see below).



Heating the mixed base to refluxing hexane (ca. 69 °C) causes its slow decomposition to butene, potassium hydride, and lithium *t*-butoxide (8). Heating this mixture is necessary, however, to ensure the formation of dianion since the first formed mono-anion is insoluble and does not undergo further metalation to the dianion without some difficulty. We expect the anions of *m*-xylene to be thermally more stable than butyllithium since they do not possess a β hydrogen, the path through which decomposition occurs for the butyl anion, and hence can withstand the elevated temperatures necessary for its formation. The functionality of the dianion was determined by reacting **1** with chlorotrimethylsilane, yielding the carbosilane **2** (see Figure 1). Results of GC and ^1H NMR analysis confirm product **2** was typically synthesized in > 90% yields which is consistent with previously reported yields of dianion **1** (9). Figure 1 represents the ^1H NMR spectra of **2**. The aromatic proton resonances can be identified as three separate signals 'a', 'b' and 'c' (δ 7.05 triplet, δ 6.73 doublet, and δ 6.67 doublet, respectively). The remainder of the spectrum consists of a singlet for the methylene protons 'd' (δ 2.02) and a singlet for the methyl protons 'e' (δ -0.01) bound to silicon.

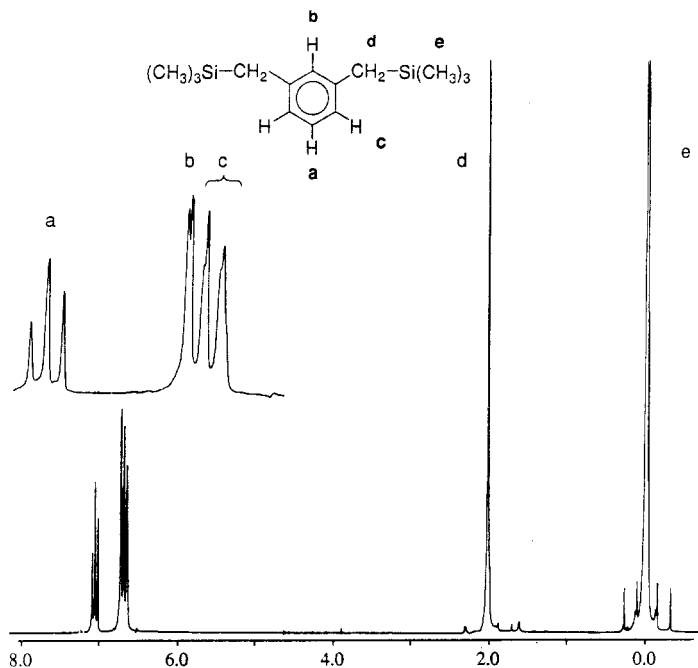


Figure 1. ^1H NMR of 2, α, α' -bis(trimethylsilyl)-*m*-xylene.

Synthesis of Polymers

Isoprene polymerizations were performed by initiating with dianion **1** suspended in THF. A suspension of **1** was made since the dianion was only sparingly soluble in THF. Base initiator solutions were used within a few hours of preparation and no loss of activity, presumably through metalation of the solvent, was noticed. Initiation was performed heterogeneously until sufficient amount of monomer had been added to produce a homogeneous solution of isoprenyl oligomers. Initiation occurred by the nucleophilic addition of **1** to isoprene, yielding isoprenyl potassium. Addition of isoprene continues until the monomer is depleted. Once this has occurred, the reaction was either terminated with methanol, or continued by the addition of 1,1-diphenylethylene, followed by the addition of *N,N*-dimethylacrylamide at -78°C . Diphenylethylene was added to the isoprenyl potassium in order to prevent carbonyl addition to the ensuing acrylamide monomer (10). The copolymer was terminated similar to polyisoprene, by the addition of methanol.

The DMA-IP-DMA block copolymer was extracted with various solvents to check for any homopolymer impurity. It was first extracted in hexane, which is a non-solvent for PDMA, and then with isopropanol, a non-solvent for PI (11). All of the material dissolved completely in both solvents, which implied block formation.

Characterization of Polymers

GPC analysis of the isoprene polymers consistently reflected relatively broad molecular weight distributions (average M_w/M_n of 1.5 for polyisoprene and 1.6 for copolymer, see Table 1). The distribution of these materials were broader than expected for a living anionic system.

Heterogeneous initiation conditions invariably adversely affects the molecular weight distributions of these polymers but was unavoidable since α,α' -dipotassio-*m*-xylene was insoluble in THF, or other commonly used solvents. The use of this dianion in anionic polymerization results in heterogeneous initiation and as a consequence molecular weight distributions may not be as narrow as in homogeneous systems. Additionally, organopotassium reagents are known to be more reactive than their organolithium analogs (6) and require more stringent reaction conditions to avoid deleterious side reactions. The septa and syringe techniques employed in these experiments may not be sufficient to achieve narrow molecular weight distribution polymers.

In the synthesis of polyisoprene three possible modes of monomer addition exist (1,2; 3,4; 1,4), resulting in several geometrical isomers. The relative amounts of these isomers can be determined by ^1H NMR analysis (12) and are summarized in Table 2. Under the polymerization conditions used, 50% of the addition occurred by the 3,4 mode, 23% by the 1,2 mode and 27% by 1,4 mode. The *cis* and *trans* isomers of 1,4 addition could not be distinguished, although it is reasonable to expect the *trans* isomer to predominate. These results are in agreement with previously reported findings of polyisoprene synthesized with a potassium counter ion in THF as a solvent (13).

Polymerization of isoprene by **1** was quantitative. If the polymerization was not terminated but additional DMA monomer added, the polymerization would continue until the DMA monomer was depleted and yield a triblock copolymer of DMA-IP-DMA. Figure 2 represents a typical ^1H NMR spectrum of the DMA-IP-DMA block copolymer. The signals due to the IP segment are identified in Table 2. The methylene protons (ordinarily seen at δ 1.7) on the backbone of the DMA segment cannot be distinguished because of the stronger isoprenyl resonance signals for similar protons. The methine proton and amide methyl protons, however, give separate signals between δ 2.5-2.7 and δ 2.7-3.2, respectively. To distinguish whether this procedure yielded a blend of homopolymers or the block copolymers, solvent extraction experiments were conducted. The synthesized copolymer was extracted with solvents that would not ordinarily dissolve both polyisoprene and polydimethylacrylamide homopolymers, but would dissolve a copolymer containing these polymer segments. Since the monomers were added sequentially and it was shown that the polymerization of isoprene was quantitative, block formation is expected. These copolymers are, therefore, not a blend of their respective homopolymers and it is clear from the NMR spectrum (Figure 2) that both segments exist in this polymer.

Table 1. Molecular Weight Information^a

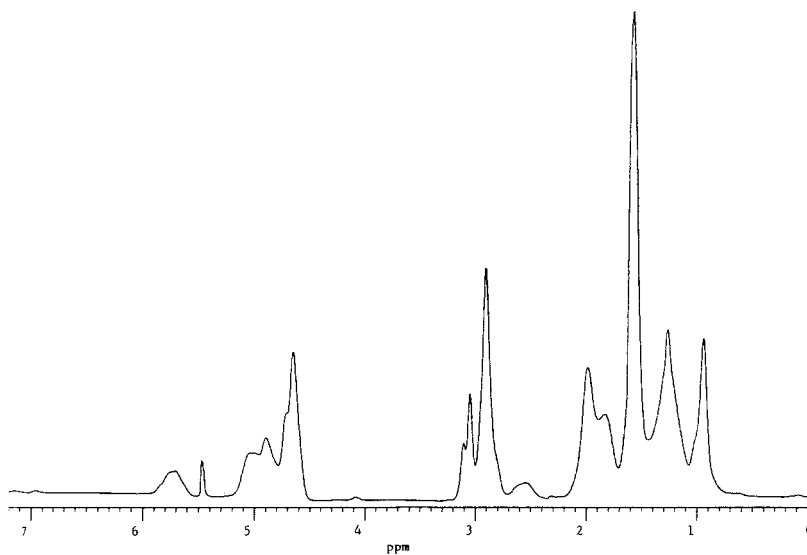
Polymer ^b	Mn (g/mol)	Mw (g/mol)	Mw/Mn	DMA ^c
PI-1	25,000	39,700	1.59	0%
PI-2	28,700	40,400	1.41	0%
PI-3	26,000	39,400	1.52	0%
DMA-IP-DMA-4	21,500	36,400	1.69	23%
DMA-IP-DMA-5	27,500	43,600	1.59	23%
DMA-IP-DMA-6	76,000	110,000	1.45	22%

a. Molecular weights are relative to polystyrene standards. b. PI represents polyisoprene and DMA-IP-DMA represents poly(N,N-dimethylacrylamide-isoprene-N,N-dimethylacrylamide). c. Predicted weight percent of N,N-dimethylacrylamide in the block copolymer.

Table 2. Relative Concentrations of the Geometrical Isomers of Polyisoprene by ^1H NMR

	1,2 addition		3,4 addition		1,4 addition	
	$\text{---CH}_2\text{---}\overset{\text{CH}_3}{\underset{\text{~}}{\text{C}}}\text{---CH=CH}_2$		$\text{CH}_2=\overset{\text{CH}_3}{\underset{\text{~}}{\text{C}}}\text{---CH---CH}_2\text{---}$		$\text{---CH}_2\text{---}\overset{\text{CH}_3}{\text{C}}=\text{CH---CH}_2\text{---}$	
Peak	5.75	=CH ₂	4.65	=CH ₂	5.00	-CH-
Shift	5.00	-CH=	1.25	-CH ₂ -	2.00	-CH ₂ -
ppm ^a	1.25	-CH ₂ -	1.60	-CH ₃	1.60	-CH ₃
	0.95	-CH ₃	2.00	-CH-		
	23 mole %		50 mole %		27 mole %	

a. Unresolved peaks were cross-referenced to lower molecular weight compounds (12).

**Figure 2.** ^1H NMR of DMA-IP-DMA-4 block copolymer.

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