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Anionic Polymerization of Hexamethylcyclotrisiloxane with Acetylacetone Initiator To Form Telechelic Polymer

ALOK KUMAR AND B. E. EICHINGER*

Department of Chemistry, University of Washington, Seattle, Washington 98195

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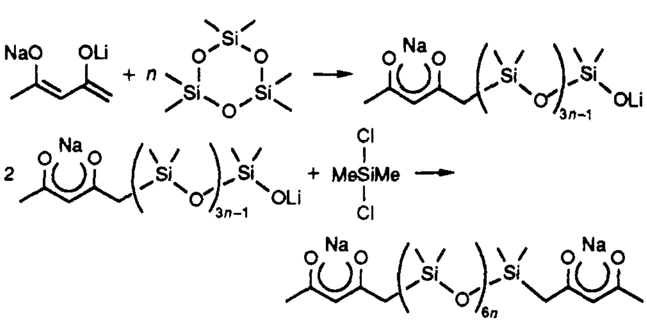
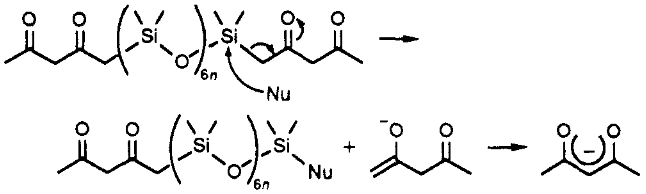
Recently, Liao and Eichinger[1] and Iwamoto[2] reported the synthesis of a telechelic polysiloxane end-capped with acetylacetone (acac) groups. The end-capping agent containing acac was synthesized and coupled to the polysiloxane in high yield. While this is a reliable method for the synthesis of telechelic polymers, the synthesis of end-capping agent is tedious. We here report the synthesis of acac end-capped polysiloxane by anionic polymerization.

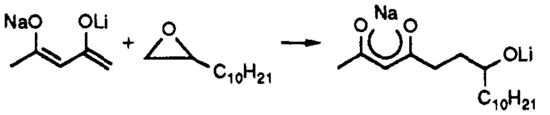
We first attempted to use the dianion of acac[3] for ring-opening polymerization of hexamethylcyclotrisiloxane using the following scheme:



After polymerization, the solvent was evaporated to give the Na salt of the polymer. NMR, IR, and UV spectroscopy confirmed that acac was the end group in the polymer. However, all attempts to neutralize the polymer led to partial or complete loss of the functionality. A survey of the literature showed that if a carbanion at the carbon α to the Si is stabilized by some group, then the Si–C bond is easily hydrolyzable,[4] probably by the following mechanism:



To introduce more carbon atoms between the acac carbonyl and the active anion, we tried to react the dianion of acac with formaldehyde. Unfortunately, aldol condensation gives many side products.[5] An epoxide ring-opening step was then successfully introduced to separate the carbonyl group from Si according to the following, previously characterized,[6] reaction. 1,2-Epoxydodecane was used because it is easily dried in vacuo.



Na(acac) (240 mg, 1.97 mmol) was placed in a flask. Ampules[7] of t-BuLi and 1,2-epoxydodecane, each containing 1 equiv, were attached to the flask. This was then sealed to a vacuum line and pumped for 3 h. Dry THF, 15 mL, was distilled in, and the flask was removed from the vacuum line by sealing at the constriction. The mixture was cooled to −78 °C, and t-BuLi was added by breaking the seal of the ampule. The contents were stirred at −78 °C for 10 min and at 0 °C for 2 h. 1,2-Epoxydodecane was added by breaking its seal, and the solution was stirred at 0 °C for 6 h and at room temperature for an additional 24 h.

D_3 (5 g, 22.5 mmol) was dried over CaH_2 at 70 °C, sublimed into an ampule, dissolved in 35 mL of cyclohexane, and sealed by heating at the constriction. An ampule of 182 mg (0.99 mmol) of dichlorodimethylsilane in cyclohexane was made (terminator). Ampules of monomer, initiator, terminator, and THF (30 mL) were attached to a reaction vessel, which was sealed to a vacuum line and pumped overnight. This was removed from the vacuum line by sealing at the constriction. The seals of monomer and initiator ampules were broken, and the solution was stirred for 20 min. Then THF was added for the propagation of polymerization. The mixture was then stirred for 1 day, and the terminator was added. LiCl precipitated out. The solution was diluted with diethyl ether and treated with 5% HCl and a cold saturated solution of NH_4Cl, dried over $MgSO_4$, and the solvent was evaporated. The polymer was pumped on the vacuum line and heated at 70 °C for 2 days to remove the solvent completely. The recovered yield of the polymer was >95%. The polymer was characterized by NMR and UV spectroscopy. NMR showed peaks at δ 2.02, 2.2, and 5.5, showing the presence of an acac group. UV showed a peak at 273 nm. The concentration was 0.85 mg/mL, and using $\epsilon = 5265$,[6] the molecular weight is calculated to be 5100. The molecular weight of the polymer by VPO was found to be 5500.

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References and Notes

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(3) The position of Na and Li can be interchanged throughout this paper.
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(7) Standard vacuum-line techniques were used. Morton, M.; Fetters, L. J. *Rubber Chem. Technol.* **1975**, *48*, 359.

Registry No. Na(acac), 15435-71-9; *t*-BuLi, 594-19-4; Cl_2SiMe_2, 75-78-5; 1,2-epoxydodecane, 2855-19-8.

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