Telechelic Star Poly(dimethylsiloxane)s of Highly Defined Structure

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ABSTRACT: The synthesis of amine telechelic, star-shaped poly(dimethylsiloxane)s of highly defined structure is reported. These polymers are prepared via utilization of a unique, blocked amine functional anionic initiator, which is soluble in nonpolar solvents. Once intitiated, a living anionic polymerization of D_3 is terminated with tetrachlorosilane to form the blocked, star polymer. After the unblocking, four-armed star, amine telechelic poly(dimethylsiloxane)s of controlled molecular weights, narrow molecular weight distributions, and theoretical functionalities are formed.

Introduction

A considerable body of work exists in the literature describing the preparation of increasingly well-defined polymers. Included in this body have been reports about advances in the synthesis of both end-reactive and star-shaped polymers. More recent work has combined these two areas of advancement so that ways now exist to prepare highly defined, end-reactive star polymers.[1-10] These telechelic star polymers have been prepared by the initiator-transfer methods pioneered by Kennedy,[1-8] via multifunctional delocalized anionic initiators followed by functional termination,[9] and by the method of blocked functional anionic initiators with multifunctional termination.[10]

The above-mentioned preparative methods all have their advantages and disadvantages with regard to their potential for the preparation of highly defined telechelic star polymers. The "inifer" method of Kennedy has succeeded in the preparation of quantitatively functional three-armed stars via cationic polymerization. However, this method is limited with regard to the types of monomers available for use, does not result in polymers of low polydispersity, and has never been utilized to prepare star polymers of more than three arms. The recent method of multifunctional delocalized anionic initiators can result in the preparation of star polymers of low polydispersity from potentially many monomers; however, this method has never been used to prepare star polymers of more than three arms.[10]

The blocked functional anionic initiator method pioneered by Schulz[10] offers the most advantages with the fewest disadvantages. Since this method involves the use of anionic "living" polymerization, the resulting star polymers have controlled molecular weights and low polydispersities.[11] Additionally, since these star polymers are prepared by multifunctional termination of living polymer chain ends, the arm number of the resulting star polymers can be readily controlled as shown in the work of Fetters.[12] This method can also employ the many monomers available for use in anionic living polymerizations. The disadvantage of this method lies in the lack of solubility of available blocked functional anionic initiators in nonpolar solvents. This solubility problem prohibits the use of this method in the preparation of poly(dimethoxysiloxane)s. Similarly, the nonpolar insolubility of blocked functional anionic initiators limits the use of this method in controlling the microstructure of diene polymers.

This paper reports the preparation of highly defined, amine telechelic poly(dimethylsiloxane) star polymers utilizing our previously reported nonpolar-soluble blocked amine functional anionic initiator.[11] The polymers formed are of controlled molecular weight, low polydispersity, controlled arm number, and theoretical functionality. Further, this method is sufficiently general so as to prepare star polymers of many different arm numbers and to extend the use of the blocked functional anionic initiator method to the preparation of controlled microstructure polydienes.

Experimental Section

Materials. *p*-(*N*,*N*-Bis(trimethylsilyl)amino)styrene was prepared as previously described.[11] Chlorotrimethylsilane, dichlorodimethylsilane, and tetrachlorosilane were obtained from Aldrich, distilled, and titrated prior to use. *sec*-Butyllithium in cyclohexane was received from Aldrich and titrated prior to use.[11] Ionol, diphenylacetic acid, molecular sieves, and D_3 were prepared as previously described.[11] Hexane, cyclohexane, hexamethylphosphoramide (HMPA), and benzene were obtained and purified as previously described.[11]

Preparation of an Amine End-Functional, Four-Armed, Star Poly(dimethylsiloxane). In a clean, dry, argon-filled, round-bottom flask was generated 0.000 93 mol of the blocked amine functional anionic initiator in 40 mL of benzene as previously described.[11] To this was added 3.91 mL (2.0 g) of the D_3 solution followed by 0.60 mL of HMPA. After 2.5 h of propagation at room temperature, 1 mL of the reaction mixture was removed and terminated by chlorotrimethylsilane for use in gel permeation chromatography and then to the reaction mixture was added 0.23 mL (0.000 24 mol) of tetrachlorosilane solution. After termination was allowed to proceed for 2 days at room temperature, an infrared spectrum of the blocked polymer was recorded. The polymer was then unblocked using 2 N aqueous HCl as described previously[11] and finally transferred to a separatory funnel where the polymer was neutralized and washed with dilute aqueous sodium hydroxide and distilled water. Complete unblocking was confirmed by using infrared spectroscopy, and the solution was filtered into a round-bottom flask, followed by removal of the solvent by rotary evaporation. The residue was then dried under vacuum for 20 h at 65 °C to give 2.08 g of oily polymer (essentially quantitative yield). Polymer samples were characterized by gel permeation chromatography, vapor-phase osmometry, NMR, and infrared spectroscopy as described below.

Measurements. Infrared spectroscopy, NMR, gel permeation chromatography (GPC), vapor-phase osmometry, and appropriate titrations were performed as previously described.[11]

Results and Discussion

Previous work has shown how our new blocked amine functional anionic initiator could be generated and used to prepare telechelic poly(dimethylsiloxane)s of controlled molecular weight, low polydispersity, and theoretical end reactivity. The present report extends this work to the preparation of equally well-defined star-type polymers.

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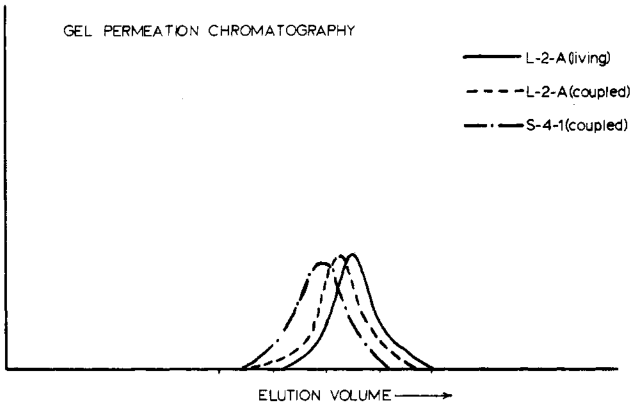

Figure 1. Gel permeation chromatograms of amine-terminated poly(dimethylsiloxane)s. L-2-A(living) is the living siloxane capped with $ClSiMe_3$. L-2-A(coupled) is the linear telechelic made by coupling living siloxane with Cl_2SiMe_2. S-4-1(coupled) is the four-arm, star telechelic made by coupling with $SiCl_4$.

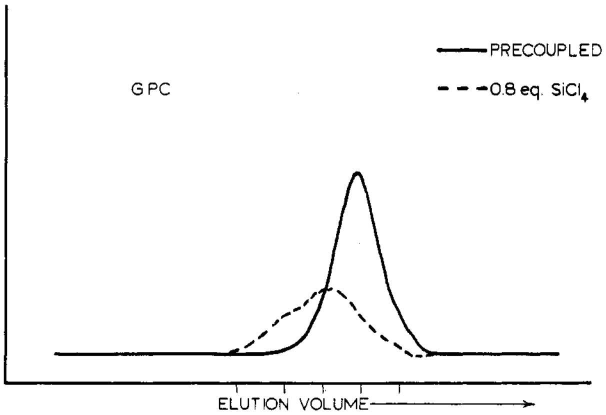

Figure 2. Gel permeation chromatograms for uncoupled and partially coupled siloxane polymers. M_n of uncoupled polymers is approximately 4000. The partially coupled sample was prepared by coupling of living siloxane with 0.8 equiv of tetrachlorosilane.

Table I
Molecular Weights, Functionality, and Polydispersity of Linear and Star Amine Telechelic Polysiloxanes

polymer[a]	M_n (theo)[b]	M_n (found)[c]	functionality[d]	M_w/M_n[e]
L-I	1500	1600	1.9	1.32
L-II	1700	2100	2.0	1.13
ST-I	3200	2600	4.1	1.32
ST-II	5100	3900	3.7	1.20
ST-III	9000	6190	3.7	1.31
ST-IV	16000	17000	4.1	1.32
ST-V	24000	24000	4.3	1.27

[a] L designates linear telechelic siloxanes formed by coupling with dichlorodimethylsilane. ST designates four-armed stars formed by coupling with tetrachlorosilane. [b] Theoretical M_n based on (monomer)/(initiator)(monomer MW). [c] M_n found via vapor-phase osmometry, chloroform at 37 °C. Polymers ST-IV and ST-V M_n based on GPC extrapolation. [d] Functionality determined via infrared spectroscopy of 1600-cm^{-1} phenyl ring vibration combined with M_n data. [e] M^w/M_n based on polystyrene calibrated GPC in THF with no correction for broadening.

The preparation of star polymers via living polymerization followed by multifunctional termination with chlorosilanes has proven to be a very effective method.[12] This method has resulted in well-defined star polymers of up to 18 arms.[12] Other methods for the preparation of star polymers do not allow such good control over polydispersity, molecular weight, and arm number.

The star polymers prepared in this report were characterized by GPC, NMR, vapor-phase osmometry, and quantitative infrared spectroscopy. Figure 1 shows the GPC results of the coupling reactions of a living poly(dimethylsiloxane) with the appropriate chlorosilanes to prepare one-, two-, and four-arm polymers. As can be seen, the coupling reactions result in the formation of higher molecular weight polymer cleanly, without broadening of the peaks or any formation of multimodal distributions. Controlled experiments demonstrated the sensitivity of GPC analysis to improper coupling. A sample of living siloxane (M_n = 4000) coupled using 0.8 equiv of tetrachlorosilane exhibited a broadened GPC trace with a distinct shoulder at low elution volume (Figure 2). The shoulder corresponds to a four-armed star, while the major peak is a three-armed star, the expected major product, and a two-armed (linear) polymer.

Table I summarizes the results of the star-type polymers prepared in this work. The molecular weights found were in reasonable agreement with that theoretically expected. The M_n of the two linear polymers and stars I–III were determined by vapor-phase osmometry; however, the M_n of stars IV and V were determined via GPC. By use of stars I–III as standards, a GPC calibration curve was constructed and the M_n of the two highest molecular weights were determined via extrapolation. The ^1H NMR spectra were in agreement with the proposed structures, showing, in addition to the methyl protons from the siloxane block fixed at 0 ppm, the protons from the end group (aromatic at 6.5–7.2 ppm, amine singlet at 3.9 ppm, and unresolved aliphatic protons at 0.6–2.0). Functionality determination was performed with infrared spectroscopy owing to difficulties in the titration method. Clearly, the polymers formed were of low polydispersity, controlled molecular weight, and near theoretical functionality. Although only linear and four-arm star telechelic polymers were prepared, this method of synthesis is clearly of such generality so as to allow for the preparation of star polymers of various arm numbers using reported methods.[12] Similarly, the styryl anion nature of the blocked functional initiator should allow the use of several different monomers to prepare star polymers via living polymerization followed by multifunctional termination.

This work has significant implications for the preparation of highly defined polymer structures. First, this work represents the first preparation of well-defined, telechelic, star poly(dimethylsiloxane)s. Second, due to the favorable solubility properties of the new initiator, the possibility of preparing well-defined high 1,4- and high *cis*-1,4-polydienes now exists. Finally, these new polymers open up the possibility of preparing well-defined model networks and novel star–block copolymers for new studies and uses.

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Spin-Label-Induced Selective ^{13}C Nuclear Relaxation: Structures of the γ-Cyclodextrin–Tempone and α-Cyclodextrin–Di-*tert*-butyl Nitroxide Inclusion Complexes in Solution

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ABSTRACT: The relative positions of the guest molecules in the γ-cyclodextrin–Tempone and the α-cyclodextrin–di-*tert*-butyl nitroxide inclusion complexes have been determined from spin-label-induced ^{13}C nuclear relaxation rates. The structures of the complexes are consistent with the sizes of the nitroxide guests relative to the hydrophobic cavity of the cyclodextrins and with the thermodynamics of complex formation. Selective proton-decoupled ^{13}C spectra demonstrate that the assignments of C2 and C5 are reversed in γ-cyclodextrin relative to α- and β-cyclodextrins.

Cyclodextrins (CDs[1]) are α-1,4-linked cyclic oligomers of D-glucopyranose that form inclusion complexes with a variety of small molecules.[2] The structure of α-CD is shown in Figure 1. Interest in the properties of these complexes has been stimulated by their suitability as model systems for probing the physical and chemical basis of molecular recognition. CDs are water soluble, have a hydrophobic cavity for specific binding of substrates, and either have catalytic groups or have sites for the introduction of such catalytic groups. Consequently, one of the most interesting applications of CDs is as simple model enzyme systems for physical and chemical study.[3] In addition, the CDs have intriguing practical applications as solubilizing agents for drug delivery and as selective reagents in extractions and separations.[4]

An important step toward understanding the forces responsible for formation of CD inclusion complexes is characterizing the structure and dynamics of the complexes in solution. Magnetic resonance spectroscopies have been applied successfully to study both structure and dynamics in a variety of CD complexes.[5] The majority of ESR studies have focused on complexes between β-CD and nitroxide-free radicals because nitroxides complexed by this molecule exhibit significant changes in *g* values and hyperfine splitting constants compared to uncomplexed radicals. Complexes formed between nitroxides and either α-CD or γ-CD have received relatively little attention because the changes in the ESR spectra that accompany complexation are relatively small. However, one of us (M.P.E.) has recently shown that Heisenberg exchange rates can be used to determine the thermodynamics and kinetics of α-CD and γ-CD complex formation with nitroxides;[6] this has expanded the number of CD–nitroxide complexes that can be studied by ESR.

NMR spectroscopy has been widely used for the study of CDs in both the solution and solid state. Several studies have used cross relaxation and chemical shifts to determine geometries and location of substrates in the CD cavity.[7] A potentially powerful technique that has not been widely used in studying CD complexes is paramagnetically induced relaxation of nuclear spins. This technique, introduced by Mildvan and co-workers,[8] has been used advantageously for the study of macromolecular systems. In favorable cases, it has provided a very detailed picture of the structure and dynamics of bimolecular and trimolecular complexes of enzymes with a variety of substrates and cofactors. To our knowledge, only two reports using this technique on CD complexes have appeared.[9] Ohara and Kobayashi observed the effects of several nitroxides on the ^{1}H spectra and ^{1}H T_1s of β-CD and showed that some resonances were selectively relaxed by the nitroxides. However, the results were not quantitatively analyzed to provide details on the position of the nitroxide in the inclusion complex because the ^{1}H spectra are poorly resolved. Although the effects of paramagnetic molecules on ^{13}C relaxation rates are smaller than their effects on ^{1}H relaxation rates, the effects are readily detectable, and the greater resolution of ^{13}C spectra make this nucleus an attractive probe for macromolecular systems.[10] This paper reports the effects of nitroxide-induced relaxation on the ^{13}C relaxation rates of nitroxide–CD inclusion complexes and shows that this method gives direct measures of the positions of the nitroxide substrates in the inclusion complex.

Experimental Methods

α-CD and γ-CD were purchased from Advanced Separation Technologies, Inc., Whippany, NJ, and used as received. The proton and carbon NMR spectra were consistent with the absence of any impurities. Tempone and di-*tert*-butyl nitroxide (DTBN) were purchased from Aldrich Chemical Co. Sodium ascorbate was obtained from Sigma. Solutions for NMR analysis were prepared by dissolving 50–100 mM of CD in 2.5 mL of degassed 20% or 99% D_2O/H_2O and adjusting the pH to between 6.8–7.8 with HCl and NaOH. Reported pH values are uncorrected pH meter readings. The concentration dependence of the nuclear relaxation rates was determined by titrating aliquots (10–40 μL)

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