Stereoregular Precursors to Poly(*p*-phenylene) via Transition-Metal-Catalyzed Polymerization. 1. Precursor Design and Synthesis

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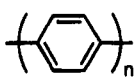
Abstract: 1,4-Linked, stereoregular precursors to poly(*p*-phenylene) (PPP) are synthesized by transition-metal-catalyzed polymerization of heteroatom-functionalized 1,3-cyclohexadienes. *cis*-5,6-Bis(trimethylsiloxy)-1,3-cyclohexadiene (TMS-CHD), a derivative of a microbial oxidation product of benzene, is polymerized stereospecifically in a cis-1,4-fashion by bis[(η^3-allyl)(trifluoroacetato)nickel(II)] with yields up to 96%. This polymerization system not only affords a highly 1,4-linked, stereoregular polymer but also permits a degree of molecular weight control. The resulting polymer, 1,4-poly(TMS-CHD), is a soluble, processable, semicrystalline material. Although 1,4-poly(TMS-CHD) cannot be pyrolyzed to yield PPP directly, the trimethylsilyl ethers on the polymer can be easily transformed to better leaving groups such as acetates to give the corresponding stereoregular acetoxy polymer (100% acetylation; 93% overall yield). NMR analysis of the acetoxy polymer is consistent with the polymer having either a highly isotactic or a highly syndiotactic cis-1,4-linked structure.

Introduction

Poly(*p*-phenylene) (PPP) is an insoluble, intractable, rigid-rod polymer that has long been sought after as both a structural and an electronic material because of its unique combination of physical properties.[1] Its relatively low density,[1b] high me-



PPP

chanical strength,[2] excellent thermal stability, and remarkable chemical resistance make it ideally suited for use as a light-weight, high-performance engineering material in extreme environments.[1a,b] Because of its conjugated π-electron system, PPP can also be converted from an electrical insulator in its pristine form ($\sigma \leq 10^{-12}$ S/cm) to a highly conductive charge transfer complex ($\sigma \leq 500$ S/cm) when treated with dopants such as AsF_5.[1a,b] PPP also possesses useful optical properties such as electroluminescence.[3] Other potentially useful material properties of PPP are its excellent radiation resistance and its intrinsic paramagnetism.[1a]

Undoubtedly, there is a broad range of potential technological applications for PPP.[1a,c] However, its development for commercial applications has been hampered by the fact that the same structural properties that make PPP such an attractive engineering polymer (i.e., its high strength, insolubility, thermal stability, and intractability) also make it extremely difficult to synthesize and process. All previous synthetic routes to PPP have been unable to generate a high molecular weight polymer with a completely 1,4-linked structure and/or incorporate a degree of processability for facile fabrication of the material into useful forms. In fact, the majority of the materials commonly called "PPP" in the literature are more accurately described as polyphenylene or phenylene oligomers because of their low molecular weight and/or regiochemical defects.[1]

Direct synthetic routes to PPP, such as oxidative polymerization of benzene, metal-catalyzed coupled of 1,4-dihalobenzenes, and Diels−Alder polycondensation of 1,4-diethynylbenzene with 1,4-phenylenebis(pyrones), all afford only low-quality polyphenylenes. Direct polymerizations of benzene using electrochemical[4] and chemical oxidation techniques[1a] only produce oligomers as a result of the inherent insolubility of the growing polyphenylene chains [number average degree of polymerization (DP) of 15−30]. These polyphenylene oligomers also contain substantial amounts of structural defects such as condensed polynuclear aromatic regions.[1a] Metal-catalyzed coupling of 1,4-disubstituted benzenes[5] and 4,4′-disubstituted biphenyls[5e,6] usually yield polyphenylenes containing significant amounts of nonlinear 1,2- and 1,3-linkages which are detrimental to the structural and electronic properties expected of the final material. Although some metal-catalyzed coupling reactions do generate completely 1,4-linked products,[5g−m] the growing PPP chains also precipitate from solution before high molecular weight material can be formed. High-temperature Diels−Alder polycondensation of 1,4-phenylenebis(pyrones) with 1,4-diethynylbenzenes also generates polyphenylene; however, model reactions indicate that 10% 1,3-linkages are typically introduced into the polymers via this route.[7] In addition, the polyphenylenes made from these Diels−Alder polycondensations often contain residual pyrone and/or carboxylic acid groups.[7] Pro-

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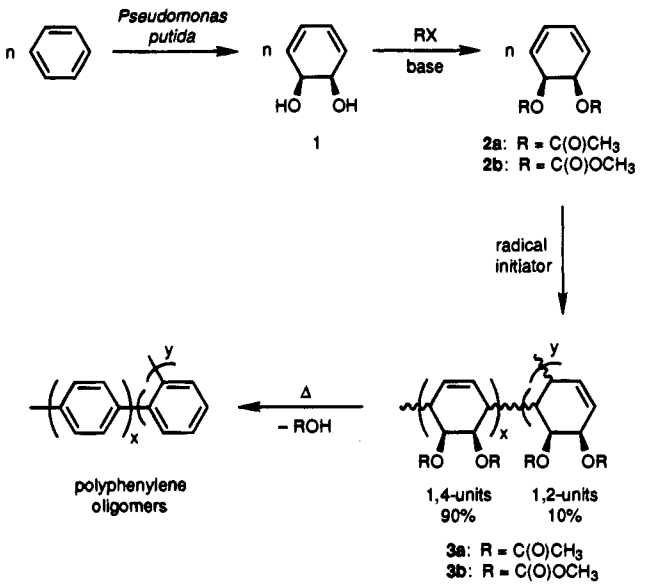
cessing of the polyphenylenes made from all of these direct routes is virtually impossible because the polyphenylene is formed directly as an insoluble, semicrystalline powder.

In order to circumvent the synthetic limitations associated with the direct synthesis of PPP, two divergent strategies have been developed. One strategy has been the synthesis of soluble, substituted PPPs.[1a,8] The solubility of these polymers insures that the molecular weight is no longer limited by premature precipitation and that direct postsynthesis processing should be possible. Unfortunately, many routes to substituted PPPs still introduce significant amounts of nonlinear defects into the polymers.[8a,b,h-l] In addition, the solubilizing side chains on these polymers impart physical properties to the materials that are very different from those sought in PPP.[8h-k]

The second strategy has been the development of precursor routes to PPP. By utilizing a processable, high molecular weight intermediate polymer that can be chemically converted to PPP, precursor routes offer processability without sacrificing any of the desirable physical properties of the final material. Unfortunately, all PPP precursor routes to date have achieved only limited success in terms of synthesis and processing. Initial precursor routes to PPP employing poly(1,3-cyclohexadiene) as the precursor polymer only yield poor-quality polyphenylene and offer poor processability. The polycyclohexadienes used in these routes contain a significant percentage of 1,2- and 1,3-units,[9] and the aromatization procedures used to convert the precursor polymers to polyphenylene usually do not proceed to completion.[9a,b,d] More recent precursor strategies based on functionalized cyclohexadiene precursor polymers offer excellent processability but again afford poor-quality final products.[10,11] The ICI process (Scheme 1),[10] for example, involves the synthesis of soluble precursor polymers (**3a,b**) via the radical polymerization of monomers (**2a,b**) derived from *cis*-5,6-dihydroxy-1,3-cyclohexadiene (**1**), a microbial oxidation product of benzene. These precursors are subsequently converted to polyphenylene via thermally-induced acid elimination in solution or the solid state to yield powders, films, or fibers.[10c] Unfortunately, the ICI process suffers from two inherent problems as a result of the nonstereospecific nature of the radical polymerization process: (1) The radically polymerized precursors contain approximately 10% 1,2-linkages that become nonlinear defects in the final polyphenylene.[10b] (2) The precursors fracture during the thermal converstion step as a result of the random backbone stereochemistry and/or the presence of the 1,2-linkages.[12] In addition, the radical polymerization process provides little if any control over the molecular weight of the polymers. A more recent precursor route to PPP has also been developed that utilizes nickel-catalyzed step growth polymerization of an ester-functionalized, 1,4-dihalobenzene to produce soluble, substituted PPP.[13] This ester-functionalized PPP is subsequently hydrolyzed and then decarboxylated to afford unsubstituted PPP. Although this route produces a completely 1,4-linked precursor polymer, the kinetics of the step growth polymerization process do not readily permit molecular weight control. In addition, the processability of the method is very limited because the conversion process involves refluxing a quinoline solution of the precursor with significant quantities of copper salts. The resulting PPP can only be obtained as a intractable powder precipitate.[13]

Scheme 1



Our objective was to develop a superior precursor route to PPP that would yield a high molecular weight, structurally regular final product and incorporate the exceptional processability inherent in the original ICI process. Specifically, what we sought was a method for polymerizing derivatives of compound **1** that would provide three things: (1) regiochemical control to yield completely 1,4-linked precursors to 100% para-

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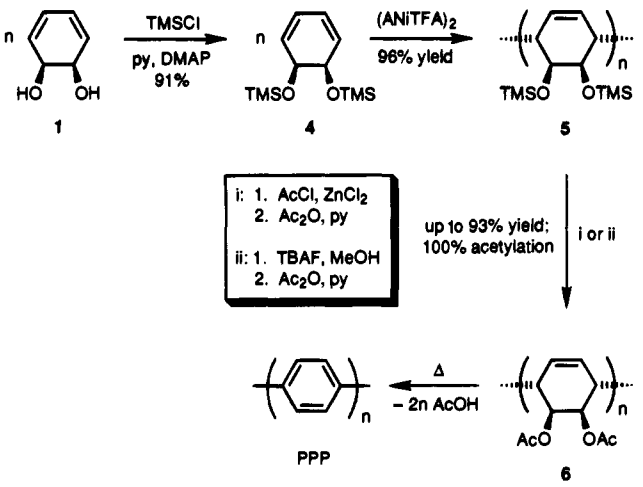
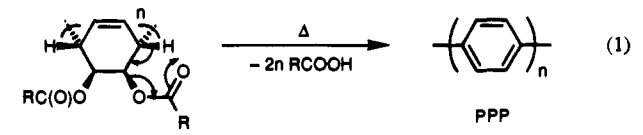
Scheme 2



linked poly(phenylene), (2) stereochemical control to yield precursors with the optimum stereochemistry for facile acid elimination without chain scission, and (3) a degree of molecular weight control during polymer synthesis. The optimum repeat unit stereochemistry for acid elimination in this case would be the 1,4-*SSRR* repeat unit structure[14] depicted in eq 1. Since the



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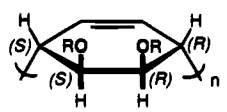


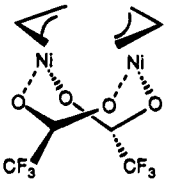
optimum pyrolytic elimination of acid from the ICI precursors is believed to involve a cis six-membered ring transition state,[10b] the precursor repeat unit should not only be 1,4-linked but also have the bridging C–C bonds in a cis relationship on the face of the cyclohexenyl ring away from the pendant functional groups.

Unfortunately, few initiators typically employed for the polymerization of 1,3-dienes offer the combination of high 1,4-regioselectivity, high cis stereospecificity, and the capability for the molecular weight control required for the synthesis of 1,4-linked, stereoregular PPP precursors. As demonstrated in the original ICI process (Scheme 1)[10] and in a similar synthetic approach used by McKean and Stille,[11] conventional radical initiators are unable to provide this level of control. Anionic and cationic initiators have also proven to be unequal to the task since both of these types of initiators afford polymers with mixtures of 1,4- and 1,2-linkages when used to polymerize 1,3-cyclohexadiene.[9] What we have developed is a high-yield, multistep synthesis of 1,4-linked, stereoregular precursors to PPP which utilizes a transition-metal catalyst to provide stereochemical and molecular weight control, protecting group chemistry to provide catalyst/functional group compatibility, and functional group interconversion chemistry to provide an avenue for facile aromatization of the precursors (Scheme 2). Essentially, our new synthetic strategy combines the stereochemical and regiochemical controls afforded by transition-metal polymerization catalysts with the efficiency and processability of the ICI process.

(14) In describing the stereochemistry of the different repeat units possible for polymers of derivatives of **1**, the following labeling scheme is used: A two number prefix is used to describe the regiochemistry of the linkages (e.g., 1,4- or 1,2-linked) and a series of four italicized letters is used to indicate the absolute configuration (i.e., *R* or *S*) of the four stereocenters on the repeat units, as read from left to right with the cyclohexene ring laying flat and the cis heteroatom functionalities pointing up. See eq 1 for an example of this labeling system.

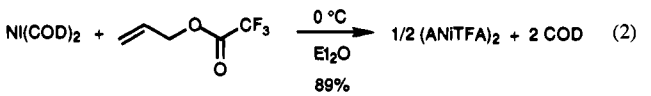
Results and Discussion

In the development of a transition-metal catalyst system for the stereospecific polymerization of derivatives of monomer **1**, two fundamental concerns needed to be addressed: (1) stereochemical control during the polymerization and (2) catalyst/functional group compatibility. Many transition-metal polymerization catalysts are known to perform stereospecific polymerization of 1,3-dienes.[15] For example, Ziegler–Natta-type systems afford highly 1,4-linked polymers of 1,3-butadiene[15] and 1,3-cyclohexadiene.[9b] However, the strong Lewis acid cocatalysts in these Ziegler–Natta systems generally cannot tolerate the types of heteroatom functionalities on the ICI monomers (**2a,b**) required for efficient conversion of the precursors to polyphenylene. Metal–π-allyl catalyst systems are also known to afford highly 1,4-linked polymers of 1,3-dienes.[15] Although a great deal of research has been performed on these catalysts with purely hydrocarbon 1,3-dienes (e.g., 1,3-butadiene and 1,3-cyclohexadiene),[16] little has been done with heteroatom-functionalized 1,3-dienes. In fact, the only successful polymerizations of heteroatom-functionalized 1,3-dienes using metal–π-allyl complexes have been copolymerizations with 1,3-butadiene.[17] The corresponding homopolymerizations of these functionalized monomers were unsuccessful using these catalysts. The most successful of these copolymerizations employed bis[(η^3-allyl)(trifluoroacetato)nickel(II)] [(ANiTFA)$_2$] as the catalyst system.[18] Consequently, (ANiTFA)$_2$ was an excellent starting point for our investigations.



(ANiTFA)$_2$

(A) The Catalyst Bis[(η^3-allyl)(trifluoroacetato)nickel(II)] [(ANiTFA)$_2$]. (ANiTFA)$_2$ is an air- and water-sensitive compound that can easily be prepared by the oxidative addition of allyl trifluoroacetate to bis(1,5-cyclooctadienyl)nickel(0) [Ni(COD)$_2$] (eq 2).[19] (ANiTFA)$_2$ not only exhibits a partial



(2)

tolerance to heteroatom functionalities in 1,3-butadiene polymerizations[18] but also has been used for the "living" polymer-

(15) For brief overviews of transition-metal catalyst systems which perform stereospecific polymerization of 1,3-butadiene, see: (a) Odian, G. *Principles of Polymerization*, 2nd ed.; John Wiley and Sons: New York, 1981; p 631. (b) Atlas, S. M.; Mark, H. F. *Catal. Rev.* **1976**, *13*, 1.

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(18) Borge-Visse, F.; Dawans, F. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 2481.

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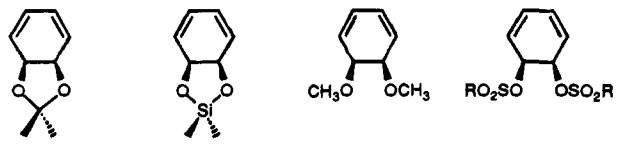
ization of the monomer, exhibiting >98% 1,4-regioselectivity.[20] In addition, nickel–π-allyl complexes such as $(ANiTFA)_2$ exhibit high cis stereospecificity in 1,3-diene polymerizations. The polymerization is believed to proceed via a syn-coordinative insertion mechanism.[21-23] This unique combination of characteristics makes $(ANiTFA)_2$ an ideal candidate for the synthesis of highly 1,4-linked, stereoregular precursors to PPP from derivatives of compound **1**. Unfortunately, no previous work has been done with this catalyst with cyclic 1,3-dienes or highly functionalized cyclic dienes.

(B) Model Studies and Catalyst/Functional Group Compatibility. Initial experiments with $(ANiTFA)_2$ focused on 1,3-cyclohexadiene (CHD) polymerizations. The purpose of these initial experiments was to determine whether the catalyst could polymerize the 1,3-cyclohexadiene moiety, the polymerizable group on derivatives of **1**. CHD was found to be readily polymerized by $(ANiTFA)_2$ at temperatures of 50 °C or higher in a variety of noncoordinating aromatic solvents, affording polymer yields of 70–90%. The resulting polycyclohexadiene is an insoluble, highly crystalline white powder that precipitates from solution during the course of the polymerization. In general, the more polar aromatic solvents (e.g., chlorobenzene and *o*-dichlorobenzene) were found to enhance catalyst activity and provide the highest yields of polymer.

Unfortunately, attempts to polymerize the acetyl (**2a**) and methoxycarbonyl (**2b**) derivatives of compound **1** using $(ANiTFA)_2$ under similar conditions were unsuccessful. ^1H NMR analysis of the reaction mixtures revealed that, instead of initiating polymerization, $(ANiTFA)_2$ aromatizes a stoichiometric amount of **2a** or **2b**. Possibly the acid or alcohol eliminated during the aromatization of these monomers decomposes the catalyst.

Subsequent investigations revealed that $(ANiTFA)_2$ is incompatible with carbonyl-containing groups in general. For example, the addition of a small amount of purified ethyl acetate to an active CHD/$(ANiTFA)_2$ polymerization system resulted in dramatically lower polymer yields or no polymer formation at all. Most likely, the Lewis basic carbonyl groups compete with the 1,3-diene moieties for coordination to the electrophilic nickel centers of the catalyst. Thus, the functional groups best suited for facile conversion of the precursor polymers to PPP (i.e., esters and carbonates) are completely incompatible with the catalyst.

Additional catalyst/functional group compatibility studies revealed that $(ANiTFA)_2$ is also incompatible with the parent monomer **1** and many of its other common derivatives. Attempts to polymerize **1** directly using $(ANiTFA)_2$ were unsuccessful and only resulted in aromatization of the monomer to phenol and water. Use of the acetonide (**2c**) and silyl

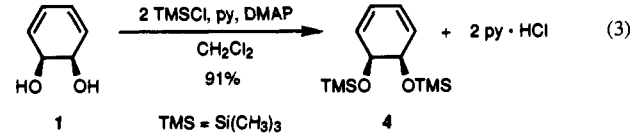


2c **2d** **2e** **2f**

acetonide (**2d**) derivatives of **1** did produce immediate decomposition of the catalyst; however, the two monomers could not be polymerized. Unfortunately, attempts to synthesize simple alkyl ether derivatives of **1** (e.g., **2e**) in sufficient purity for polymerization studies with $(ANiTFA)_2$ were unsuccessful using literature procedures.[10b] Thus, simple compatibility studies of 1,2-diethers with the catalyst were performed by adding small amounts of purified 1,2-dimethoxyethane (DME) to an active CHD/$(ANiTFA)_2$ polymerization reaction. The addition of DME to a CHD polymerization reaction quickly resulted in catalyst decomposition and afforded only very low polymer yields. A plausible rationalization for this incompatibility is that 1,2-diether oxygens can chelate to the electrophilic nickel centers to deactivate the catalyst. Due to the difficulty of synthesizing bis(sulfonic ester) derivatives of **1** (**2f**), similar compatibility studies were performed for sulfonic esters by using ethyl tosylate as an additive. Only a small amount of poly(CHD) formed in the presence of ethyl tosylate, probably as a result of a similar competitive coordination effect from the Lewis basic S=O groups.

More exotic derivatization of **1** (e.g., substitution of the hydroxy groups with halides) was not attempted due to the inherent thermal and hydrolytic instability of the material. Compound **1** spontaneously aromatizes to form phenol and water in the presence of acid or at temperatures in excess of 60 °C.[10b] In fact, **1** must be stored as a solid at sub-zero temperatures or as a basic solution (e.g., in pyridine) to minimize aromatization. As a result, derivatization of this compound is limited to procedures which employ relatively low temperatures and basic or near neutral conditions.[10b]

(C) *cis*-5,6-Bis(trimethylsiloxy)-1,3-cyclohexadiene: A Compatible Monomer via Protecting Group Chemistry. A derivative of **1** compatible with $(ANiTFA)_2$ was obtained by masking the hydroxy groups on the parent monomer as trimethylsilyl ethers. *cis*-5,6-Bis(trimethylsiloxy)-1,3-cyclohexadiene (**4**) was prepared by reacting compound **1** with 2 equiv of chlorotrimethylsilane (TMSCl) in a mixture of pyridine and methylene chloride using 4-(dimethylamino)pyridine (DMAP) as a catalyst (eq 3). Monomer **4** can be polymerized in high



(3)

yields by $(ANiTFA)_2$ at a temperature of 50 °C or higher in a variety of aromatic solvents or as a neat liquid (eq 4).[24] Chlorobenzene was found to be the best solvent for the polymerization in terms of polymer yield and catalyst activity. Typically, with a monomer-to-catalyst ratio of 80:1 and a monomer concentration of 1.5 M in chlorobenzene, the polymer is obtained in 93% yield with a number average degree of polymerization (M_n) of 38 000 and a polydispersity index (PDI) of 1.64, as determined by Viscotek GPC analysis.[25] Under these reaction conditions, the mixture of $(ANiTFA)_2$ and **4** in chlorobenzene changes from an initial clear orange solution to a dark red solution and finally to an opaque coffee-colored mixture over a period of approximately 15–20 min at 50 °C. The active reaction mixture then remains black for the duration of the polymerization, becoming progressively more viscous until a gel forms (usually after approximately 24 h). The resulting TMS ether polymer (**5**) is a white powder which is soluble in hexanes, diethyl ether, THF, and $CHCl_3$.

Unlike the other derivatives of **1**, monomer **4** is believed to be compatible with the catalyst for two reasons: (1) The steric

(20) Hadjiandreou, P.; Julemont, M.; Teyssié, P. *Macromolecules* **1984**, *17*, 2455.
(21) Durand, J. P.; Dawans, F. Teyssié, P. *J. Polym. Sci., Part B* **1968**, *6*, 757.
(22) Yakovlev, V. A.; Dolgoplosk, B. A.; Tinyakova, E. I.; Yakoleva, O. N.; *Vysokomol. Soedin.* **1969**, *A11*, 1645.
(23) Porri, L.; Aglietto, M. *Makromol. Chem.* **1976**, *177*, 1465.
(24) Monomer **4** can also be polymerized with similar nickel–π-allyl complexes containing a relatively nonbasic ancillary ligand (i.e., bis[(η^3-allyl)(pentafluorophenoxy)nickel(II)] and bis[(η^3-allyl)(pentafluorobenzoato)nickel(II)]). However, $(ANiTFA)_2$ was found to be the easiest to prepare and the most active.
(25) Viscotek GPC analysis was performed by the Analytical and Physical Sciences Group at ICI Chemicals and Polymers Ltd., Runcorn, U.K.

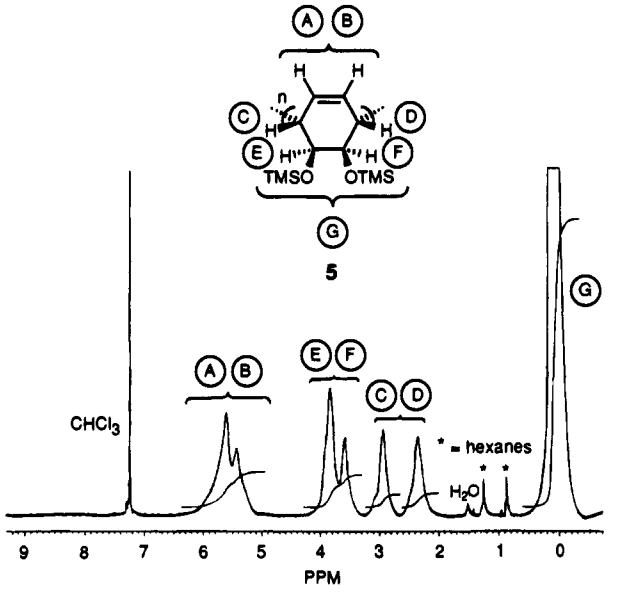
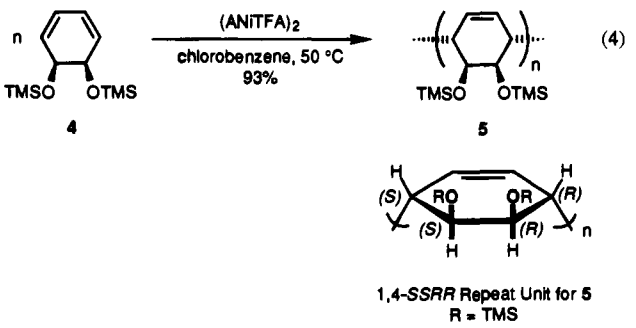


Figure 1. 400-MHz ^{1}H NMR spectrum of polymer **5** in $CDCl_3$.

bulk of the large TMS protecting groups effectively prevents the oxygen atoms of the monomer from coordinating to the catalyst and interfering with the polymerization. (2) The TMS ethers are very poor leaving groups compared to esters and carbonates, thus monomer aromatization leading to catalyst decomposition is inhibited. The bulky TMS groups may also play a tertiary role in the polymerization by directing the insertion of the monomer into the propagating polymer chain. The bulky TMS groups can not only sterically shield the oxygen atoms but also effectively block off one face of the cyclohexadiene ring of **4**. Thus, **4** should preferably approach and coordinate to the propagating Ni catalyst via its unhindered face away from the large TMS ethers. This π-facial selectivity afforded by the TMS ethers, coupled with the cis stereospecificity[21-23] and the 1,4-regioselectivity[19a,20] of the $(ANiTFA)_2$ system, should yield polymer **5** as a completely 1,4-linked, stereoregular polymer with the 1,4-*SSRR* repeat unit depicted in eq 4.



(D) Characterization of Polymer 5: Confirmation of the Inferred 1,4-Stereoregular Structure. The proposed 1,4-linked structure for **5**, as inferred from the factors discussed above, was confirmed by ^{1}H NMR analysis. 1,2-Units in radically synthesized polymers of derivatives of compound **1** typically exhibit a proton resonance in the 1.8–2.1 ppm range of the ^{1}H NMR spectrum.[11] 1,4-Linkages of these polymers do not exhibit any proton signals in this region of the spectrum.[11] As can be seen from the 400 MHz ^{1}H NMR spectrum of **5** (Figure 1), the polymer does not exhibit any proton signals in this region, consistent with a highly 1,4-linked structure for the polymer. Further support for this assignment was provided by comparing the 500 MHz ^{1}H NMR spectrum of **5** made using $(ANiTFA)_2$ (Figure 2a) with that of radically polymerized

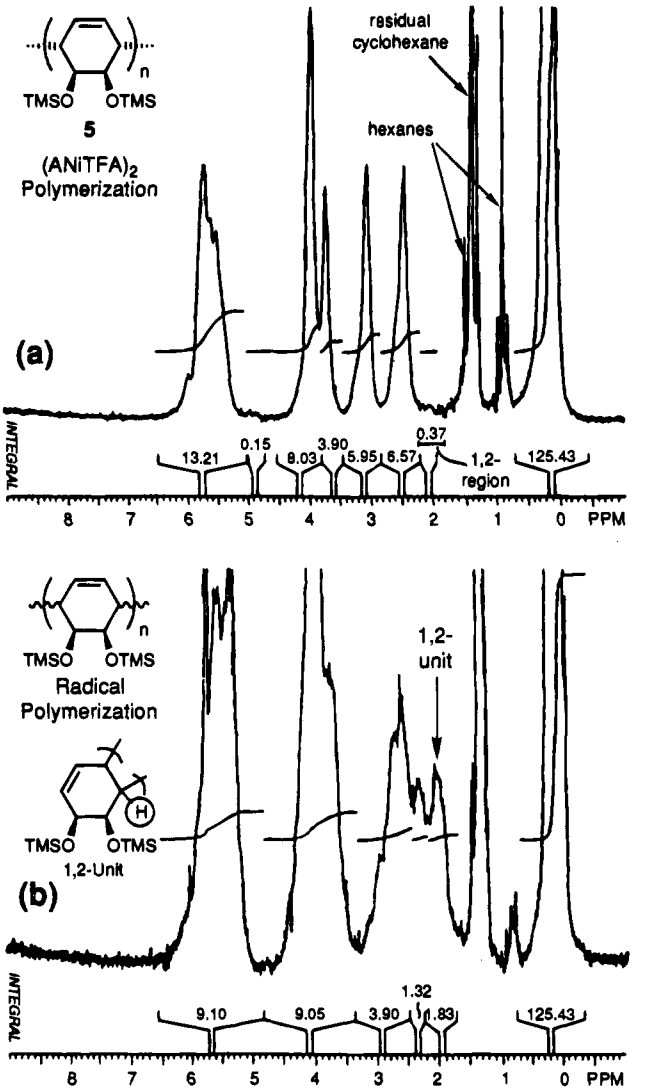


Figure 2. 500-MHz ^{1}H NMR spectra of (a) polymer **5** and (b) radically polymerized oligomers of **4** in cyclohexane-d_{12}. The ^{1}H NMR signals at δ 0.9 and overlapped with the cyclohexane solvent peak at δ 1.4 are due to residual hexanes trapped in the polymer during workup.

oligomers of **4** (Figure 2b).[26] Only the radically polymerized oligomers of **4** exhibit a proton signal at 1.9 ppm characteristic of 1,2-units.

Although ^{1}H NMR analysis was consistent with a highly 1,4-linked regioregular structure for **5**, this technique was not able to provide any conclusive information on the tacticity (backbone stereochemistry) of the polymer. For a completely stereoregular polymer, the symmetric 1,4-*SSRR* repeat units inferred for polymer **5** (eq 4) can be connected in two regular fashions: (1) the same throughout (an isotactic structure) and (2) a perfectly alternating fashion (a syndiotactic structure) (Figure 3).[27] Since cyclohexene molecules in solution typically undergo rapid half-chair–half-chair conformational inversion (eq 5),[28] one would

expect that on the NMR time scale there would be a plane of

(26) Comparative 500-MHz ^{1}H NMR spectra of **5** and radically polymerized oligomers of **4** were provided by Dr. Denis Ballard and Dr. David Haddleton at ICI Chemicals and Polymers Ltd., Runcorn, U.K. Even though the monomer was 99.7% pure by GC analysis, neat **4** was difficult to radically polymerize with traditional radical initiators. Only oligomers with a DP of approximately 12 were recovered in 15% yield. Because of the low molecular weight and low polymer yields obtained, the solution and solid-state conformations of radically polymerized oligomers of **4** have not been determined.

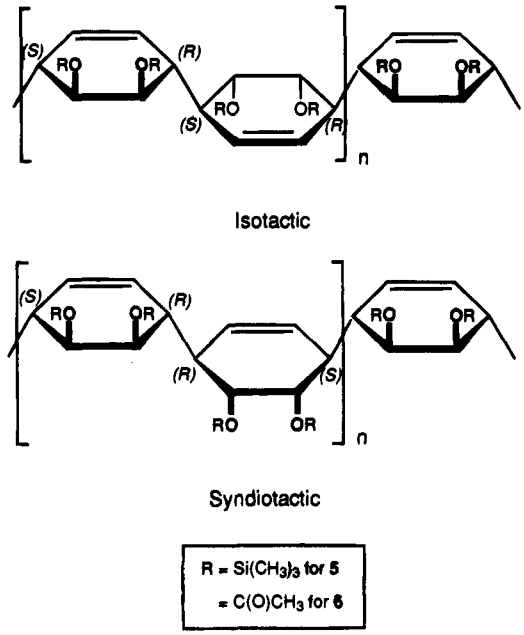


Figure 3. Isotactic and syndiotactic structures for conformationally nonrigid polymers **5** and **6** with the 1,4-*SSRR* repeat unit.

symmetry bisecting each cyclohexenyl repeat unit in the two possible regular tacticities for **5** (Figure 3). If this were the case, the 1,4-*SSRR* isotactic and syndiotactic structures possible for **5** would both exhibit only three nonequivalent ^{1}H signals from the protons on the cyclohexene rings from symmetry arguments. However, the actual ^{1}H NMR spectrum of **5** (Figure 1) shows different chemical environments for *each* of the six protons on the cyclohexenyl ring of the repeat units. Variable-temperature ^{1}H NMR analysis of **5** in toluene-d_8 revealed that the six different proton resonances did not coalesce even at 100 °C. Attempts to obtain more information on the stereochemistry of **5** using conventional solution ^{13}C NMR analysis were unsuccessful. ^{13}C NMR analysis of **5** dissolved in a variety of solvents (e.g., C_6D_6, $CDCl_3$, THF-d_8) with different concentrations only yielded spectra with extremely poor signal-to-noise and poor resolution.

In order to further elucidate the structure of **5**, the polymer was also analyzed by a variety of secondary characterization techniques. Wide-angle powder X-ray diffraction (PXRD) analysis revealed that **5** is a partially ordered polymer in the solid state, exhibiting a single diffraction peak at 9.725 Å and a diffuse, amorphous halo over the 3–6-Å region (Figure 4). This type of PXRD profile is typically exhibited by rodlike molecules such as nematic liquid crystals and liquid-crystalline polymers.[29,30] Viscotek GPC analysis of **5** also revealed that the polymer has a relatively high Mark–Houwink coefficient

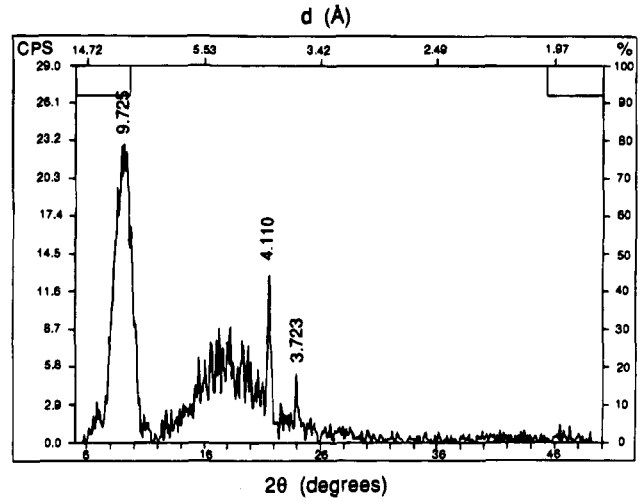


Figure 4. PXRD profile of polymer **5**. The reflections at 4.110 and 3.723 Å are diffractometer artifacts.

a of 0.9–1.1 in THF.[25] Such a high value for this viscosity parameter is consistent with strong polymer–solvent interactions and an extended or elongated polymer chain conformation in solution.[31] This unexpected rodlike conformation for polymer **5** is probably the reason why a high-resolution, solution ^{13}C NMR spectrum of the polymer could not be obtained. The rodlike conformation of the polymer chains probably makes tumbling of the polymer chains in solution extremely slow on the NMR time scale, thereby resulting in severe chemical shift anisotropy, poor signal-to-noise, and poor signal resolution. In fact, benzene and toluene solutions of **5** are usually thixotropic. That is, these initial free-flowing polymer solutions often form gels upon standing but return to their original fluid state upon mechanical agitation.

Taken altogether, these observations suggest that polymer **5** is highly 1,4-linked with a rodlike conformation and solid-state order characteristic of a polymer with a highly regular structure. We believe that **5** has either the isotactic or syndiotactic structure with the 1,4-*SSRR* repeat unit (Figure 3), as would be expected from the stereospecificity of the monomer addition reaction (eq 4). We also believe that the inconsistency in the number of observed nonequivalent ring protons in its ^{1}H NMR spectrum with that expected from the symmetry of the two stereoregular structures is most likely a consequence of the unexpected rodlike polymer conformation. The polymer chains adopt a rodlike secondary structure that slows down the rate of half-chair–half-chair interconversion and effectively locks the cyclohexene repeat units into a single half-chair conformation on the NMR time scale. This loss of normally rapid conformational equilibrium (i.e., "ring-flipping") (eq 5) removes the expected plane of symmetry within each repeat unit on the NMR time scale, resulting in six nonequivalent ring protons instead of the three expected (see Figure 5). The rodlike conformation and the locked half-chair repeat unit inferred for **5** are most likely the result of the steric interactions of the bulky TMS ethers. (These rationalizations on the stereoregular structure and conformation of polymer **5** will be directly confirmed in subsequent sections of this study.)

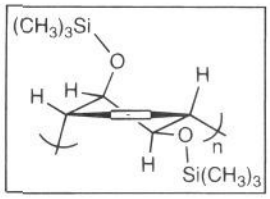
(27) Due to the complexity in assigning the different tacticities possible for polymers of derivatives of **1**, a simple labeling scheme analogous to that used to describe the tactic structures of polypropylene and polyacetaldehyde is employed. The term isotactic refers to a backbone with the same repeat unit connectivity throughout and a symmetry plane relating the stereocenters of adjacent units. The term syndiotactic refers to a backbone with an alternating connectivity and a C_2 axis relating the corresponding stereocenters of adjacent units. See: Odian, G. *Principles of Polymerization*, 2nd ed.; John Wiley and Sons: New York, 1981; pp 566–574.

(28) The conformation of cyclohexene in solution is described as a half-chair with a staggered structure similar to that depicted in Figure 5. Cyclohexene half-chair conformers undergo rapid inversion with an activation energy for ring inversion of 5.3 kcal/mol. This activation energy is approximately one-half that for the ring inversion of cyclohexane. See: Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, Part A: Structure and Mechanisms*, 3rd ed.; Plenum: New York, 1990; pp 131–141.

(29) Vertogen G.; de Jeu, W. *Thermotropic Liquid Crystals, Fundamentals*; Springer-Verlag: Berlin, 1988; Chapter 1.

(30) Ballauff, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28* (3), 253.

(31) The exponential factor a in the Mark–Houwink equation $[\eta] = KM^a$, which relates molecular weight (M) to intrinsic viscosity ($[\eta]$), can be used to extrapolate the conformation of the polymer in solution: The parameter a is 0 for compact spheres, 0.5 for statistical coils, approximately 1 for semicoils (ellipsoids), and 1.8–2.0 for perfect rigid-rod molecules. Higher values of a also imply better solvent–polymer interactions. See: (a) Seymour, R. B.; Carraher, C. E., Jr. *Polymer Chemistry, An Introduction*; Marcel Dekker: New York, 1981; pp 66–75. (b) Sperling, L. H. *Introduction to Physical Polymer Science*; John Wiley & Sons: New York, 1986; pp 81–83.



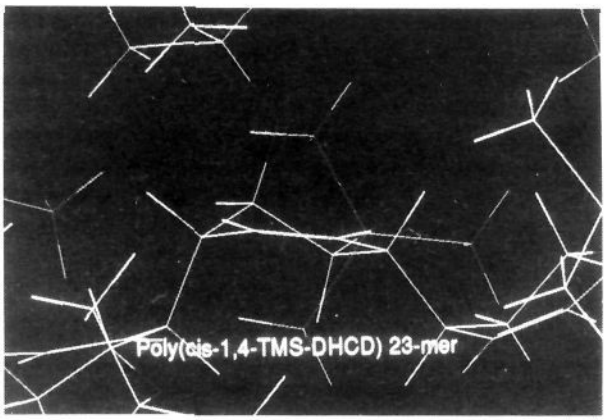


Figure 5. Locked half-chair conformation for the 1,4-*SSRR* of polymer **5** with the isotactic structure, as suggested by computer modeling.

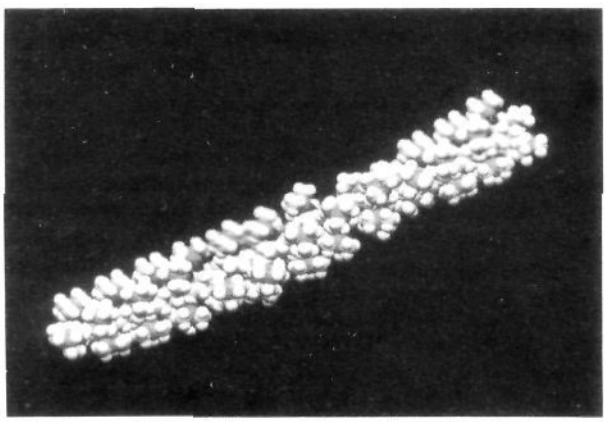


Figure 6. Rodlike secondary structure for the 1,4-*SSRR* isotactic structure of polymer **5**, as suggested by computer modeling.

To help visualize these concepts, computer-modeled images of the locked 1,4-*SSRR* repeat unit and the inferred rodlike conformation for polymer **5** are presented in Figures 5 and 6, respectively. It should be noted that the images presented in these figures are of a local energy minimum conformation for the isotactic structure of **5** shown in Figure 3, modeled using Biograf with MM2 force-field parameters.[32] Similar modeling of the corresponding 1,4-*SSRR* syndiotactic structure of **5** afforded an elongated helix rather than a rodlike structure as in the isotactic case.

(E) Preliminary Kinetic Analysis of the (ANiTFA)$_2$/Monomer 4 Polymerization System. In order to determine whether the (ANiTFA)$_2$/**4** polymerization system has the potential for molecular weight control, several aspects of its polymerization kinetics were examined. For example, the efficiency of the (ANiTFA)$_2$/monomer **4** polymerization system in chlorobenzene was found to have a strong dependence on the initial monomer concentration. At a constant monomer-to-catalyst mole ratio of 80:1, the yield of **5** increases asymptotically up to 93% with increasing initial monomer concentration. Below a critical monomer concentration (0.14 M), however, polymerization does not proceed (Figure 7). To determine whether the polymerization system was "living",[33] the M_n of the polymer was examined as a function of percent monomer conversion using a constant monomer-to-catalyst mole ratio of 75:1. As can be seen in Figure 8, the M_n vs percent conversion relationships for the system in chlorobenzene, toluene, and neat monomer are not linear. Instead, the polymer M_n rises quickly at low percent conversion and then levels out for the remainder of the reaction. These M_n vs percent conversion relationships are consistent with a typical chain addition polymerization[34] with termination and chain transfer processes, rather than a "living" polymerization process.[33]

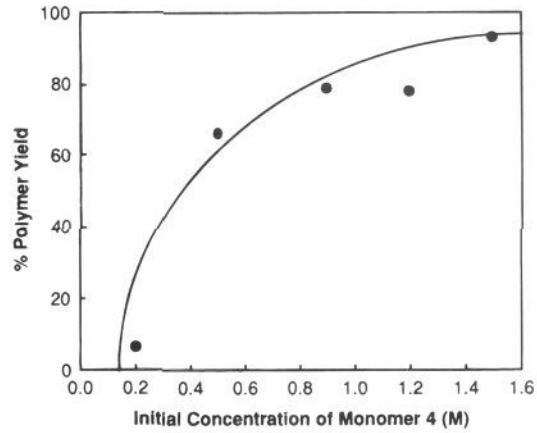


Figure 7. Plot of percent polymer yield vs initial monomer concentration for the (ANiTFA)$_2$/monomer **4** polymerization system in chlorobenzene. (Polymerization temperature = 50 °C; monomer-to-catalyst ratio = 80:1; reaction time = 24 h.)

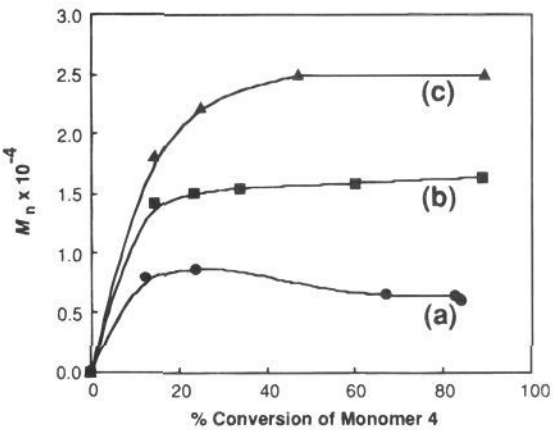


Figure 8. Plots of the M_n of polymer **5** vs percent monomer conversion for the (ANiTFA)$_2$/monomer **4** polymerization system: (a) neat; (b) in toluene, [**4**] = 2.0 M; (c) in chlorobenzene, [**4**] = 0.7 M. All polymerizations were performed at 50 °C with a monomer-to-catalyst ratio of 75:1. M_n values in a and b were determined by Viscotek GPC analysis. The M_n values in c were determined by GPC analysis referenced to polystyrene molecular weight standards.

Despite its non-"living" kinetic behavior, the (ANiTFA)$_2$/**4** system does have the potential for molecular weight control. Blocking experiments, performed by addition of fresh aliquots of monomer to the propagating system at approximately 75%

(32) Typically, structures were built up from a single energy-minimized repeat unit by expanding successively to a dimer, tetramer, octamer, etc., minimizing at each step using MM2 or Dreiding force fields in Biograf Version 2.20. The roughly minimized structures (usually 23-mers) were then finally minimized over 1000 iterations using MM2 parameters and BatchMin Version 3.1d. For **5** with the 1,4-*SSRR* isotactic structure, a final energy of 94.3 kJ/mol was obtained after 1000 iterations (6261 cpu s) of energy minimization using MM2 parameters.

(33) For a review of features characteristic of a "living" polymerization process, see: Quirk, R. P.; Lee, B. *Polym. Int.* **1992**, *27* (4), 359.

(34) For a brief overview of features characteristic of typical chain addition processes, see: Cowie, J. M. G. *Polymers: Chemistry and Physics of Modern Materials*, 2nd ed.; Chapman and Hall: New York, 1991; p 81.

Table 1. Blocking Experiment: Effect of Adding Fresh Aliquots of Monomer to the Active $(ANiTFA)_2$/Monomer **4** Polymerization System In Chlorobenzene

equiv of fresh monomer 4 added[a]	polymer 5		
	M_n (Viscotek GPC)	DP	PDI
75	1.78×10^4	69	2.06
70	3.31×10^4	129	1.84
247[b]	5.14×10^4	200	2.03

[a] Addition of fresh aliquots of monomer performed at approximately 75% conversion of the previous aliquot. The monomer aliquots were diluted to maintain an initial monomer concentration of 0.7 M at each addition. [b] A larger amount of **4** was required at this point in the experiment due to increasing viscosity in the reaction mixture. The lower than expected M_n from this final blocking experiment is a result of gel formation stopping the reaction prematurely before all the added monomer could be consumed.

Table 2. Effect of Increasing the Monomer-to-Catalyst Ratio on the M_n and Percent Yield of Polymer **5** for the $(ANiTFA)_2$/Monomer **4** Polymerization System in Chlorobenzene[a]

monomer-to-catalyst ratio	polymer 5			
	M_n (Viscotek GPC)	DP	PDI	% yield
50:1	2.22×10^4	87	1.75	80
100:1	2.73×10^4	106	2.00	83
200:1	3.47×10^4	135	1.84	66

[a] [**4**] = 1.5 M; reaction time = 24 h; polymerization temperature = 50 °C.

conversion, resulted in predictable molecular weight increases in the resulting polymer *without* detectable broadening of the PDI or generation of a multimodal molecular weight distribution (Table 1). These facts suggest that there is a well-defined active species present during the course of the polymerization reaction which can be utilized (under the proper conditions) to systematically increase polymer molecular weight.

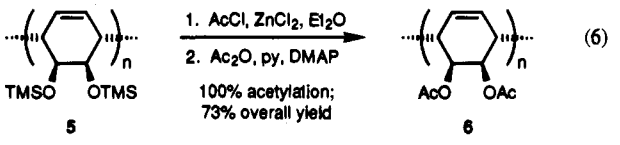
The M_n of the polymer was also found to increase with increasing initial monomer-to-catalyst ratios (Table 2). However, the linear relationship is not a direct one, and lower polymer yields are generally obtained with increasing monomer-to-catalyst ratios at a constant monomer concentration of 1.5 M. These lower than expected M_n values and polymer yields are very likely due to the rapid gelation observed during the reaction from accumulation of polymer **5** under the concentrated reaction conditions. This gel formation stops the reaction prematurely before all of the monomer can be consumed. By employing more dilute reaction mixtures to reduce the extent of gelation (i.e., [**4**] = 1.2 M), recovered yields of **5** as high as 96% have been achieved with a monomer-to-catalyst ratio of 140:1 for a 20-g-scale polymerization of **4**. The polymer obtained under these reaction conditions has an M_n of 5.31×10^4 (DP ~ 207) and a PDI of 1.31.

Although a high degree of molecular weight control and excellent polymer yields can be achieved under the appropriate reaction conditions, the exact nature of the system's polymerization kinetics has not yet been determined. We do know that the rate-determining step in chain transfer and termination in this system is not the conventional β-H elimination of a propagating metal–allyl species as suggested by Teyssié for the $(ANiTFA)_2$/butadiene system.[20] If β-H elimination were the rate-determining step in chain transfer and termination, a difference in the M_n of homopolymers made from the $(ANiTFA)_2$-catalyzed polymerization of ring-deuterated **4** and **4** should be observed as a result of a kinetic isotope effect. However, the M_n and PDI of homopolymers of ring-deuterated **4** and **4** synthesized under identical reaction conditions were found to be identical (see the supplementary material).[35]

Unfortunately, a more detailed examination of the dark brown-black active catalyst species responsible for this polymerization behavior was not possible. Attempts to analyze the propagating species using ^1H NMR spectroscopy only afforded spectra with extremely broad signals with poor signal-to-noise. The difficulties experienced in NMR analysis may be due to the presence of a paramagnetic nickel complex or a highly fluxional species. Attempts to isolate the black active species were also unsuccessful due to its high solubility in solvents typically used to precipitate organometallic intermediates (e.g., pentane and hexanes) and its instability in coordinating solvents.

(F) Thermal Analysis and Pyrolysis of Polymer 5. Although the $(ANiTFA)_2$/monomer **4** polymerization system produces a 1,4-linked polymer and possesses a degree of molecular weight control, the resulting polymer **5** does not yield PPP upon pyrolysis. DSC and TGA studies revealed that **5** is thermally stable up to approximately 327 °C under argon and has neither a T_g nor a T_m prior to its decomposition temperature. IR analysis of the pyrolysis product after heating **5** past its decomposition temperature did not reveal any bands in the 650–850-cm^{-1} region characteristic of PPP.[36] In addition, elemental analysis of the pyrolytic residue from **5** revealed a substantial amount of residual Si in the material. Although the poor leaving ability of the TMS ethers is essential for preventing monomer **4** from aromatizing under the polymerization conditions, it does however prevent the pyrolytic aromatization of polymer **5** to PPP. In order to overcome this obstacle, the TMS protecting groups on **5** were transformed to more facile leaving groups.

(H) Functional Group Transformations on Polymer 5. Only a handful of efficient functional group interconversion reactions on polymers have been documented.[37–39] However, two methods were found for completely transforming the TMS ethers of **5** to more facile leaving groups such as acetates. The first method involved treating **5** with acetyl chloride using $ZnCl_2$ as a catalyst (eq 6). The combination of an acid chloride and



5 6 (6)

$ZnCl_2$ has been used to provide almost quantitative conversion of TMS ethers to ester groups in one step in the case of small molecules.[40] When applied to polymer **5**, these reagents convert 96% of the TMS ethers to acetate groups. The remaining 4% of unreacted TMS ether groups are hydrolyzed to hydroxy groups upon workup. The fully acetylated polymer (**6**) is obtained by treating this material with acetic anhydride in pyridine containing a catalytic amount of DMAP. Complete acetylation is indicated by the disappearance of the proton signal at 3.9 ppm due to residual hydroxy groups in the ^1H NMR spectrum of the crude polymer. The overall yield of this two-step procedure is 73% recovery of 100% acetylated product.

The second procedure for transforming the TMS ether groups of **5** to acetate groups was inspired by the retreatment process employed in the first procedure. Instead of attempting to convert the TMS ethers to acetates in one step, **5** is first deprotected by tetra-*n*-butylammonium fluoride (TBAF) and methanol to give

(35) Ring-deuterated **4**-d_6 was synthesized from **1**-d_6, which is obtained from the microbial oxidation of benzene-d_6 by *Pseudomonas putida*. Samples of **1**-d_6, were donated by ICI Chemicals and Polymers Ltd., Runcorn, U.K.

(36) Assignments for the IR bands used to qualitatively gauge the molecular weight and regioregularity of PPP were obtained from the following: (a) ref 1a and (b) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; John Wiley and Sons: New York, 1972, p 189.

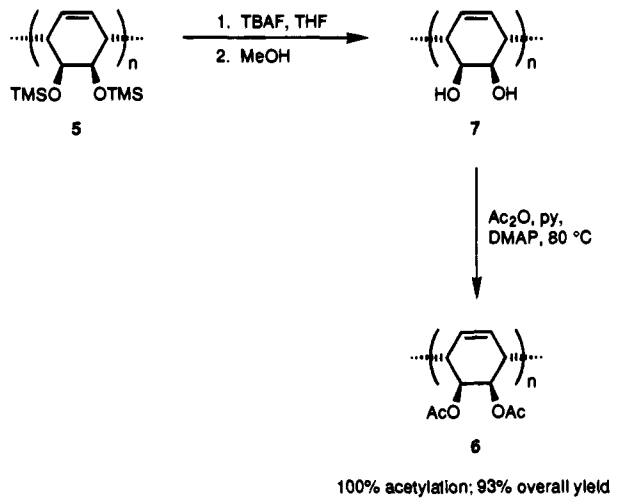
(37) Sogah, D. Y.; Webster, O. W. *Macromolecules* **1986**, *19*, 1775.

(38) Risse, W.; Grubbs, R. H. *Macromolecules* **1989**, *22*, 1558.

(39) Chung, T. C. *Chemtech* **1991**, *21* (8), 496 and references therein.

(40) Kim, S.; Lee, W. J. *Synth. Commun.* **1986**, *16* (6), 659.

Scheme 3



the corresponding hydroxy polymer **7**.[41] Polymer **7** is completely acetylated to polymer **6** by treatment with a mixture of pyridine, acetic anhydride, and catalytic DMAP at 80 °C (93% recovered overall yield over two steps) (Scheme 3).

Both procedures result in 100% conversion of the TMS ethers to acetate groups without detectably affecting any of the stereocenters on the polymer. The acetoxy polymer **6** is, in fact, a 1,4-linked, stereoregular analog to the radically polymerized precursor **3a**, originally used in the ICI process (Scheme 1). Unfortunately, the first procedure (eq 6) appears to be limited to acetyl substitution. The use of other acyl chlorides such as benzoyl chloride, for example, did not produce the corresponding benzoate polymer from **5**. The second procedure (Scheme 3) appears to be a much more general process for the synthesis of ester derivatives of **5**. Treatment of **7** with pyridine, catalytic DMAP, and the appropriate acid anhydride afforded the corresponding 1,4-linked benzoate, propionate, and hexanoate polymers.[42] Unfortunately, it was not possible to synthesize the stereoregular analog to the radically polymerized methoxycarbonyl polymer **3b** using methyl chloroformate or dimethyl pyrocarbonate by either of the above procedures.[43]

Characterization of Polymer 6: Confirmation of the cis-1,4-Stereoregular Structure. Polymer **6** was characterized by NMR spectroscopy, Viscotek GPC analysis, low-angle laser light scattering (LALLS) analysis, and PXRD analysis.[44] In contrast to polymer **5**, a highly 1,4-linked, stereoregular structure for polymer **6** could be directly confirmed by NMR analysis. Superficially, a comparison of the ^1H and ^{13}C NMR spectra of **6** with those of its radically polymerized counterpart **3a** suggests a stereoregular structure for polymer **6**. As can be seen in Figures 9 and 10, **6** exhibits ^1H and ^{13}C resonances with chemical shifts identical to those of its radically polymerized

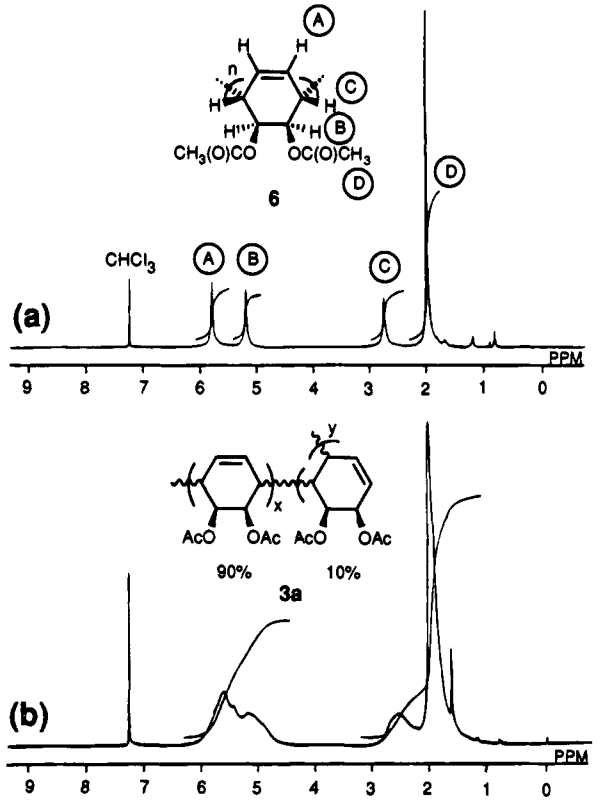


Figure 9. 400-MHz ^1H NMR spectra of (a) stereoregular acetoxy polymer **6** and (b) its radically polymerized analog **3a** in $CDCl_3$.

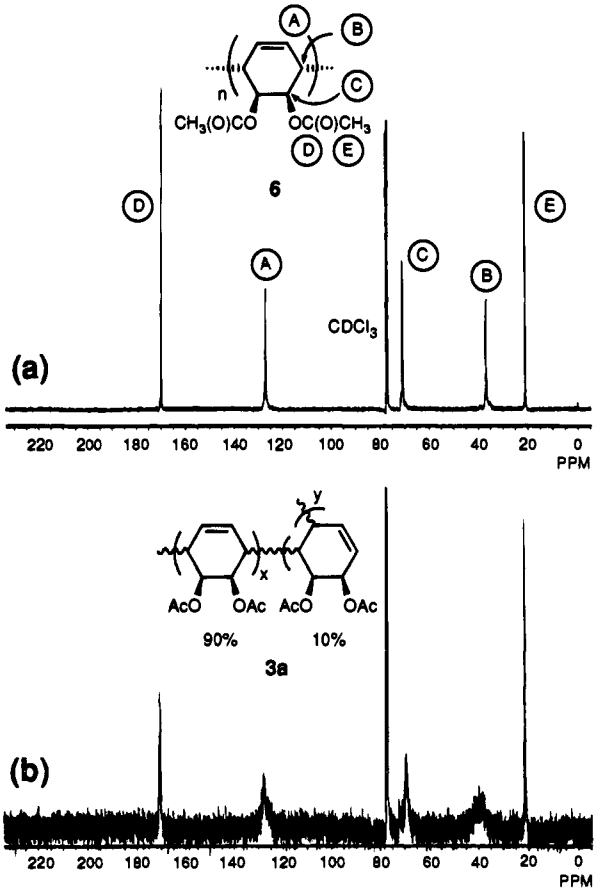


Figure 10. 100-MHz ^{13}C NMR spectra of (a) stereoregular acetoxy polymer **6** and (b) its radically polymerized analog **3a** in $CDCl_3$.

analog **3a**, which has 10% 1,2-linkages and random backbone stereochemistry. However, the individual resonances of **6** are much narrower and more symmetric, as would be expected for a stereoregular polymer. Unfortunately, the presence of any

(41) We have not attempted to convert the hydroxy polymer **7** back to **5** by treatment with TMSCl and base to determine whether the reaction is reversible.

(42) The propionate and hexanoate derivatives of **7** were synthesized by Curtis A. Hastings at the California Institute of Technology using variations of the acylation procedures described in the Experimental Section.

(43) (a) There was no reaction of $ZnCl_2$ and methyl chloroformate with **5** in diethyl ether. Only partially hydroxylated **5** was recovered due to acid-catalyzed protonation of some of the TMS ether groups during workup in MeOH. (b) When dimethyl pyrocarbonate was added to **7** suspended in a solution of pyridine and catalytic DMAP, the dimethyl pyrocarbonate reacted violently at room temperature with the liberation of a gas. Only and insoluble brown material was recovered from the reaction mixture. Possibly, the DMAP initiated a base-catalyzed decomposition of the dimethyl carbonate. Methyl chloroformate reacted similarly with pure pyridine when the mixture was heated above room temperature.

(44) DSC was also performed on **6**; however, the polymer did not exhibit a discernible T_g or T_m prior to its thermal decomposition at approximately 320 °C (ramp rate = 5 °C/min).

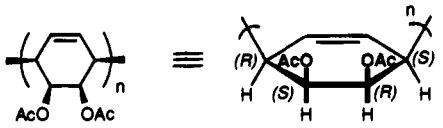


Figure 11. Two representations of the 1,4-*RSRS* repeat unit possible for polymer **6**.

1,2-units in **6** could not be detected by ^{1}H NMR analysis. The proton signal from the acetate methyl groups masks the 1.8–2.1-ppm region where protons from 1,2-linkages normally appear.[11] However, the ^{1}H NMR spectrum of the corresponding stereoregular benzoate polymer, which was similarly derived from polymer **5**, did not exhibit any proton resonances in the 1.8–2.1-ppm region (see the supplementary material). This observation is again consistent with polymer **5** and its derivatives (such as **6**) having essentially only 1,4-linkages.

With respect to the stereoregular structure of the polymer, both the sharpness and the number of unique signals in the ^{1}H and ^{13}C NMR spectra of **6** suggest two things about the polymer: (1) it has a highly tactic (i.e., stereoregular) structure with a plane of symmetry bisecting each repeat unit and (2) it is conformationally nonrigid. As can be seen from Figures 9a and 10a, polymer **6** exhibits four sharp ^{1}H NMR signals and five sharp ^{13}C NMR signals, thus indicating the presence of only four nonequivalent protons and five nonequivalent carbons in the polymer. This fact implies that there must be a plane of symmetry bisecting *each* repeat unit of the polymer, making both halves of the cyclohexene rings equivalent by NMR analysis along the entire polymer chain. As discussed for polymer **5**, both isotactic and syndiotactic 1,4-*SSRR* structures for **6** (Figure 3) would introduce a plane of symmetry through each repeat unit, provided that the polymer is conformationally flexible and the cyclohexene repeat units undergo rapid half-chair–half-chair interconversion.[45] This conformational flexibility and backbone symmetry would make the protons and carbons on both halves of each cyclohexene ring equivalent throughout the polymer and give rise to exactly four chemically nonequivalent protons and five chemically nonequivalent carbons by NMR spectroscopy, as is observed experimentally.

Although an isotactic or a syndiotactic structure consisting of 1,4-*RSRS* repeat units (Figure 11) would give the same number of observed NMR signals, it is highly unlikely that **6** consists of these repeat units, considering the π-facial selectivity afforded by the bulky TMS ethers of **4** during the synthesis of the parent polymer **5** (see section B). Polymer **6** also cannot be an atactic polymer (random backbone stereochemistry) containing the 1,4-*SSRR* repeat unit or a polymer containing substantial amounts of 1,2-units or trans (1,4-*SSRS* or 1,4-*RSRR*) repeat units if it exhibits the observed ^{1}H and ^{13}C NMR spectra. An atactic polymer would have very low symmetry. 1,2-Units and 1,4-trans (1,4-*SSRS* and 1,4-*RSRR*) repeat units do not possess a plane of symmetry (Figure 12). These latter structures would contain many more chemically nonequivalent protons and carbons than the 1,4-*SSRR* isotactic and syndiotactic cases. The ^{1}H and ^{13}C NMR spectra for polymers containing mixtures of these latter structures would tend be much broader and more asymmetric due to the large number of slightly different proton and carbon environments. This is indeed what is observed for **3a**, which is atactic and has a combination of all three possible repeat unit structures as a result of nonstereospecific radical polymerization (see Figures 9b and 10b). Consequently, **6** must have a highly isotactic or syndiotactic structure with the 1,4-*SSRR* repeat unit, as shown in Figure 3.

(45) In the absence of conformational flexibility, as assumed for the parent polymer **5**, the cyclohexene rings of the repeat units would assume a locked half-chair conformation that has neither a plane nor a center of symmetry. See Figure 5.

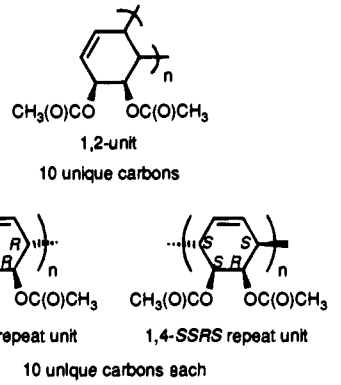


Figure 12. Repeat units that *do not* have the symmetry required to generate the ^{1}H and ^{13}C NMR spectra observed for polymer **6**.

Table 3. Comparison of Viscotek GPC and LALLS Molecular Weight Data for Polymers **6** and **3a**

	Viscotek GPC analysis			LALLS analysis
polymer	M_n	M_w	PDI	M_w
6	2.68×10^4	4.17×10^4	1.56	4.94×10^4
3a	3.57×10^4	9.32×10^4	2.61	1.10×10^5

In order to confirm that the sharpness and symmetry of the ^{1}H and ^{13}C NMR signals observed for **6** are the result of a stereoregular structure and not due to very low molecular weight material, the absolute molecular weight of the polymer was determined by Viscotek GPC[25] and LALLS analyses.[46] The results of these analyses are presented in Table 3 and compared to similar data obtained from radically polymerized **3a**. The molecular weight of **6** is approximately one-half to two-thirds that of **3a**. These molecular weights for **6** are in good agreement with the number average degree of polymerization obtained by Viscotek GPC for **5**, the polymer from which **6** is derived. Consequently, the differences observed between the ^{1}H and ^{13}C NMR spectra of **6** and **3a** cannot be attributed to very low molecular weight polymer **6**. Instead, they must be attributed to differences in polymer stereochemistry.

The conformationally flexible secondary structure inferred for **6** from the symmetry of its NMR spectra was also supported by PXRD and Viscotek GPC analysis. Whereas PXRD analysis of **5** suggested a rodlike structure and nematic-type order in the solid state (Figure 4), PXRD analysis of **6** revealed an absence of sharp reflections, thus suggesting that the polymer has an amorphous, flexible backbone. In fact, the PXRD profile of **6** is similar to that of its radically polymerized analog **3a**, which is reported to be completely amorphous and have a coiled chain structure in the solid state.[10b] Viscotek GPC analysis of **6** in THF indicated that the polymer has a relatively small Mark–Houwink coefficient a of 0.5–0.6, similar to that of its radically polymerized counterpart **3a**.[25] This relatively low a value is characteristic of weak polymer–solvent interactions and a coiled, compact polymer chain conformation in solution.[31] Computer molecular modeling[47] of the 1,4-*SSRR* isotactic and syndiotactic structures of **6** yielded helical chain conformations for the polymers. Unfortunately, more detailed dynamic

(46) LALLS analysis of **6** was performed by the Analytical and Physical Sciences Group at ICI Chemicals and Polymers Ltd., Runcorn, U.K.

(47) Molecular modeling of the 1,4-*SSRR* isotactic and syndiotactic structures possible for **6** was performed at a very simple level using Biograf Version 2.20 to build the structures and MM2 force-field parameters to minimize them. Typically, the structures were built up from a single minimized repeat unit by expanding successively to a dimer, tetramer, octamer, etc., minimizing at each step using MM2 or Dreiding force fields. The roughly minimized structures (usually 32-mers) were then finally minimized over 1000 iterations using MM2 parameters and BatchMin Version 3.1d.

molecular mechanics analysis must be performed before any information on the conformational flexibility of **6** can be inferred.

The fact that NMR, PXRD, and Viscotek GPC analyses are all consistent with a conformationally flexible, highly 1,4-linked stereoregular structure for **6** also confirms all of our initial assumptions on the 1,4-stereoregular structure and conformation of the parent polymer **5**. It was originally assumed that **5** is a stereoregular polymer with either a 1,4-*SSRR* isotactic or a 1,4-*SSRR* syndiotactic structure (Figure 3) and that its unusual ^{1}H NMR spectrum and physical properties are the result of a rodlike chain conformation in which the repeat units are conformationally locked (Figures 5 and 6). By simply changing the bulky TMS ethers on **5** to acetate groups, the resulting polymer **6** exhibits spectroscopic properties expected for a conformationally flexible, stereoregular polymer, even though the backbone stereochemistry of the two polymers is identical. This observation clearly indicates that the unusual ^{1}H NMR spectrum and physical properties of **5** are *not* the result of an unusual backbone tacticity but rather the result of conformational effects due to the bulky TMS ether side chains. The increase in conformational flexibility upon conversion of **5** to **6** is probably due to a reduction in steric interactions upon replacement of the bulky TMS protecting groups by less sterically demanding acetyl groups.

In summary, NMR, PXRD, and Viscotek GPC analyses are all consistent with **6** being a conformationally flexible, highly 1,4-linked stereoregular polymer with either the 1,4-*SSRR* isotactic or the 1,4-*SSRR* syndiotactic structure shown in Figure 3. Unfortunately, there is no simple spectroscopic method for directly determining which of the two tacticities the polymer actually has because of the similar symmetry elements in the two structures.[48] Fortunately, for the production of high-quality PPP, the tacticity of the precursor polymer is not as important as the 1,4-regiochemistry and the geometric relationships within each repeat unit. The linear structure of the polyphenylene depends entirely on the 1,4-regiochemistry of the precursor, whereas the ease of the acid elimination should depend on just the stereochemical (cis) relationship between the pendant ester group and the adjacent bridgehead proton within *each* repeat unit (see eq 1). Both the 1,4-*SSRR* isotactic and the 1,4-*SSRR* syndiotactic structures inferred for polymer **6** meet these two criteria for the formation of high-quality PPP.

Conclusions

1,4-Linked, stereoregular precursor polymers to poly(*p*-phenylene) (PPP) are possible via the transition-metal-catalyzed polymerization of derivatives of the microbially synthesized monomer *cis*-5,6-dihydroxy-1,3-cyclohexadiene (Scheme 2). By masking the hydroxy groups on the monomer as trimethylsilyl ethers, *cis*-5,6-bis(trimethylsiloxy)-1,3-cyclohexadiene (**4**) can be polymerized exclusively in a cis-1,4-fashion by bis[(η^3-allyl)-(trifluoroacetato)nickel(II)] with yields up to 96%. This polymerization system not only affords a highly 1,4-linked, stereoregular polymer but also permits a degree of molecular weight control. The resulting stereoregular polymer **5** is a soluble, processable, partially crystalline material which unfortunately does not yield PPP directly upon pyrolysis. Polymer **5** can be subsequently transformed to the corresponding stereoregular acetoxy polymer **6**, which has more facile leaving groups for better conversion to PPP (100% acetylation; up to 93% overall yields). NMR analysis of **6** is consistent with the polymer having either a highly isotactic or a highly syndiotactic 1,4-linked structure with the symmetric repeat unit depicted.

(48) Polymer **6** cannot be a mixture of isotactic and syndiotactic chains because the two tactic structures would have slightly different ^{1}H and ^{13}C chemical shifts in their NMR spectra. A mixture of these two stereoregular structures would generate a ^{13}C NMR spectrum in which the number of ^{13}C resonances would be doubled. Figure 10a clearly shows only five sharp, single-line ^{13}C resonances, indicating polymer **6** exists in only one stereoregular form.

Experimental Section

General Considerations. All manipulations of air- and/or water-sensitive compounds were performed using standard high-vacuum or Schlenk line techniques. Argon was purified by passage through columns of BASF RS-11 catalyst (Chemlog) and 4 Å molecular sieves (Linde). Solids were transferred and stored in a nitrogen-filled Vacuum Atmospheres drybox. All distillations were performed under argon flush. All solvents and liquid reagents were degassed by repeated freeze–pump–thaw cycles and stored under argon in flasks fitted with PTFE valves. Solid reagents and monomers were degassed in vacuo and stored in the drybox prior to use. Solution polymerizations were all performed in 50-mL capacity, thick-walled glass Schlenk tubes fitted with 8-mm-diameter PTFE valves.

Materials and Reagents. All solvents were purchased from the Aldrich Chemical Co., EM Science, or Fisher Scientific. *n*-Pentane, toluene, benzene, diethyl ether, THF, and DME were vacuum-transferred from sodium/benzophenone. *n*-Pentane and *n*-dodecane were made olefin-free prior to vacuum transfer by successively stirring over concentrated H_2SO_4 and washing with deionized water until the acid layer became colorless. *n*-Dodecane was vacuum-distilled prior to use. Methylene chloride was vacuum-transferred from calcium hydride. Chlorobenzene, and *o*-dichlorobenzene were distilled from calcium hydride. Ethyl acetate was purified by distillation. Anhydrous methanol was obtained by distilling over Mg powder. Methanol and hexanes for polymer precipitations were used without further purification.

1,3-Cyclohexadiene, chlorotrimethylsilane, acetyl chloride, acetic anhydride, tetra-*n*-butylammonium fluoride (TBAF) hydrate, 2,6-di-*tert*-butyl-4-methylphenol (BHT), 4-(dimethylamino)pyridine (DMAP), and $ZnCl_2$ were all purchased from the Aldrich Chemical Co. 1,3-Cyclohexadiene was distilled from sodium borohydride or calcium hydride prior to use. Chlorotrimethylsilane was purified by distillation from magnesium filings. Acetyl chloride was simply distilled prior to use whereas acetic anhydride was distilled from anhydrous sodium sulfate. TBAF hydrate (98%), BHT (99+%), DMAP (99%), and $ZnCl_2$ (99.999%) were all used without further purification. Benzoic anhydride (97%) was purchased from the Sigma Chemical Co. and degassed in vacuo prior to use. Pyridine was purchased from Baker Chemicals and purified by distillation from calcium hydride. Allyl trifluoroacetate was prepared according to a literature synthesis by refluxing distilled allyl alcohol with trifluoroacetic acid (Aldrich) in a reverse Dean–Stark apparatus.[19a] Bis(1,5-cyclooctadienyl)nickel(0) [Ni(COD)$_2$] was obtained from the Strem Chemical Co. and recrystallized from toluene prior to use. *cis*-5,6-Dihydroxy-1,3-cyclohexadiene (**1**), its acetyl (**2a**) and methoxycarbonyl (**2b**) derivatives, and the corresponding radically polymerized polymers (**3a**,**b**) were all donated by ICI Chemicals and Polymers Ltd., Runcorn, U.K. Compound **1** was obtained as a 50 wt % solution in pyridine. It was purified by removing the pyridine in vacuo, precipitating the crude material in pentane, and recrystallizing from 30 °C ethyl acetate using charcoal as a decolorizer. The acetyl and methoxycarbonyl derivatives **2a**,**b** required no further purification. Monomers **1** and **2a**,**b** were stored as solids under anhydrous, sub-zero conditions and degassed in vacuo prior to use. The radically polymerized precursor polymers **3a**,**b** also required no further purification prior to use. Basic alumina was purchased from the Fluka Chemical Co. and dried under dynamic vacuum at 130 °C for 24 h prior to use. Millex-SR Luer-Lok syringe filter units for nonaqueous solutions were purchased from the Waters-Millipore Co. Glass microfiber paper for cannula filtration was purchased from Whatman and oven-dried prior to use.

Instrumentation. NMR spectra were recorded using a JEOL GX-400 (399.65-MHz ^{1}H, 100.40-MHz ^{13}C) spectrometer. Infrared spectra were recorded using a Perkin-Elmer 1600 series FT-IR spectrometer. Gas chromatography was performed using a Hewlett-Packard HP 5890 Series II gas chromatograph equipped with 30-m-long SE-30 (OV-1) capillary column and an HP 3396 Series II integrator. General gel permeation chromatograms were obtained on a home-built system

consisting of two American Polymer Standards columns, a Waters Ultrastyragel column, an Altex Model 110A pump, and a Knauer differential refractometer using HPLC grade methylene chloride (Burdick and Jackson brand) as the eluant at a flow rate of 1.0 mL/min at room temperature. Viscotek gel permeation chromatograms were obtained on a system consisting of a set of three Polymer Labs mixed B columns (300 mm, 5 μm) and a Viscotek differential refractometer/viscometer detector using THF as the eluant at a flow rate of 1 mL/min at 35 °C. Low-angle laser light scattering (LALLS) analysis was performed on a Chromatrix KMX-6 light-scattering apparatus using THF as the solvent. Powder X-ray diffraction profiles were obtained on a Scintag/USA PAD V powder X-ray diffractometer using Ni filtered, Cu Kα radiation. Differential scanning calorimetry and thermogravimetric analysis were performed on Perkin-Elmer PC Series DSC7 and TGA7, respectively. Molecular modeling calculations were performed on a Silicon Graphics Iris 4D/220GTX computer employing Biograf Version 2.20 and BatchMin Version 3.1d programs. Space-filling (CPK) images of the modeled structures were displayed using the MacroModel program. Elemental analysis was performed at Oneida Research Services Inc., Whitesboro, NY, and Galbraith Laboratories Inc., Knoxville, TN.

Preparation of Bis[(η^3-allyl)(trifluoroacetato)nickel(II)] [(ANiTFA)$_2$]. In the drybox, recrystallized bis(1,5-cyclooctadienyl)nickel-(0) [Ni(COD)$_2$] (5.00 g, 18.2 mmol) was ground to a fine powder using a mortar and pestle and loaded into a 250-mL Schlenk flask containing a stirbar. The canary yellow powder was suspended in 100 mL of rapidly stirred diethyl ether and then added to a 250-mL Schlenk flask containing allyl trifluoroacetate (5.60 g, 35.4 mmol) at 0 °C in 10-mL aliquots via a wide-bore cannula over a period of 10 min. The mixture was stirred in the absence of light at 0 °C for 90 min or until all of the yellow Ni(COD)$_2$ was consumed. The resulting clear dark red solution was then quickly filtered into another Schlenk flask using a cannula fitted with a plug of glass micrifiber at one end (cannula filtration). Three-quarters of the solvent was removed in vacuo with the mixture maintained below room temperature in order to induce precipitation of the (ANiTFA)$_2$. An equal volume of −78 °C olefin-free pentane was then added to precipitate the remainder of the catalyst as a red-brown powder. The product was washed with 2 × 10-mL aliquots of −78 °C olefin-free pentane and dried in vacuo overnight at ambient temperature. Yield: 3.43 g (89%) of ANiTFA)$_2$. ^{1}H NMR (400 MHz, C_6D_6): δ 4.80−5.30 (1H), 2.45 (2H), 1.60−1.90 (2H). (It is important to perform this synthesis as quickly as possible in one session to minimize the amount of time the product remains in solution.)

A Typical Polymerization of 1,3-Cyclohexadiene Using (ANiTFA)$_2$. In the drybox, (ANiTFA)$_2$ (0.010 g, 0.024 mmol) was dissolved in 2.3 mL of solvent (e.g., benzene, chlorobenzene, or *o*-dichlorobenzene) to give a clear orange solution. After transferring the catalyst solution to a Schlenk tube containing a stirbar, 1,3-cyclohexadiene (1.1 mL, 0.89 g, 0.011 mol) that had been previously filtered through a short plug of basic alumina, was then added to the orange catalyst solution via syringe. After approximately 5 min, the initially clear orange reaction mixture became turbid due to initial polymer formation at room temperature. The reaction vessel was then sealed and placed under an atmosphere of argon after repeated freeze−pump−thaw cycles. The turbid orange reaction mixture was placed in a 50−51 °C oil bath and rapidly stirred for 24 h. During the course of the reaction, the polymerization mixture became progressively more difficult to stir due to the rapid buildup of insoluble polymer. At the end of the reaction, the crude polymer was suspended in methanol (25 mL) containing 0.1% BHT and isolated by suction filtration. The resulting light orange powder was subsequently resuspended in benzene (50 mL) and reisolated from methanol as before. After drying overnight in vacuo, the polymer was obtained as an off-white, insoluble powder. Yield: 0.79 g (88%) of polycyclohexadiene. PXRD: 5.292, 4.517, 3.907 Å. Anal. Calcd for $(C_6H_8)_n$: C, 90.00; H, 10.00. Found: C, 85.34; H, 9.49.

Preparation of *cis*-5,6-Bis(trimethylsiloxy)-1,4-cyclohexadiene (4). *cis*-5,6-Dihydroxy-1,3-cyclohexadiene (**1**) (20.00 g, 0.178 mol) and a catalytic amount of DMAP were dissolved in a mixture of methylene chloride (650 mL) and pyridine (43.2 mL, 0.536 mol) in a 2-L round-bottom flask containing a stirbar. With the pale yellow solution rapidly stirring under argon and the temperature moderated with a cool water bath, chlorotrimethylsilane (50.0 mL, 0.393 mol) was added dropwise via a pressure-equalizing addition funnel. After stirring for 1.5 h, olefin-free pentane (200 mL) was cannulated into the cloudy white suspension to precipitate the pyridinium hydrochloride, which was subsequently removed by filtration under argon. The solvent was removed from the filtrate in vacuo at room temperature to yield a pale yellow oil. High-vacuum distillation of the oil using a short-path distillation apparatus, an 80 °C oil bath, and a liquid nitrogen cooled collection flask yielded **4** as a viscous, colorless, clear liquid (bp: ca. 47 °C at ca. 10 μm Hg of pressure). The final product was stored in the drybox freezer. Yield: 41.6 g (91%) of monomer **4**. ^{1}H NMR (400 MHz, C_6D_6): δ 5.73−5.88 (4H), 4.12 (2H), 0.14 (18H). IR (neat): 3042, 2954, 2795, 1412, 1373, 1325, 1251, 1176, 1119, 1051, 986, 925, 888, 841, 764, 696, 643, 578 cm^{-1}.

A Typical Polymerization of *cis*-5,6-Bis(trimethylsiloxy)-1,4-cyclohexadiene (4) Using (ANiTFA)$_2$. In the drybox, (ANiTFA)$_2$ (0.140 g, 0.329 mmol) was dissolved in chlorobenzene (10.2 mL) to give a dark orange-red solution. This solution was filtered through a 0.5-μm-porosity, Millex-SR, nonaqueous filter unit into a Schlenk tube via a gas-tight syringe. To this catalyst solution were added a stirbar and monomer **4** (6.75 g, 26.3 mmol) that had been passed through an equal volume of dry, basic alumina to remove trace impurities. The clear orange reaction mixture (monomer-to-catalyst mole ratio = 80:1, monomer concentration = 1.5 M) was then degassed via repeated freeze−pump−thaw cycles and sealed under an atmosphere of argon. The reaction mixture was placed in a 50−51 °C oil bath and rapidly stirred for 48 h. The initial clear orange solution became deep red-brown after a period of 5 min. After approximately 30 min, the reaction mixture became opaque and coffee-colored. After 48 h, a dark brown gel was usually obtained. The polymer was dissolved in an equal volume of hexanes or THF and precipitated into rapidly stirred methanol (800 mL) containing 0.1% BHT. The resulting off-white powder was isolated by suction filtration, washed with fresh methanol, and dried in vacuo overnight. Yield: 6.25 g (93%) of polymer **5**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.1−6.2 (2H), 3.3−4.1 (2H), 2.7−3.2 (1H), 2.1−2.6 (1H), −0.4−0.5 (18H). IR (KBr mull): 2957, 2898, 1251, 1111, 1087, 1046, 837, 748 cm^{-1}. PXRD: 9.725 Å and an amorphous halo centered at 5.5 Å. Anal. Calcd for $(C_{12}H_{24}O_2Si_2)_n$: C, 56.19; H, 9.43; Si, 21.90. Found: C, 55.91; H, 9.34; Si, 22.21.

A Typical Experiment for Determining the M_n vs Percent Conversion Relationship of the (ANiTFA)$_2$/Monomer 4 Polymerization System. A typical M_n vs percent conversion plot for the (ANiTFA)$_2$/**4** polymerization system was obtained by withdrawing samples from an active polymerization reaction at various times, determining the amount of unreacted monomer at each point by quantitative GC analysis, and measuring the molecular weight of the polymer isolated from each sample by GPC. For example, for a polymerization system in toluene with a [**4**] of 2.0 M and a monomer-to-catalyst mole ratio of 75:1, (ANiTFA)$_2$ (0.110 g, 0.259 mmol), monomer **4** (5.00 g, 19.4 mmol, 5.43 mL), toluene (3.44 mL), and *n*-$C_{12}H_{26}$ (0.664 g, 3.90 mmol) were combined in a 50-mL Schlenk tube according to the aforementioned polymerization procedure. After placing the reaction mixture in a 50−51 °C oil bath, aliquots of the reaction mixture (containing varying proportions of polymer and unreacted monomer) were withdrawn at various times under argon flush. Each aliquot was then injected into 10 mL of methanol containing 0.1 wt % BHT to precipitate the polymer. After mixing the resulting suspension well and then allowing the polymer to settle, 5−10 μL of the green supernatant was transferred to a 1.00-mL volumetric flask and diluted with methanol. The amount of unreacted monomer in the supernatant of each aliquot was then determined by quantitative GC analysis using a 1.0-μL injection volume, an injector temperature of 160 °C, a detector temperature of 250 °C, an initial temperature of 80 °C, an initial time of 2 min, a ramp rate of 10 °C/min, a final temperature of 200 °C, and a final time of 4 min. The amount of unreacted **4** was calculated by comparing the area of its GC trace with that of the added internal standard, *n*-$C_{12}H_{26}$, after applying an appropriate response correction factor. (The relative GC response factor between the monomer and the internal standard was determined by averaging the ratio of the integral of the monomer to that of the standard for a series of standard solutions.) The precipitated polymer **5** from each sample aliquot was individually purified and isolated by centrifuging the crude material, washing it with fresh methanol, redissolving it in THF (1 mL), and finally precipitating it into methanol. The M_n of

each sample of **5** was determined by Viscotek GPC analysis at ICI, Runcorn, U.K.

Preparation of the Stereoregular Acetoxy Polymer 6: Method 1. A 500-mL capacity Schlenk flask was charged with polymer **5** (2.41 g), anhydrous zinc chloride (2.69 g, 19.7 mmol), and a stirbar in the drybox. On the Schlenk line, diethyl ether (250 mL) was cannulated into the reaction vessel under argon flush. The mixture was rapidly stirred at ambient temperature for 1 h to completely dissolve the zinc chloride. Neat acetyl chloride (5.62 mL, 79.0 mmol) was then syringed into the colorless clear solution. The mixture was stirred at room temperature for 18 h, during which time a pale yellow, gelatinous solid formed. The reaction mixture subsequently was decanted into methanol (1600 mL) to precipitate the polymer as a white powder. The polymer was isolated by suction filtration, washed with fresh methanol, and dried in vacuo overnight at ambient temperature. Yield: 1.43 g (78%) of crude acetoxy polymer **6**.

This crude polymer **6** typically has a small percentage (4%) of hydroxy groups as indicated by a signal at 3.9 ppm in its ^{1}H NMR spectrum. These residual hydroxy groups were acetylated by treating the crude polymer with pyridine and acetic anhydride according to the following procedure: A 50-mL Schlenk tube was charged with a stirbar, the crude acetoxy polymer **6** (1.13 g), and a catalytic amount of DMAP. The solids were degassed in vacuo, placed under an argon atmosphere, and dissolved in methylene chloride (10 mL). To this clear pale yellow solution were added pyridine (1.72 mL, 21.2 mmol) and acetic anhydride (1.72 mL, 18.2 mmol) as neat liquids by syringe under argon flush. The sealed reaction mixture was then stirred at 40 °C for 13 h. After the mixture was cooled to ambient temperature, the volatiles were removed in vacuo. The remaining light orange, glassy solid was dissolved in methylene chloride (50 mL) and washed sequentially with saturated aqueous $NaHCO_3$ (2 × 50 mL), saturated aqueous NaCl (2 × 50 mL), and deionized water (50 mL). The organic phase was dried over anhydrous Na_2SO_4, concentrated down to approximately 10 mL, and added dropwise to stirred hexanes (100 mL) containing 0.1% BHT to precipitate the polymer. The white precipitate was isolated by suction filtration, washed with more hexanes, and dried in vacuo overnight at ambient temperature. Yield: 1.02 g (90%, based on the crude material) of fully acetylated polymer **6**. The resulting polymer **6** has the same ^{1}H NMR spectrum as the material made via acetylation of polymer **7**: no hydroxy proton signal at 3.9 ppm is present after retreatment of the crude polymer.

Method 2. (a) Preparation of the Stereoregular Hydroxy Polymer 7 from Polymer 5. A 1-L Schlenk flask was charged with a stirbar and TBAF monohydrate (34.7 g, 0.133 mol). The TBAF monohydrate was dried in vacuo at room temperature for 2.5 h, placed under an argon atmosphere, and then dissolved in THF (250 mL). A filtered solution of dry, degassed **5** (5.00 g in 80 mL of dry THF) was added dropwise over 30 min to the rapidly stirred solution of TBAF monohydrate. A thick yellow gum immediately precipitated from the reaction mixture. After rapidly stirring for 6.5 h at room temperature, anhydrous methanol (100 mL) was then syringed into the reaction mixture. The resulting cloudy suspension was stirred for a further 36 h under argon before the off-white solid was isolated by suction filtration. After washing with methanol (2 × 10 mL) and then hexanes (2 × 10 mL), the precipitate was dried in vacuo for 48 h to afford quantitative yields of polymer **7** as an amorphous off-white polymer which is insoluble in common solvents. Consequently, it has not been well characterized spectroscopically. Polymer **7** is extremely hygroscopic and should be stored in a dessicator. PXRD: amorphous (no sharp reflections). Anal. Calcd for $(C_6H_8O_2)_n$: C, 64.27; H, 7.19. Found: C, 62.20; H, 7.84; N, 0.55; Si, below detection limit (100 ppm).

(b) Acetylation of Polymer 7. A 50-mL capacity, thick-walled glass Schlenk tube was charged with a stirbar, finely powdered polymer **7** (0.553 g), and a catalytic amount of DMAP. The solids were degassed in vacuo, placed under an argon atmosphere, and then suspended in dry pyridine (6.0 mL, 74 mmol). Acetic anhydride (2.6 mL, 28 mmol) was added by syringe, and the slurry was stirred at 80 °C for 1.5 h or until the reaction mixture cleared. The resulting clear yellow-orange mixture was then cooled to ambient temperature, and the volatiles were removed in vacuo. The remaining yellow glassy solid was dissolved in methylene chloride (50 mL) and washed sequentially with saturated aqueous $NaHCO_3$ (25 mL) and saturated NaCl (25 mL) solutions. The organic phase was dried over anhydrous Na_2SO_4, concentrated down to approximately 5 mL, and then added dropwise to stirred hexanes (150 mL) containing 0.1% BHT to precipitate the polymer. The pale yellow precipitate was isolated by suction filtration, washed with more hexanes, and dried in vacuo overnight. Yield: 0.968 g of completely acetylated polymer **6** (93% over two steps, based on starting polymer **5**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.6−6.0 (2H), 5.0−5.4 (2H), 2.5−2.9 (2H), 1.8−2.2 (6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169 (C=O), 127 (C=C), 71 (C−OR), 36 (C−C=C), 21 (CH_3). Anal. Calcd for $(C_{10}H_{12}O_4)_n$: C, 61.22; H, 6.16. Found: C, 60.45; H, 6.14; Ni, <0.0041. IR (film cast on NaCl): 1747, 1431, 1371, 1232, 1165, 1055, 1024, 923, 765 cm^{-1}. PXRD: amorphous (two amorphous halos centered at 10.4 and 18.9 Å.)

Preparation of the Stereoregular Benzoate Derivative of Polymer 5. A 50-mL Schlenk tube was charged with a stirbar, finely powdered polymer **7** (0.103 g), and a catalytic amount of DMAP. The solids were degassed in vacuo, placed under an argon atmosphere, and suspended in pyridine (5.0 mL, 60 mmol) to give a light gray slurry. Degassed benzoic anhydride (2.09 g, 9.20 mmol) was then added to the reaction vessel under argon flush. The flask was sealed, and the reaction mixture was stirred at 80 °C for 18 h. During that time, the suspended polymer in the initial slurry dissolved, affording a clear pale yellow solution. The mixture was then cooled to ambient temperature, and the volatiles were removed in vacuo to yield a glassy solid residue. The crude polymer was worked up and isolated by the same procedure used for **6**. Yield: 97% of the benzoate derivative of polymer **5**. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.2−7.9 (10H), 6.3 (2H), 5.6 (2H), 3.2 (2H). PXRD: amorphous (no sharp reflections).

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Supplementary Material Available: Figures showing 400-MHz ^{1}H NMR spectra of $(ANiTFA)_2$ and compound **4**; FT-IR spectra of compounds **3a**, **4**, **5**, and **6**; a photograph of a CPK space-filling model of monomer **4** showing the steric shielding of the oxygens atoms and the π-facial selectivity afforded by the bulky TMS protecting groups; tabulated Viscotek GPC data for polymers **3a**, **5**, and **6**; LALLS plots and tabulated molecular weight data for **3a** and **6**; PXRD profiles of polymers **3a** and **6**; comparative Viscotek GPC plots of the two homopolymers made from $(ANiTFA)_2$-catalyzed polymerization of ring-deuterated **4**-d_6 and regular **4** under identical reaction conditions; and a 400-MHz ^{1}H NMR spectrum of the benzoate derivative of polymer **5** (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.