

Living Polymerization of Butadiene at Both Chain Ends via a Bimetallic Nickel Initiator. Preparation of Hydroxytelechelic Poly(butadiene) and Symmetric Poly(isocyanide-*b*-butadiene-*b*-isocyanide) Elastomeric Triblock Copolymers

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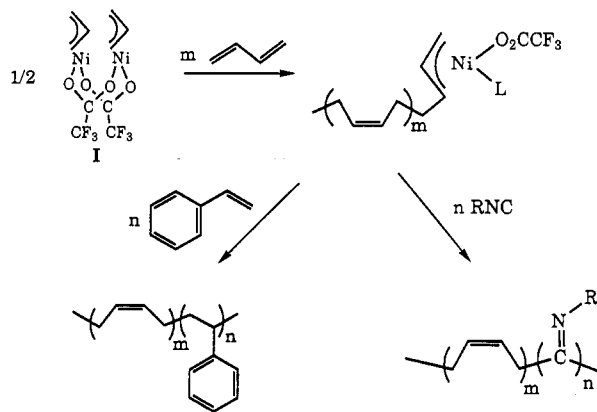
Abstract: A bifunctional nickel initiator, bis(μ -trifluoroacetato)(η^3 : η^3 -2,2'-biallyl)dinickel(II), IV, was synthesized to promote the living polymerization of butadiene to high *cis*-1,4-content polymer with both chain ends active. Other potential initiators, [1,4-phenylenebis((η^3 -1-allyl)nickel trifluoroacetate)]_n, II, and [1,4-cyclohexanediylbis((η^3 -1-allyl)nickel trifluoroacetate)]_n, III, were found to be completely ineffective due to intermolecular carboxylate bridges which gave the complexes polymeric structures. The intramolecular bridges in IV and its molecular weight were confirmed by X-ray crystallography. IV cocrystallizes in space group *P*1̄ with 0.5 equiv of 2,3-bis((trifluoroacetoxy)methyl)-1,3-butadiene in the unit cell with constants of $a = 9.5600(8)$ Å, $b = 9.6554(9)$ Å, $c = 11.7615(10)$ Å; $\alpha = 73.711(7)^\circ$, $\beta = 73.537(7)^\circ$, $\gamma = 71.938(7)^\circ$; $V = 967.50(15)$ Å³; and $Z = 2$. Refinement of the model, which contained a disordered C₆H₈ unit, led to convergence with $R_F = 5.8\%$, $R_wF = 6.9\%$, and GOF = 2.21 for 276 variables refined against those 2852 data with $|F_o| > 3.0\sigma(|F_o|)$. The living polybutadiene samples were successfully used to prepare triblock copolymers of the structure poly(1-phenylethyl isocyanide-*b*-butadiene-*b*-1-phenylethyl isocyanide), which have been characterized using gel permeation chromatography, differential scanning calorimetry, ¹³C NMR, elemental analysis, and transmission electron microscopy. The bifunctional living polybutadiene was also successfully end-capped with *p*-(trifluoromethyl)-benzaldehyde to afford a telechelic polymer with hydroxy functionalities at both chain ends.

Introduction

Bifunctional polymers, polymers with functionality at both ends of the polymer chains, are very desirable materials. If the end groups are simple functional groups (i.e. carboxylic acids, alcohols, etc.), then these polymers can serve as "macromers", high molecular weight building blocks.¹ If the functionality is present as a polymer chain with a different repeat unit, then triblock copolymers are formed. Triblock copolymers have physical properties unique to their class of materials, many behaving as thermoplastic elastomers.² Furthermore, if homopolymers with vastly different properties are combined to create block copolymers, materials which retain the dissimilar properties of their components can be produced which possess valuable properties (i.e. hydrophilic and hydrophobic blocks can be combined to produce a semipermeable membrane).² We propose a facile synthetic method for preparing polybutadiene, living at both chain ends, as well as triblock polymers and bifunctional polymers using a new, unprecedented bimetallic nickel initiator.

[(η^3 -Allyl)Ni(trifluoroacetate)]₂, I, has been documented to initiate the living polymerization of butadiene to yield, under various conditions, either the *trans*- or the *cis*-1,4-addition

Scheme 1. Preparation of Diblock Copolymers Using I



polymer.³ Since this polymerization is living, the polymer chain end remains active, and it has been shown that diblock copolymers can be prepared by addition of a suitable comonomer after polymerization of the butadiene (Scheme 1). Diblock copolymers of butadiene with styrene⁴ and 1-phenylethyl isocyanide⁵ have been reported. One advantage of the system utilizing I over anionic techniques for preparing a styrene-butadiene diblock copolymer is that the nickel initiator gives far superior control over the polybutadiene microstructure (1,2- versus 1,4-addition) than is observed under anionic conditions.⁴ Isocyanides cannot be polymerized anionically, and so the isocyanide-butadiene diblock polymer can only be prepared through nickel catalysis.⁵

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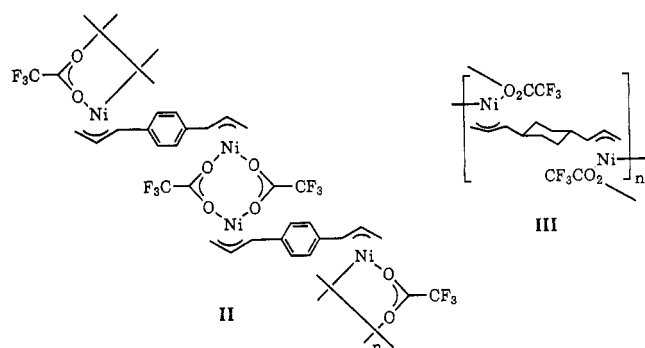
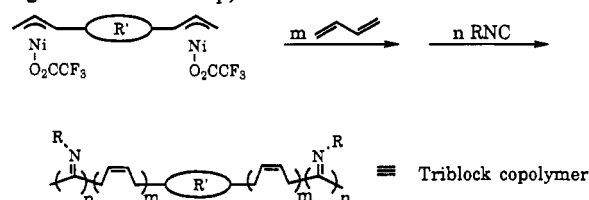
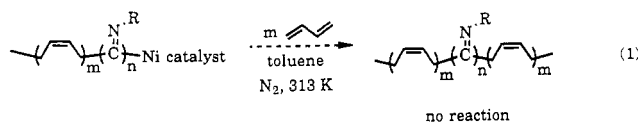


Figure 1. Polymeric complexes II and III.

Scheme 2. Preparation of Triblock Copolymers Using Linked η^3 -Allylnickel Trifluoroacetate Units (R' Is an Organic Linker Group)



Prompted by our success in preparing isocyanide-butadiene diblock polymers, we desired a means to prepare the isocyanide-butadiene-isocyanide triblock polymers, which would possess the hard-soft-hard chain architecture found in thermoplastic elastomers. The straightforward, "linear", approach toward preparation of these polymers, namely, consecutive addition of isocyanide, butadiene, and isocyanide to I (eq 1), was ruled out

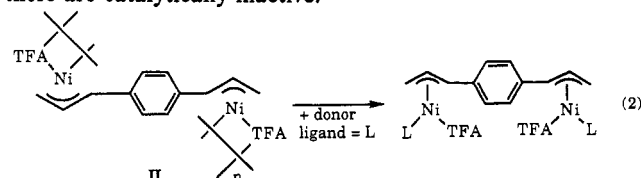


due to the "change of mechanism" nature of the polymerization system. Once I is reacted with isocyanide, it is no longer an active polymerization initiator for butadiene, and so butadiene must always be polymerized before isocyanide.⁵ Our solution to this problem was a bifunctional initiator where the allyl groups in two allylnickel trifluoroacetate units were joined covalently by some organic linker which would then form the center of the polymer chain (Scheme 2). Thus, by linking the two chain ends together, we would ultimately obtain a polymer with both chain ends connected to active initiator centers. Addition of a second monomer (e.g. isocyanide) then affords the triblock polymer in a fashion analogous to preparation of the diblock copolymers.

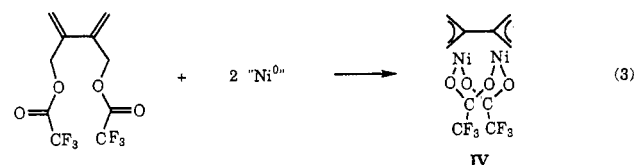
Results and Discussion

Living Bifunctional Polymerization of Butadiene. The first linker groups we had designed for the bifunctional initiator were 1,4-phenylene and 1,4-cyclohexanedyl, where the nickel complexes (II and III, respectively) are as shown in Figure 1. II was found to be very thermally unstable, and both were found to be completely insoluble in all nondonor solvents (alkanes, arenes, and halocarbons as well as in diene monomer). The insolubility of these complexes resulted in their being completely inactive as diene polymerization initiators. Furthermore, any donor solvent or ligand used to solubilize the complexes (THF, pyridine, dioxane, acetonitrile, DMSO, DMF, phosphines, phosphites, and ketones) effectively acted as potent initiator poisons. We believe that intermolecular carboxylate bridges (see Figure 1) were responsible for the insolubility of complexes II and III. Although complex I is dimeric due to these bridges,⁶ linkage of the allyl groups in II and III in conjunction with intermolecular bridges give rise

to polymeric complexes. Donor groups can break the carboxylate bridges and yield molecular complexes (eq 2), yet, as stated, these are catalytically inactive.

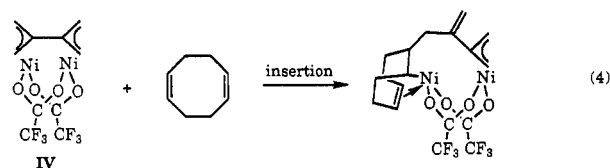


In effort to develop an initiator with linked η^3 -allyl groups which remains soluble in nondonor solvents, we searched the literature for any complexes filling these criteria. A seemingly ideal candidate model complex was bis(μ -trifluoroacetato)(η^3 : η^3 -2,2'-biallyl)dipalladium(II) (Scheme 3), which has η^3 -allyl groups linked in very close proximity so that intramolecular carboxylate bridges are formed.⁷ Consequently, the complex was reported to be monomeric and soluble in a nondonor solvent (chloroform). Unfortunately, the synthesis of the palladium complex is not applicable for preparation of the nickel analog. η^3 -Allyl nickel complexes are far less stable than those of palladium and would not survive the protic conditions in the synthesis. In order to prepare our desired complex, bis(μ -trifluoroacetato)-(η^3 : η^3 -2,2'-biallyl)dinickel(II), IV, we envisioned synthesis from 2,3-bis((trifluoroacetoxy)methyl)-1,3-butadiene and a source of nickel(0) (e.g. Ni(COD)₂, COD = 1,5-cyclooctadiene, or Ni(CO)₄) (eq 3). This oxidative addition route is analogous to the



synthesis of I, which is very general and usually proceeds in high yield.⁶

Preparation of 2,3-bis((trifluoroacetoxy)methyl)-1,3-butadiene was planned from 2,3-bis(hydroxymethyl)-1,3-butadiene, a known compound.⁸ Following the literature methodology, 2,3-bis((trifluoroacetoxy)methyl)-1,3-butadiene was successfully prepared in six steps from diethyl malonate, yet only in an unsatisfactory overall 0.5% yield. Consequently, we designed a three-step synthesis which gave the target ligand in gram quantities in an overall 21% yield starting from allene (Scheme 4).⁹ Double oxidative addition of the ligand to 2 equiv of Ni(COD)₂ was found to almost exclusively produce not IV but a compound in which IV had inserted 1 equiv of COD into an allyl group (eq 4). We had observed similar decomposition reactivity in prep-



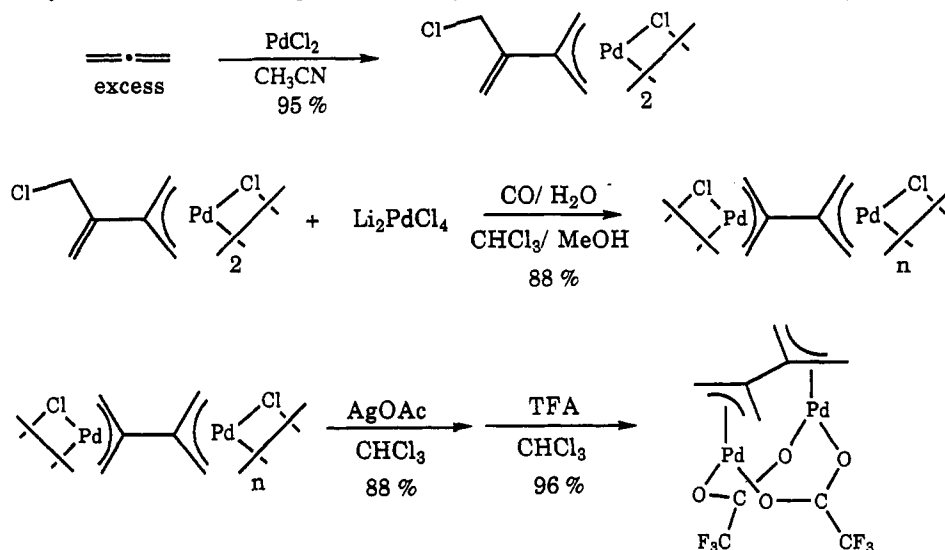
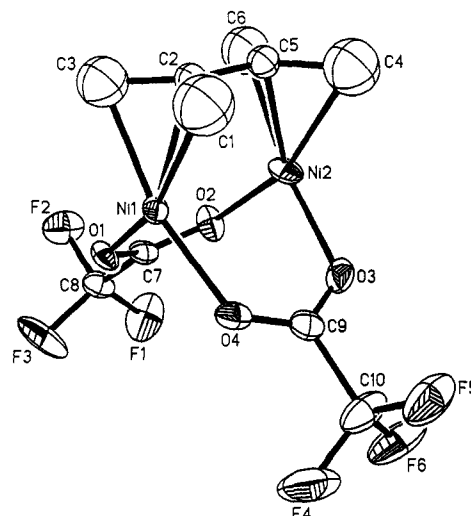
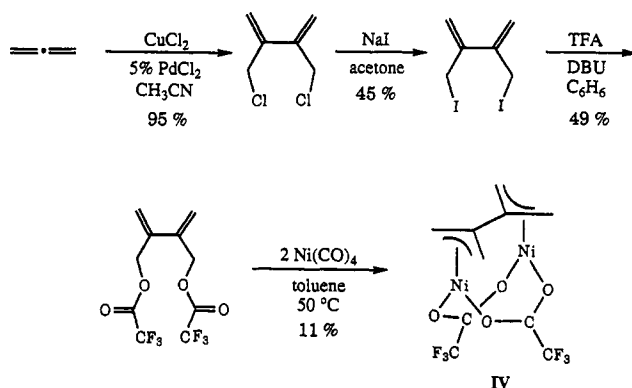
arations of I where the mixture was allowed to warm to room temperature or was stirred too long. Lower reaction temperatures, shorter reaction times, or different solvents did not solve this problem in preparations of IV. This was primarily due to the sluggishness of the oxidative addition reaction which was slowed as well as the decomposition reaction so that large amounts of starting materials were obtained. Other sources of nickel(0) (e.g.

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Scheme 3. Reported Synthetic Scheme for Preparation of Bis(μ -trifluoroacetato)(η^3 : η^3 -2,2'-biallyl)dipalladium(II)**Scheme 4.** Synthetic Scheme for Synthesis of 2,3-Bis((trifluoroacetoxy)methyl)-1,3-butadiene and Conversion to IV**Figure 2.** X-ray structure of IV·1/2(2,3-bis((trifluoroacetoxy)methyl)-1,3-butadiene).

(1,5,9-cyclododecatriene)Ni,¹⁰ (norbornene)₃Ni,¹¹ Ni(PF₃)₄, and Ni(AcAc)₂/(EtO)AlEt₂ were also not successful, and best results were finally obtained using Ni(CO)₄ (CAUTION: Ni(CO)₄ is very toxic even at very low concentrations! All manipulations using this reagent must be performed in an efficient fume hood). Here, CO insertion into the allyl group was a competing reaction, yet practical quantities of IV were obtained under controlled conditions.

Once isolated, crystalline IV (IV cocrystallizes with 0.5 equiv of 2,3-bis((trifluoroacetoxy)methyl)-1,3-butadiene, which can be removed by selective solvent extraction, Figure 2) proved to be very robust and highly soluble in nondonor solvents (diethyl ether and arenes). Most importantly, IV was found to be an active initiator for the polymerization of butadiene. Polymer was obtained in very high yield (>95%) and possessed a microstructure (ca. 70% *cis*-1,4 and 30% *trans*-1,4) identical to that seen for material prepared using I under identical conditions.⁵ It seemed to us that, once initiated, polymerizations utilizing IV behaved exactly as systems using I: initially deep red solutions of IV were observed shortly after addition of monomer to change to the characteristic orange/brown color of polymerizations with I. Since the polymerization of butadiene using I is a living system,³ we were eager to determine if the polymerization of butadiene using IV equally displayed living behavior at both metal centers. To examine the reaction in detail, we measured the kinetic and molecular weight properties of the polymerization system.

The rate law for polymerization of butadiene using I is second order: first order in monomer as well as in I. The rate constant for this reaction in C₆D₆ was found to be $k_t(313\text{ K}) = 4.11(5) \times 10^{-3}\text{ M}^{-1}\text{ s}^{-1}$ (Figure 3). For the analogous system using IV, a large (ca. 1 day at 40 °C) induction period was found to occur before polymerization initiation (Figure 4). We believe this induction period was due to the high stability of IV once isolated as a pure compound. In essence, the processes required to break apart the polycyclic structure of IV to allow insertion of butadiene monomer units (by either breaking the carboxylate linkages or isomerizing the allyl group from η^3 to η^1) must be much slower than the processes required to initiate polymerizations with I. Once the polymerizations are underway, the active sites should be identical (i.e. polybutadiene-substituted allylnickel trifluoroacetate species). The stability of IV can be discussed relative to its Pd analog. In the Pd complex, there are four ¹H NMR resonances for the η^3 : η^3 -biallyl ligand which have been assigned to a twisting of the ligand necessary to accommodate the two Pd atoms (the Pd–Pd separation in η^3 -allylpalladium acetate dimer is 2.94 Å, smaller than the sum of van der Waal radii (3.20 Å), while the overall length of the planar η^3 : η^3 -biallyl ligand is only 2.82 Å).⁷ The smaller ionic radius of Ni versus Pd (0.49 vs 0.64 Å, respectively)¹² makes for a better fit of the metal atoms into the structure of IV, which is reflected in a planar (or very fluctuational) η^3 : η^3 -biallyl ligand (only two ¹H NMR resonances),

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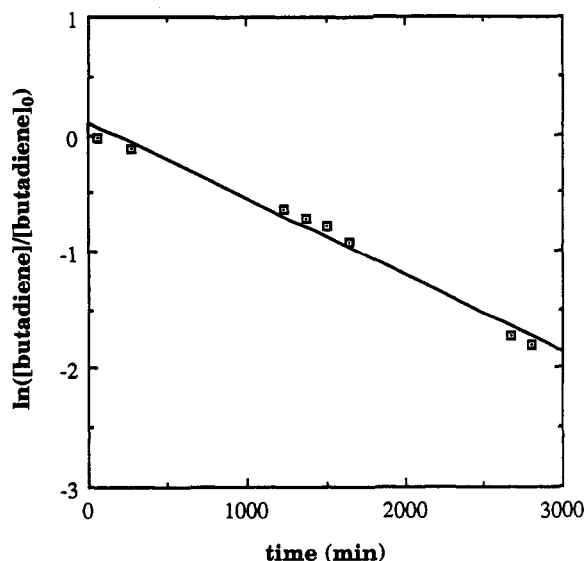


Figure 3. Butadiene kinetics using I. $T = 40\text{ }^{\circ}\text{C}$; $[I] = 3.3\text{ mM}$.

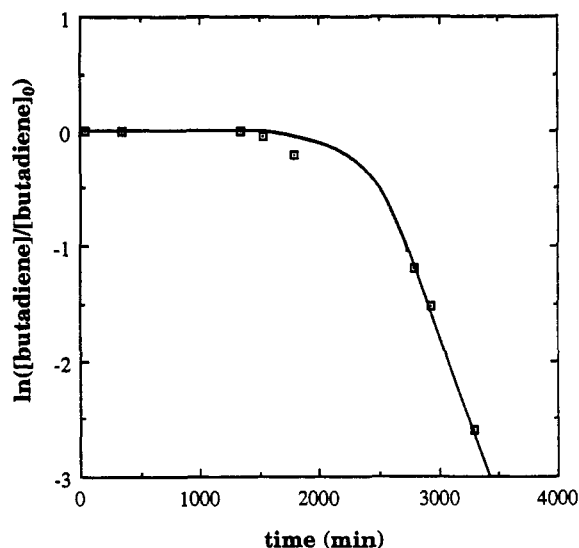
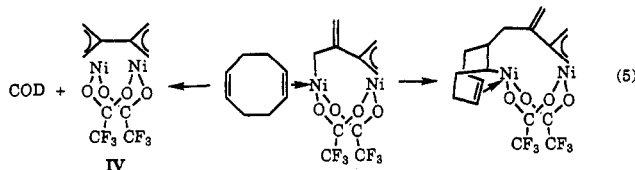


Figure 4. Butadiene kinetics using IV. $T = 40\text{ }^{\circ}\text{C}$; $[IV] = 12\text{ mM}$.

giving a very stable polycyclic compound. Our results (*vide supra*) of IV being very unstable relative to the insertion of ligands (e.g. COD) now seem unfounded except that these insertions most probably occur *before* the stable structure of IV is assembled (i.e. oxidative addition product can either dissociate a COD or CO ligand and generate IV, or it can insert the ligand and produce a byproduct) (eq 5). It has not been determined whether pure,



isolated IV will react appreciably with either COD or Ni(0) sources.

After the induction period, polymerization gradually begins and then the propagation rate constant reaches a constant maximum value at *ca.* 15% conversion of monomer. This limiting rate is first order in both monomer and initiator and gave a rate constant of $k_{IV}(313\text{ K}) = 4.15(5) \times 10^{-3}\text{ M}^{-1}\text{ s}^{-1}$ (Figure 4). This value was, as expected, nearly identical to k_I and illustrates that the propagation reactions are mechanistically identical and that there is no chain termination in polymerizations with IV.¹³ Next, we examined the molecular weight of polybutadiene produced as

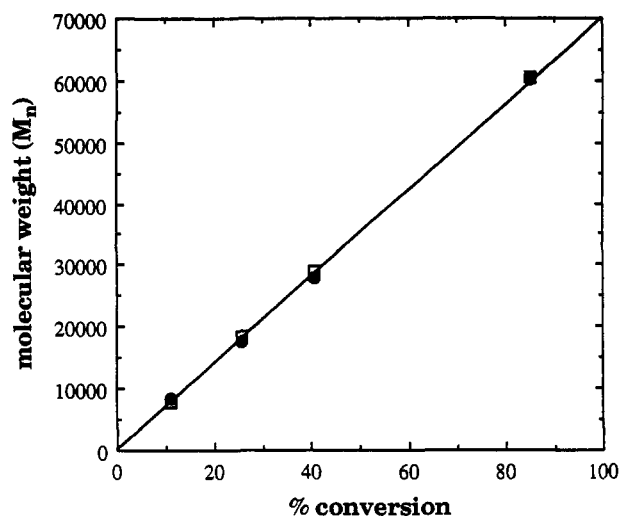


Figure 5. M_n of polybutadiene samples versus percent conversion of monomer. White squares are theoretical M_n values; black circles are experimental M_n values. Polymerization catalyst is IV.

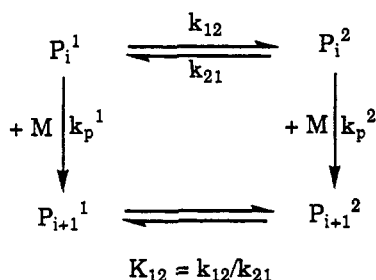
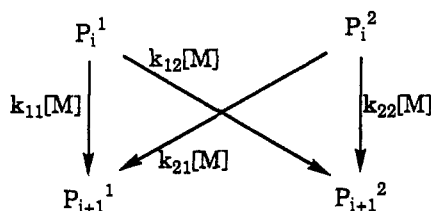
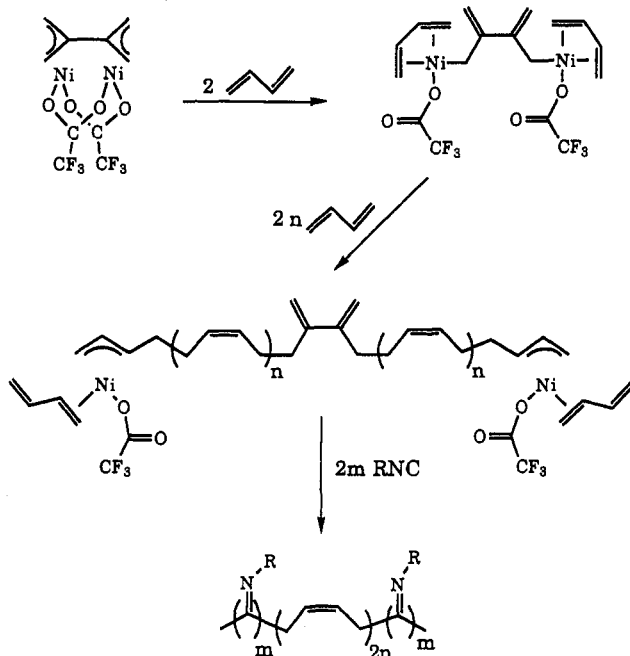
a function of the percent conversion of monomer. Using IV, we were able to obtain polybutadiene samples whose molecular weights varied linearly with percent conversion and agreed well with molecular weight values which were calculated from the molar monomer to initiator ratio at desired degrees of conversion ($M_n = 2[\text{butadiene}]/[\text{Ni}]$) (Figure 5). The linearity of this plot shows that no chain transfer is occurring over the course of the polymerization reaction.¹³ Since the propagation rate constants for I and IV are nearly identical, we can conclude that both of the metal centers in IV are active in the polymerization process. If not, then the rate constant for IV would be much less (i.e. it would equal $1/2$ of k_I if only one metal center were active). In summary, the mixture of butadiene with initiator IV showed all of the characteristics of a polymerization system in which both ends of the polymer are living.

The samples of polybutadiene prepared using IV (and I) were noticeably polydisperse ($M_w/M_n \approx 2\text{--}3$). This does not conflict with the polymerization system being termed living.¹³ The broad distributions are most probably due to interconversion between different active species throughout the course of the polymerization. Interconversion between differently active species broadens the molecular weight distribution (MWD) by the effect of having active chains which grow at different rates. The source of this phenomenon in this case can be different monomer/ligand coordination modes on the nickel center (i.e. η^2 -versus η^4 -coordination of butadiene),³ which can interconvert by loss or reorientation of ligands (Scheme 5; where P_1^1 and P_2^2 are living *i*-mers in states 1 and 2, respectively).¹⁴ If the exchange rate between the different species is very fast, the effect of this process is negligible. However, if the exchange rate is very slow relative to propagation, multiple distributions will result: one corresponding to each active species. For intermediate cases, a broad MWD results where the nonuniformity can be modeled using expressions derived by Böhm.¹⁵ Furthermore, these different species can form polymers of different microstructure (i.e. *cis*-versus *trans*-1,4-addition polymer which is seen with I as initiator), where the stereochemistry of the ultimate mer (the one bound

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Scheme 5. Equilibration Interconversion between Different Active Sites**Scheme 6.** Monomer Insertion Interconversion between Different Active Sites**Scheme 7.** Preparation of Triblock Copolymers using IV

to the nickel center) can then affect the propagation rate of the initiator center. These stereochemical effects, which will also broaden the MWD, give different catalytic species which can only interconvert through insertion of additional monomer to the polymer chain (Scheme 6).¹⁴

Preparation of Triblock Copolymers. It has been proposed that the living polymerization of butadiene mediated by I (and hence IV) propagates via an η^3 -allylnickel trifluoroacetate species with the polymer chain bound to one end of the allyl group.³ We note that this active propagating species is identical to I with respect to the catalysis of living isocyanide polymerizations (i.e., both contain nucleophiles (allyl groups) and electron-withdrawing groups).⁵ Therefore, the polymerization of isocyanides using active nickel initiators derived from butadiene polymerizations with IV, as described above, should afford isocyanide/butadiene/isocyanide triblock copolymers (Scheme 7).

Treatment of butadiene with a catalytic amount of IV followed by subsequent treatment of the reaction mixture with 1-phenylethyl isocyanide afforded the block copolymers. Differential scanning calorimetry (DSC) performed on selected block co-

polymers showed glass transitions (T_g 's) = -94°C , which corresponded well with T_g 's = -95°C measured for pure polybutadiene ($\sim 75\%$ *cis*) prepared using IV under identical reaction conditions. These DSC results show² that significant butadiene chains (blocks) exist in these copolymers as opposed to small, random segments. The blocklike nature of these copolymers was also confirmed by use of $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. $^{13}\text{C}\{^1\text{H}\}$ NMR showed only resonances for the parent homopolymers, and none were detectable which could be assigned to butadiene/isocyanide copolymer linkages, indicating that these were few in number. Elemental analyses (C, H, and N) of the copolymers revealed the presence of both monomer components at percentages which closely matched the feed compositions. The unique element (N is present only in the isocyanide component) allowed fairly precise determination of copolymer composition, permitting us to use these results with confidence.

GPC analysis of these materials showed unimodal distributions with polydispersities ranging from 2.1 to 3.0, yet gave molecular weights which decreased upon addition of isocyanide blocks. In an experiment where only a small amount of isocyanide was added to a high molecular weight living butadiene polymer, no low molecular weight peak for homopolyisocyanide was detected. This prompted us to assume that copolymers were indeed formed and that the anomalous GPC data were due to some as yet unexplained phenomenon which resulted in the hydrodynamic properties of the triblock polymers being drastically different from butadiene homopolymer. Since polybutadiene and these triblock copolymers undoubtedly have very different solution properties and because of the relative nature of GPC measurements, apparent molecular weights could very well decrease upon lengthening of the polymer chain.¹⁶

Simple rheological measurements (Ubbelohde tube viscosities) were undertaken as another method of molecular weight determination. For the sample 1-phenylethyl isocyanide/butadiene/1-phenylethyl isocyanide (b) (Table 1), the intrinsic viscosity of the initial polybutadiene segment ($[\eta](\text{THF}, 28.5^\circ\text{C})$) was found to be 0.563. Using published Mark-Houwink parameters,¹⁷ the viscosity average molecular weight, M_v , was found to be 28 000, a value very close to the GPC-determined molecular weight. For the copolymer, $[\eta](\text{THF}, 28.5^\circ\text{C})$ was found to be 0.701, significantly larger than the value for the polybutadiene segment: a good sign that this material is a copolymer. Without the Mark-Houwink parameters for this copolymer, no true molecular weight can be calculated. That these materials are in fact copolymers was confirmed by selective solvent extraction experiments. Lack of homopolybutadiene contamination was confirmed for the same 1-phenylethyl isocyanide/butadiene/1-phenylethyl isocyanide (b) by Soxhlet extraction of the copolymer with *n*-heptane, a solvent for polybutadiene but not for poly(1-phenylethyl isocyanide). Since this sample should contain mostly 1-phenylethyl isocyanide (ca. 80 wt %), the copolymer should not be soluble in *n*-heptane; however, any homopolybutadiene would readily dissolve in this solvent. No polymer was found in solution, indicating that these materials are copolymers. As such, we were able to calculate rough molecular weights from the elemental analysis data described above (Table 1).

The physical properties of these triblock copolymers were not examined in detail; however, crude inspections showed them to exhibit very different properties from the corresponding polyisocyanide/polybutadiene diblock copolymers. Samples of poly(1-phenylethyl isocyanide)-*b*-polybutadiene with high polybutadiene content (ca. >80%) are waxy semicrystals which readily separate if pulled apart. In contrast, poly(1-phenylethyl isocyanide)-*b*-polybutadiene-*b*-poly(1-phenylethyl isocyanide) samples of identical composition are not waxy, but are rubbery and resist when pulled apart. If not overextended, the samples will return to their original shape, displaying true elastomeric properties.²

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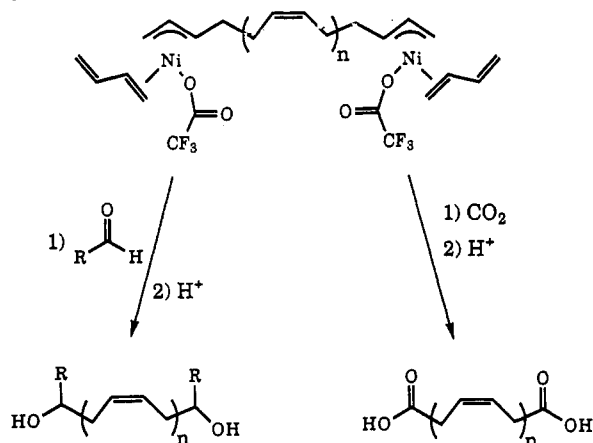
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Table 1

polymer system	$\mu\text{mol IV}$	mmol diene	mmol CNR	M_n					yield (%) ^e
				PBD ^a	PBD ^b	block ^a	block ^c	block ^d	
butadiene/IVa	11.8	3.38	4.19	15 470	18 000	77 530	68 180	9000	99
butadiene/IVb	11.8	6.66	10.75	30 095	30 510	150 000	149 560	37 600	96
butadiene/IVc	11.8	12.8	2.92	58 810	52 910	91 270	79 210	13 600	89

^a Calculated M_n of the first segment and then of the final copolymer, as determined by the monomer to catalyst ratio. ^b PBD = polybutadiene; M_n of a small aliquot of this polymer before addition of isocyanide monomer, as determined by GPC. ^c M_n of the total copolymer product, as determined by elemental analysis data. ^d M_n of the total copolymer product, as determined by GPC relative to polystyrene. ^e Total isolated yield of triblock copolymer.

Scheme 8. End-Group Modification of Living Bifunctional Polybutadiene



Telomerizations of Polybutadiene Using IV. Polymerization of butadiene using IV yields polybutadiene with η^3 -allyl nickel functional groups at both chain ends. These highly reactive end groups can be easily derivatized to many common organic functional groups through reaction with different small molecules. The resulting telomers, or bifunctionally modified polymers, are materials that can then be used for a variety of applications (e.g. macromers for graft copolymer synthesis or as polymeric cross-linking agents).¹ The limits as to which functional groups can be appended onto the ends of the polymer are directly related to the number of different types of molecules that can react quantitatively with the η^3 -allyl nickel end group. Some common reactions of this type are the reactions of aldehydes, CO, and CO₂ with η^3 -allyl nickel complexes to give homoallylic alcohols, aldehydes, and carboxylic acids, respectively.¹⁸ We wished to extend this small molecule reaction chemistry to our polymeric complexes to prepare telechelic polybutadiene with alcohol and acid end groups (Scheme 8). Alcohols and acids are complementary to each other with regard to formation of a chemical (ester) link. For example, polybutadiene end-capped with alcohol groups can be reacted with acid-bearing polymers (e.g. polyacrylic acid) to form grafts or can be reacted with the carboxylic acid termini in a polyester or polyamide to form block polymers.

Hydroxytelechelic poly(butadiene) is a commercially produced polymer which has found numerous applications including block copolymer synthesis, network formation, and chain extension.¹⁹ For most of these applications, it is important that the number of functional groups per chain (i.e. the functionality) is ≥ 2 . Commercial hydroxytelechelic poly(butadiene) is produced by the free radical polymerization of butadiene with hydrogen peroxide and is characterized as a statistical mixture of 1,4 and 1,2 repeat units and contains at least three types of hydroxy end groups.²⁰ Also, disproportionation chain termination reactions

can produce polymer chains which are monofunctional and therefore of limited use. The problems of poor stereo- and regiospecificity and lack of end-group control have been addressed by Hillmyer *et al.*, who have used ring opening metathesis polymerization (ROMP) techniques to prepare hydroxytelechelic poly(butadiene).²¹ They were able to prepare high *trans*-1,4-hydroxytelechelic poly(butadiene) with estimated functionalities of 1.7–1.9. Our methodology is complementary to this in that our poly(butadiene) has a high *cis*-1,4 content. Furthermore, since our polymerization system is living (the ROMP system relies on chain transfer reactions), we have more precise control over molecular weight and end-group modification.

In order to identify and quantify end-capping of the polybutadiene samples, we decided to use end-capping reagents which contained NMR active labels (¹⁹F and ¹³C). *p*-(Trifluoromethyl)benzaldehyde and ¹³CO₂ were added to living polybutadiene samples prepared using IV to prepare the telechelic polymers. The presence of the end groups on the polymer chains would then be confirmed by purification of the polymeric sample and observation of the end group directly using ¹³C{¹H} or ¹⁹F NMR spectroscopy. For the reaction using the aldehyde, the unreacted aldehyde has a resonance in the ¹⁹F NMR spectrum at –62.90 ppm and the end-capped polybutadiene product shows a resonance at –62.14 ppm. For comparison, the reaction of allylMgBr with the aldehyde gave a product with a resonance of –61.19 ppm. This alcohol product is structurally very similar to our polymer-substituted product and hence has a similar fluorine NMR resonance.

Quantification of the end-capping reaction was achieved through application of isocyanide polymerization chemistry.²² The polymer chains were first reacted with aldehyde and then stirred until the reaction was assumed to be complete (50 °C, 48 h). At this point, excess *p*-(trifluoromethyl)phenyl isocyanide was added to the reaction mixture, since if any unreacted η^3 -allyl nickel species are present, they will react quantitatively with the isocyanide to form polyisocyanide that is covalently linked to the polybutadiene chains.⁵ Under these conditions, even very minute quantities of unreacted polymer chains can be detected by ¹⁹F NMR because of the amplification of the fluorine signal by polymerization of the isocyanide (Scheme 9). Since both ends of the polybutadiene chains were shown earlier to possess η^3 -allyl nickel end groups, quantitative reaction of these end groups would mean that both ends of the chains were functionalized. *p*-(Trifluoromethyl)phenyl isocyanide has a resonance in the ¹⁹F NMR spectrum at –62.70 ppm, and the homopolymer shows a resonance at –61.7 ppm. When the complete sequence of experiments was performed, a yellow polymeric product was isolated. The yellow color was due to oligomeric decomposition products from the highly reactive isocyanide monomer and was removed by filtration of a toluene suspension of the product. This indicated that these oligomeric products were not covalently bound to the polybutadiene chains and probably resulted from thermal decomposition of the monomer. Indeed, when a ¹⁹F NMR spectrum was recorded of the colorless polybutadiene product, the only resonance present was the one at –62.14 ppm. On the basis of these data, we concluded that the reaction of the living polybutadiene chains

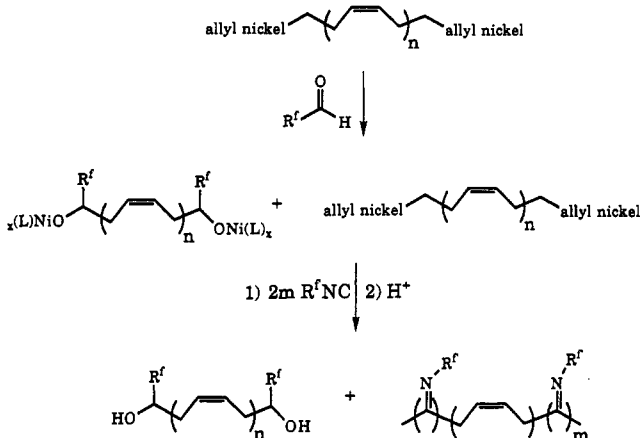
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Scheme 9. Strategy for Quantifying the End-Capping of Polybutadiene^a

^a The presence of different end groups can be identified and quantified by ¹⁹F NMR spectroscopy

with *p*-(trifluoromethyl)benzaldehyde was a quantitative reaction (i.e. the degree of functionality = 2.0) to the limits of NMR detection.

The end-capping of bifunctional polybutadiene chains with ¹³CO₂ was carried out analogously to the aldehyde-capping reaction. The expected labeled carboxylic acid end-group carbon was not observed for polymerizations using either I or IV as initiator. When *p*-(trifluoromethyl)phenyl isocyanide was added to the reaction mixture and the polybutadiene was isolated, the filtered polymer was yellow and showed resonances in the ¹⁹F NMR spectrum assignable to poly(*p*-(trifluoromethyl)phenyl isocyanide). Thus, it appears that CO₂ did not react with the chain ends and that the block copolymer between polybutadiene and the isocyanide was formed.

Conclusions

We have developed an initiator which promotes the living bifunctional polymerization of butadiene at ambient temperature. This synthetic system can be used to prepare chain-end-functionalized polybutadiene samples as well as triblock copolymers of butadiene with isocyanides. The telomers are potentially useful as macromolecular building blocks for the synthesis of a number of different polymer architectures and offer polybutadiene segments which can vary in length and consist of a regular microstructure which cannot be obtained through anionic and other techniques. The polyisocyanide-*b*-polybutadiene-*b*-polyisocyanide triblock copolymers are elastomeric, as would have been predicted since polyisocyanide chains are high melting and form crystalline structures.²³ These materials may offer some properties not obtainable in other triblock copolymer elastomers (e.g. polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) rubber), especially since the polyisocyanide segments are helical and rod-like in the solid phase.²³ The scope of polymer synthesis using IV has not yet been fully explored, and many other applications of this initiator may be awaiting discovery. For instance, styrene⁴ and allenes²⁴ have been reported to polymerize when treated with I and compounds similar to I. Hence, IV could potentially be used to prepare SBS thermoplastic elastomer or new thermoplastic elastomers based on polyallene as the hard, crystalline block.

Experimental Section

General. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Toluene, hexane, and THF were distilled from sodium benzophenone ketyl under nitrogen and were stored under nitrogen before use. Diethyl ether, THF-

*d*₈, C₆D₆, and *d*₈-toluene were vacuum transferred from sodium benzophenone ketyl. CDCl₃ was vacuum transferred from P₂O₅. ¹³CO₂ was stored over CaH₂ at 25 °C and was vacuum transferred before use. 4-(Trifluoromethyl)benzaldehyde was vacuum transferred from CaH₂ and stored under nitrogen before use. Butadiene was vacuum transferred from CaH₂ at -78 °C immediately before use. 2,3-Bis(chloromethyl)-1,3-butadiene was prepared according to the literature procedure.⁹ 1,4-Cyclohexanediylbis(1-propen-3-ol) was obtained from Tom Jenkins (Stanford University) and used as received. I and 1-phenylethylisocyanide were prepared as described in the literature. Ni(CO)₄ (Matheson), Ni(COD)₂ (Strem), and Ni(PF₃)₄ (Ozark-Mahoning Pennwalt) were used as received. Gel permeation chromatography (GPC) was performed on a Hewlett-Packard 1050 Series liquid chromatograph pump equipped with a HP Model 1047 refractive index detector and HP Model 3396A integrator. Separations were effected by 10⁵, 10⁴, 10³, and 500 Å Waters Ultrastaygel columns, and molecular weight was calibrated relative to polystyrene standards. DSC measurements were recorded on a Seiko Instruments, Inc., differential scanning calorimeter (equipped with a low-temperature attachment). NMR spectra were recorded on a Bruker AM-500 spectrometer, and ¹³C{¹H} spectra were referenced to the carbon of chloroform-*d* at δ 77.0. ¹⁹F spectra were referenced at -60.0 ppm to external C₆H₅CF₃. Ubbelohde tube viscosities were measured using a Schott-Gerate AVS 360 automated system equipped with a CT 050 constant temperature bath. The X-ray structural analysis was carried out by Dr. Joseph Ziller at the crystallographic facility, University of California at Irvine.

1,4-Phenylenebis(3-propen-1-ol). Terephthalaldehyde (2.50 g, 18.6 mmol) was dissolved in dry THF (150 mL) and cooled to -78 °C under a nitrogen atmosphere. Vinylmagnesium bromide (40 mL of a 1.0 M solution in THF, 40.0 mmol) cooled to -10 °C was then added slowly to the reaction mixture *via* cannula. Upon completion of the addition, the mixture was allowed to warm to -10 °C, whereupon water (5 mL) was added slowly. The reaction mixture was then filtered and the solvent removed from the filtrate to give the crude product. This product was washed with pentane (2 × 20 mL) to leave the product as a yellow sticky solid (2.5 g, 72%). The product was estimated to be sufficiently pure (<95% purity by ¹H NMR) for use without further characterization in catalyst preparation. IR (THF): 3500 cm⁻¹ (νOH, s br). ¹H NMR (acetone-*d*₆): δ 7.32 (m, ArH, 4H), 5.98 (m, (HO)CHCH=CH₂, 2H), 5.27 (dd, (HO)CHCH=CH₂, 2H), 5.20 (s, (HO)CHCH=CH₂, 2H), 5.03 (dd, (HO)CHCH=CH₂, 2H), 4.60 (m, (HO)CHCH=CH₂, 2H).

1,4-Phenylenebis(1-trifluoroacetyl-3-propene). 1,4-Phenylenebis(3-propen-1-ol) (500 mg, 2.63 mmol) was dissolved in THF (10 mL) and pyridine (0.53 mL, 6.55 mmol) under nitrogen in a Schlenk flask. TFAA (0.75 mL, 5.31 mmol) was added slowly with stirring, and the mixture was stirred for 10 min. The solvent was removed from the resulting mixture *in vacuo*, and the residue was extracted with dry hexanes. Evaporation of the hexanes *in vacuo* gave a yellow oil. This oil was distilled *in vacuo* (short path, 53 °C, 0.02 Torr) to give the product as a colorless oil (520 mg, 52%). The product was estimated to be sufficiently pure (>95% purity by ¹H NMR) for use without further characterization in catalyst preparation. IR (THF): 1790 cm⁻¹ (νCO, vs). ¹H NMR (toluene-*d*₈): δ 8.06 (dd, ArH, 4H), 6.86 (m, (TFAO)CHCH=CH₂, 2H), 6.55 (s, (TFAO)CHCH=CH₂, 2H), 6.45 (dd, (TFAO)CHCH=CH₂, 2H), 6.30 (m, (TFAO)CHCH=CH₂, 2H). ¹⁹F NMR (toluene-*d*₈): δ -79.8 (s, OC(O)CF₃).

[1,4-Phenylenebis((π³-1-allyl)nickel Trifluoroacetate)]_n. 1,4-Phenylenebis(1-trifluoroacetyl-3-propene) (75.0 mg, 0.196 mmol) was added to a Schlenk flask in the glovebox and then suspended in diethyl ether (3 mL). Into another Schlenk flask was placed bis(cyclooctadiene)nickel (135 mg, 0.491 mmol) which was suspended in diethyl ether (3 mL). On a Schlenk line, the ligand suspension was added to the nickel suspension *via* cannula, and the resulting mixture was stirred. After ca. 30 min a turquoise precipitate began to form, and the mixture was stirred for an additional 15 h. The blue suspension was then filtered, and the residue was washed with hexanes (3 × 3 mL) and dried under vacuum to leave the product as a turquoise powder (53 mg, 54%). The product was found to be paramagnetic and unstable (decomposes to Ni metal) in all dissolving (donor) solvents tried (e.g. THF, acetonitrile, and pyridine), and no NMR spectrum could be obtained. IR (Nujol): 1680 cm⁻¹ (νCO, vs). Anal. Calcd for C₁₆H₁₂O₄F₆Ni₂: C, 38.47; H, 2.43. Found: C, 38.90; H, 2.62.

1,4-Cyclohexanediylbis(3-trifluoroacetyl-1-propene). 1,4-Cyclohexanediylbis(1-propen-3-ol) (300 mg, 1.53 mmol) was dissolved in CH₂Cl₂ (10 mL) and pyridine (0.248 mL, 3.06 mmol) under nitrogen in a Schlenk flask. TFAA (0.454 mL, 3.21 mmol) was added slowly with stirring, and the mixture was stirred for 10 min. The solvent was removed from the resulting mixture *in vacuo*, and the residue was extracted with dry hexanes.

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Evaporation of the hexanes *in vacuo* gave the product as a colorless oil (486 mg, 82%). The product was estimated to be sufficiently pure (>95% purity by ^1H NMR) for use without further characterization in catalyst preparation. IR (hexanes): 1786 cm^{-1} (ν_{CO} , vs). ^1H NMR (CDCl_3): δ 5.30 (m, $(\text{TFAO})\text{CHCH}=\text{CH}_2$, 2H), 5.03 (d, $(\text{TFAO})\text{CHCH}=\text{CH}_2$, 2H), 4.93 (m, $(\text{TFAO})\text{CHCH}=\text{CH}_2$, 4H), 1.41, 1.26, 1.05, 0.50 (m, cyclohexyl-H, 10H). ^{19}F NMR (CDCl_3): δ -71.5 (s, $\text{OC}(\text{O})\text{CF}_3$).

[1,4-Cyclohexanediylbis($(\eta^3$ -1-allyl)nickel Trifluoroacetate)]₂. 1,4-Cyclohexanediylbis(3-trifluoroacetyl-1-propene) (100 mg, 0.258 mmol) was added to a Schlenk flask in the glovebox and then dissolved in diethyl ether (3 mL). Into another Schlenk flask was placed bis(cyclooctadiene)-nickel (177 mg, 0.645 mmol) which was suspended in diethyl ether (3 mL). On a Schlenk line, the ligand solution was added to the nickel suspension *via* cannula, and the resulting mixture was stirred. After ca. 3 min a red/orange precipitate began to form, and the mixture was stirred for an additional 1.5 h. The suspension was then filtered, and the residue was washed with hexanes ($3 \times 3\text{ mL}$) and dried under vacuum to leave the product as a red/orange powder (128 mg, 98%). The product was found to be paramagnetic in all dissolving (donor) solvents tried (e.g. THF, acetonitrile, and pyridine), and no NMR spectrum could be obtained. IR (Nujol): 1694 cm^{-1} (ν_{CO} , vs). Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_4\text{F}_6\text{Ni}_2$: C, 40.0; H, 3.60. Found: C, 39.7; H, 3.61.

2,3-Bis(iodomethyl)-1,3-butadiene. 2,3-Bis(chloromethyl)-1,3-butadiene (3.50 g, 22.6 mmol) was dissolved in acetone (10 mL) in a 250-mL round-bottom flask. NaI (10 g, 66.7 mmol) in acetone (100 mL) containing a small amount of BHT (ca. 50 mg) was added with stirring, and the mixture was stirred for 10 h while covered with Al foil. The resulting orange mixture was filtered, the solvent was removed *in vacuo*, and the residue was extracted with dry pentane (150 mL). Evaporation of the pentane *in vacuo* gave the product as a white fluffy powder (3.4 g, 45%). The product was estimated to be sufficiently pure (>95% purity by ^1H NMR) for use without further characterization in catalyst preparation. The product was stored at -40°C in the dark to avoid spontaneous polymerization. ^1H NMR (CDCl_3): δ 5.59 (s, $\text{CH}_2\text{C}=\text{CH}_2$, 2H), 5.41 (s, $\text{CH}_2\text{C}=\text{CH}_2$, 2H), 4.10 (s, $\text{CH}_2\text{C}=\text{CH}_2$, 4H).

2,3-Bis((trifluoroacetoxy)methyl)-1,3-butadiene. 2,3-Bis(iodomethyl)-1,3-butadiene (2.0 g, 5.9 mmol) was dissolved in C_6H_6 (25 mL) containing a small amount of BHT (ca. 30 mg) in a 50-mL round-bottom flask. DBU (3.0 mL, 11.9 mmol) was added with stirring followed by slow addition of TFA (1.54 mL, 11.9 mmol), and the colorless mixture was stirred for 40 h under reflux. CH_2Cl_2 (20 mL) was added to the light brown suspension, and it was washed with water ($2 \times 20\text{ mL}$). The organic layer was dried over MgSO_4 , and then solvents were removed *in vacuo* to leave a brown oil. This oil was distilled *in vacuo* (short path, 35°C , 0.07 Torr) to give the product as a colorless oil. The oil was crystallized from hexanes at -40°C as colorless needles (880 mg, 49%). The product was estimated to be sufficiently pure (>95% purity by ^1H NMR) for use without further characterization in catalyst preparation. IR (toluene): 1787 cm^{-1} (ν_{CO} , vs). ^1H NMR (CDCl_3): δ 5.50 (s, $\text{CH}_2\text{C}=\text{CH}_2$, 2H), 5.43 (s, $\text{CH}_2\text{C}=\text{CH}_2$, 2H), 5.04 (s, $\text{CH}_2\text{C}=\text{CH}_2$, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 137.3 (s, $\text{CH}_2\text{C}=\text{CH}_2$), 118.8 (s, $\text{CH}_2\text{C}=\text{CH}_2$), 67.9 (s, $\text{CH}_2\text{C}=\text{CH}_2$). ^{19}F NMR (CDCl_3): δ -73.7 (s, $\text{OC}(\text{O})\text{CF}_3$).

Bis($(\mu$ -trifluoroacetato)(η^3 -2,2'-biallyl)dinickel(II), IV. 2,3-Bis((trifluoroacetoxy)methyl)-1,3-butadiene (200 mg, 0.652 mmol) was added to a Schlenk flask in the glovebox and then dissolved in toluene (50 mL). Into this flask was injected nickel tetracarbonyl, $\text{Ni}(\text{CO})_4$, (0.40 mL, 3.07 mmol) *via* syringe. CAUTION: $\text{Ni}(\text{CO})_4$ is very toxic even at very low concentrations! All manipulations using this material should be carried out in an efficient fume hood and all exposed glassware rinsed with acetone in the hood. On a Schlenk line, a reflux condenser was connected to the flask, and the yellow solution was stirred at 50°C . After ca. 1 h, the solution became red/orange and was stirred for an additional 40 h. The solvent was removed from the resulting deep red solution *in vacuo*, and the resulting red oily solid was extracted with diethyl ether (5 mL) to give a red solution. Concentration of this solution and layering of hexanes (3 mL) upon it gave the product, after standing at -40°C for 24 h, as dark purple X-ray quality needles which contained 0.5 equiv of 2,3-bis((trifluoroacetoxy)methyl)-1,3-butadiene per unit of IV. The diene could be washed out of the crystals with cold hexanes (-40°C) to leave the pure product (30 mg, 11%). IR (toluene): 1665 cm^{-1} (ν_{CO} , vs). ^1H NMR (CDCl_3): δ 3.30 (s, η^3 -biallyl-H, 4H), 2.01 (s, η^3 -biallyl-H, 4H). ^{19}F NMR (CDCl_3): δ -77.1 (s, $\text{OC}(\text{O})\text{CF}_3$). Elemental analysis was performed on unwashed, X-ray quality crystalline material which contained the diene of crystallization. Anal. Calcd for $\text{C}_{10}\text{H}_8\text{O}_4\text{F}_6\text{Ni}_2 \cdot 1/2(\text{C}_{10}\text{H}_8\text{O}_4\text{F}_6)$: C, 31.24; H, 2.08. Found: C, 31.19; H, 2.01.

X-ray Structural Determination of IV-1/2(2,3-Bis((trifluoroacetoxy)methyl)-1,3-butadiene). Data Collection and Structure Solution. A red/purple crystal of approximate dimensions $0.16 \times 0.28 \times 0.30\text{ mm}$ was oil-mounted on a glass fiber and transferred to a Syntex P2₁ diffractometer which was equipped with a modified LT-1 low-temperature system. Determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix was carried out by standard techniques. Low-temperature (163 K) intensity data were collected *via* a θ - 2θ scan technique with Mo $\text{K}\alpha$ radiation under the conditions given in Table 2 (supplementary material).

All 3656 data were corrected for absorption and for Lorentz and polarization effects and placed on an approximately absolute scale. Any reflection with $I(\text{net}) < 0$ was assigned the value $|F_o| = 0$. There were no systematic extinctions nor any diffraction symmetry other than the Friedel condition. The two possible triclinic space groups are the noncentrosymmetric $P1$ [C_1 ; no. 1] or the centrosymmetric $\bar{P}1$ [C_1 ; no. 2]. Refinement of the model using the centrosymmetric space group proved it to be the correct choice.

Solution and Refinement of the Crystal Structure. All crystallographic calculations were carried out using either the UC Irvine-modified version of the *UCLA Crystallographic Computing Package* (*UCLA Crystallographic Computing Package*, University of California, Los Angeles, 1981, C. Strouse; personal communication) or the *SHELXTL PLUS* program set (Sheldrick, G. M., Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1990). The analytical scattering factors for neutral atoms were used throughout the analysis; both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + 0.0004(|F_c|)^2$.

The structure was solved by direct methods (*SHELXTL PLUS*) and refined by full-matrix least-squares techniques. The C_6H_8 group is disordered. Two orientations were included to account for the disorder. There is one-half molecule of $\text{C}_{10}\text{H}_8\text{O}_4\text{F}_6$ present which is located on an inversion center at (0, 1/2, 1/2). Hydrogen atoms (except those on the disordered ligand) were included using a riding model with $d(\text{C-H}) = 0.9\text{ \AA}$ and $U(\text{iso}) = 0.08\text{ \AA}^2$. Refinement of the model led to convergence with $R_F = 5.8\%$, $R_wF = 6.9\%$, and $\text{GOF} = 2.21$ for 276 variables refined against those 2852 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier map yielded $\rho(\text{max}) = 1.64\text{ e \AA}^{-3}$ at a distance of $0.98\text{ \AA}$ from Ni(2). Intramolecular distances (Table 3) and angles (Table 4), positional parameters, and isotropic displacements (Table 5) are available as supplementary material.

Butadiene Polymerization Kinetics Using I. Compound I (0.88 mg, $2.0\text{ }\mu\text{mol}$) was dissolved in C_6D_6 (0.35 mL) and placed in a thick-walled NMR tube. On a vacuum line, butadiene (0.25 mL, 2.3 mmol) was condensed into the tube, which was then sealed with a torch. The tube was subsequently thermostated in a 40°C oil bath. The reaction was monitored by ^1H NMR spectroscopy, where monomer loss was followed by monitoring loss of the vinylic monomer resonance at δ 6.22 and growth of the vinylic polymer resonance at δ 5.42. Monomer concentration as a function of time was then fit to a straight line plot using standard rate law equations to yield $k_{\text{obs}}(313\text{ K}) = 8.53 \times 10^{-4}\text{ min}^{-1}$. Conversion of units and dividing out the catalyst concentration gave $k_1(313\text{ K}) = 4.11(5) \times 10^{-3}\text{ M}^{-1}\text{ s}^{-1}$.

Butadiene Polymerization Kinetics Using IV. Compound IV (3.0 mg, $7.1\text{ }\mu\text{mol}$) was dissolved in C_6D_6 (0.40 mL) and placed in a thick-walled NMR tube. On a vacuum line, butadiene (0.20 mL, 1.8 mmol) was condensed into the tube, which was then sealed with a torch. The tube was subsequently thermostated in a 40°C oil bath. The reaction was monitored by ^1H NMR spectroscopy, where monomer loss was followed by monitoring loss of the vinylic monomer resonance at δ 6.22 and growth of the vinylic polymer resonance at δ 5.42. For three separate runs, no monomer loss was observed for ca. 1 day, whereupon monomer concentration began to decrease at an increasing rate. After ca. 20% conversion of monomer, monomer concentration as a function of time was fit to a straight line plot using standard rate law equations to yield $k_{\text{obs}}(313\text{ K}) = 2.91 \times 10^{-3}\text{ min}^{-1}$. Conversion of units and dividing out the catalyst concentration gave $k_1(313\text{ K}) = 4.15(5) \times 10^{-3}\text{ M}^{-1}\text{ s}^{-1}$.

Molecular Weight of Butadiene versus Percent Conversion Using IV. Aliquots (0.20 mL each) of a stock solution of IV (7.2 mg, $17\text{ }\mu\text{mol}$) in C_6D_6 (1.20 mL) were syringed into four separate thick-walled NMR tubes. Also into each tube was vacuum transferred butadiene (0.40 mL, 36 mmol), whereupon each tube was sealed with a torch. The percent conversion of each reaction (thermostated in a 45°C oil bath) was monitored by ^1H NMR spectroscopy as detailed above. At desired conversions, a tube was opened and the contents were precipitated into methanol which contained HCl (0.01 M) and a preservative (BHT, 0.001

M). The molecular weight distribution of each sample was then determined by GPC in THF: 11.0% conversion, $M_n = 8390$, $M_w = 17660$; 25.7% conversion, $M_n = 17670$, $M_w = 44380$; 40.7% conversion, $M_n = 27900$, $M_w = 57010$; 85.0% conversion, $M_n = 60270$, $M_w = 245340$.

Preparation of Polyisocyanide-*b*-polybutadiene-*b*-polyisocyanide Triblock Copolymers. In the glovebox, a deep red solution of IV (5.0 mg, 0.012 mmol) in toluene (0.50 mL) was added to a 100-mL thick-walled glass tube fused to a high-vacuum stopcock. The contents of the flask were frozen with $N_2(l)$ and then brought under vacuum on a Schlenk line, where butadiene (182, 360, or 694 mg; 3.38, 6.66, or 12.8 mmol for **a**, **b**, or **c**, respectively; determined by weighing the reaction flask before and after monomer addition) was vacuum transferred into the reaction mixture. After stirring at 45 °C (4 days), the contents of the reaction pots were removed (in the drybox) for GPC analysis, which showed molecular weights which varied with butadiene concentration (Table 1) and polydispersities (M_w/M_n) ranging from 2.0 to 2.4. $^{13}C\{^1H\}$ NMR analysis revealed that these polymers were generally of ca. 70% *cis*-1,4 microstructure, the remainder being *trans*-1,4 ($^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 32.1 (s, *trans* =CHCH₂), 27.9 (s, *cis* =CHCH₂); the relative ratio of microstructures was determined by comparing the intensities of the two narrow peaks). The bulk of the polymer reaction products were not isolated, but were diluted in the drybox with toluene (2, 3, or 5 mL for **a**, **b**, or **c**, respectively), and 1-phenylethyl isocyanide (550, 1410, or 384 mg; 4.19, 10.75, or 2.92 mmol for **a**, **b**, or **c**, respectively) was then added to afford, after additional stirring at 35 °C (24 h), the corresponding triblock copolymers. These copolymers were isolated by twice precipitating the product by addition of the toluene solution to methanol which contained HCl (0.01 M) and a preservative (BHT, 0.001 M). Overall isolated yields were generally greater than 90%. $^{13}C\{^1H\}$ NMR (poly(isocyanide-butadiene-isocyanide); $CDCl_3$): δ 164 (br m, CNCH(CH₃)-C₆H₅), 143 (br m, CNCH(CH₃)C₆H₅), 129.6 (s, *cis* =CHCH₂), 128 (br m, CNCH(CH₃)C₆H₅), 62 (br m, CNCH(CH₃)C₆H₅), 27.9 (s, *cis* =CHCH₂), 27 (br m, CNCH(CH₃)C₆H₅). The percentages of polybutadiene and polyisocyanide in the copolymers were calculated using the feed quantities of the two monomers. Anal. [Poly(isocyanide-butadiene-isocyanide) (**a**); (CNCH(CH₃)C₆H₅)_n/(CH₂CH)_m/(CNCH(CH₃)C₆H₅)_n] found: C, 83.0; H, 8.15; N, 7.86. Percent (CNCH(CH₃)C₆H₅)_n: calcd, 76.1; found, 73.6. Percent (CH₂CH)_m: calcd, 24.9; found, 26.4. Anal. [Poly(isocyanide-butadiene-isocyanide) (**b**); (CNCH(CH₃)C₆H₅)_{3n}/(CH₂CH)_m/(CNCH(CH₃)C₆H₅)_n] found: C, 86.86; H, 9.87; N, 3.55. Percent (CNCH(CH₃)C₆H₅)_n: calcd, 35.6; found, 33.2. Percent (CH₂CH)_m: calcd, 64.4; found, 66.8. Anal. [Poly(isocyanide-butadiene-isocyanide) (**c**); (CNCH(CH₃)C₆H₅)_n/(CH₂CH)_m/(CNCH(CH₃)C₆H₅)_n] found: C, 82.59; H, 7.84; N, 8.51. Percent (CNCH(CH₃)C₆H₅)_n: calcd, 79.7; found, 79.6. Percent (CH₂CH)_m: calcd, 20.3; found, 20.4. Percent polymer composition of each copolymer was determined by manipulation of raw C, H, and N data using N as a unique element to determine the percentage of polyisocyanide in the sample.

***p*-CF₃C₆H₄NC.** Ethyl formate (20.0 mL, 248 mmol) was heated with *p*-(trifluoromethyl)aniline (10 g, 62.1 mmol) over 3 days to give the corresponding formamide upon removal of the resulting ethanol. A portion of the formamide (5.0 g, 26 mmol) was then placed in a 250-mL three-neck flask equipped with a dropping funnel, a nitrogen inlet, and a stir bar. To the flask was also added CH₂Cl₂ (70 mL) and *N*-methylmorpholine (30 mL) to give a homogeneous solution, which was placed under a nitrogen atmosphere. Phosgene (1.93 M in toluene, 15.0 mL, 29.0 mmol) (CAUTION: phosgene is very toxic and all manipulations involving this material must be performed in an efficient fume hood; furthermore, solutions of phosgene should be cooled to avoid vaporization and all glassware must be rinsed off in the fume hood after contact with phosgene) was then added to the dropping funnel and added rapidly to the stirred formamide solution, causing precipitation of *N*-methylmorpholine hydrochloride and the evolution of gas. The resulting mixture was quenched with water (5 mL) and then washed with water (2 × 20 mL). The resulting organic layer was dried over MgSO₄ and then concentrated to leave a red oil. The oil was then distilled *in vacuo* (short path, 25 °C, 0.04 Torr) to give the isocyanide as a colorless liquid (2.9 g, 65%). IR ($CHCl_3$): 2128 cm⁻¹ (ν (NC) s). 1H NMR ($CDCl_3$): δ 7.69 (d, *ArH*, 2H), 7.51 (m, *ArH*, 2H). ^{19}F NMR ($CDCl_3$): δ -62.7 (s, CF₃).

Polymerization of *p*-CF₃C₆H₄NC with I. In the drybox, I (4.9 mg, 0.011 mmol) was dissolved in dry toluene (0.25 mL) to give an orange/red solution. *p*-CF₃C₆H₄NC (0.50 mL, 2.9 mmol) was then added via syringe to give an orange/yellow solution, which was stirred for 18 h under O₂. The resulting yellow precipitate was thinned with $CHCl_3$ (3 mL) and then added to dilute KOH (0.01 M) in methanol to precipitate

the polymer. The product was separated by centrifugation and then air dried. Reprecipitation and then drying *in vacuo* gave the polymer as a yellow/brown powder (420 mg, 84%). IR ($CHCl_3$): 1628 cm⁻¹ (ν (CN), br s). ^{19}F NMR ($CDCl_3$): δ -61.7 (br s, CF₃).

***p*-(1-Hydroxy)-3-butenyl- α,α,α -trifluorotoluene.** Allyl bromide (0.30 mL, 3.5 mmol) was added to a suspension of excess Mg turnings (1.0 g, 14 mmol) in dry ethyl ether (25 mL). The mixture was stirred at 0 °C for 15 min, whereupon a solution of 4-(trifluoromethyl)benzaldehyde (0.50 g, 2.9 mmol) in ethyl ether (5 mL) was slowly added and the mixture was stirred for an additional 30 min at 25 °C. Water (0.5 mL) was added, and a white precipitate formed instantly. The mixture was filtered, and the solvent was removed *in vacuo* to leave the product as a colorless oil (0.61 g, 99%). IR ($CHCl_3$): 3424 cm⁻¹ (ν (OH) br s). 1H NMR ($CDCl_3$): δ 7.62 (d, *ArH*, 2H), 7.47 (d, *ArH*, 2H), δ 5.78 (m, CH₂CH=CH₂, 1H), 5.18 (dd, CH₂CH=CH₂, 2H), 4.80 (m, CH(OH), 1H), 2.50 (m, CH₂CH=CH₂, 2H), 2.07 (br s, CH(OH), 1H). ^{19}F NMR ($CDCl_3$): δ -62.19 (s, CF₃).

End-Group Modification of Bifunctional Polybutadiene with 4-(Trifluoromethyl)benzaldehyde. In the glovebox, a deep red solution of IV (20.0 mg, 0.0472 mmol) in toluene (1.0 mL) was added to a 100-mL thick-walled glass tube fused to a high-vacuum stopcock. The contents of the flask were frozen with $N_2(l)$ and then brought under vacuum on a Schlenk line, where butadiene (1.00 g; 18.5 mmol; determined by weighing the reaction flask before and after monomer addition) was vacuum transferred into the reaction mixture. After stirring at 45 °C (4 days), the contents of the reaction pot were a solid, orange homogeneous gel. A small aliquot of this material was removed (in the drybox) for GPC analysis, which showed a molecular weight (M_n) of 19710 (theoretical $M_n = 21190$) and polydispersity (M_w/M_n) of 1.8. Portions of this bifunctionally living polybutadiene sample were used for all subsequent end-capping experiments. One-fourth of this sample (11.8- μ mol polymer chains) was added to a 100-mL thick-walled glass tube fused to a high-vacuum stopcock. Excess 4-(trifluoromethyl)benzaldehyde (20 mg, 110 μ mol) was syringed into the flask, which was then sealed and stirred at 50 °C for 24 h. In the drybox, *p*-CF₃C₆H₄NC (20 mg, 120 μ mol) was then added to the reaction mixture, which was stirred for an additional 24 h. The polymer was isolated by twice precipitating toluene solutions of the product from methanol which contained HCl (0.01 M) and a preservative (BHT, 0.001 M). Yellow oligomeric isocyanide impurities were removed from the toluene solutions by filtration through 0.45- μ m PTFE filters; the isolated polybutadiene sample was a colorless product (236 mg, 94%). IR (NaCl): 738 cm⁻¹ (ν (*cis* CH₂C=CH₂) vs). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 129.6 (s, *cis* =CHCH₂), 27.9 (s, *cis* =CHCH₂). ^{19}F NMR ($CDCl_3$): δ -62.14 (s, CF₃).

Attempted End-Group Modification of Bifunctional Polybutadiene with $^{13}CO_2$. One-fourth of the bifunctional polybutadiene sample prepared above (11.8- μ mol polymer chains) was added to a 100-mL thick-walled glass tube fused to a high-vacuum stopcock. Excess $^{13}CO_2$ (1.0 L (1 atm), 45 mmol) was vacuum transferred into the flask, which was then sealed and stirred at 50 °C for 48 h. In the drybox, *p*-CF₃C₆H₄NC (20 mg, 120 μ mol) was then added to the reaction mixture, which was stirred for an additional 24 h. The polymer was isolated by twice precipitating toluene solutions of the product from methanol which contained HCl (0.01 M) and a preservative (BHT, 0.001 M). The toluene solution of polymer was filtered through a 0.45- μ m PTFE filter; the isolated polymer sample was a yellow product (252 mg, 101% based upon starting polybutadiene). IR (NaCl): 738 cm⁻¹ (ν (*cis* CH₂C=CH₂) vs). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 129.6 (s, *cis* =CHCH₂), 27.9 (s, *cis* =CHCH₂). ^{19}F NMR ($CDCl_3$): δ -61.7 (br s, CF₃).

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Supplementary Material Available: Views of the disordered atoms in the structure of IV as well as a view of the entire unit cell and a cell packing diagram, tabulated experimental data for the structural analysis of IV (Table 2) and tables of intramolecular distances (Table 3) and angles (Table 4), positional parameters, and isotropic displacements (Table 5) (10 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.