New Acetylenic Monomers and Polymers from 4,5-Dicyanoimidazole

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Received December 16, 2003; Revised Manuscript Received May 19, 2004

ABSTRACT: An efficient synthesis of 1-methyl-2-ethynyl-4,5-dicyanoimidazole via Sonogashira coupling is described. Our optimized method generates 1-methyl-2-ethynyl-4,5-dicyanoimidazole in almost 80% yield from 1-methyl-2-bromo-4,5-dicyanoimidazole. Syntheses of the ethyl, propyl, and *p*-methoxybenzyl derivatives of 2-ethynyl-4,5-dicyanoimidazole are also reported. The polymerization of 1-methyl-2-ethynyl-4,5-dicyanoimidazole with transition-metal catalysts and triethylamine is described. Variation of catalyst concentration, reaction time, and temperature is also described. A more complete mechanistic picture of acetylene polymerizations, especially those with electron-withdrawing substituents, is presented. Solid samples of 1-methyl-2-ethynyl-4,5-dicyanoimidazole oligomers are EPR-active, and the number of free spins was quantified. Cyclic voltammetry was used to investigate the reduction of 1-methyl-2-ethynyl-4,5-dicyanoimidazole oligomers and other dicyanoimidazole derivatives.

Introduction

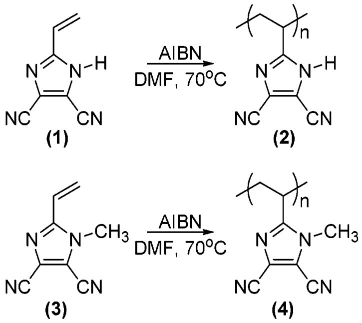
The HCN tetramer diaminomaleonitrile (DAMN) has proved to be a very convenient reagent for the synthesis of heterocyclic monomers.[1−3] There has been no work on acetylenic polymers based on DAMN, although our group has recently reported vinylic polymers derived from DAMN.[4−8] High molecular weight polymers from both 2-vinyl-4,5-dicyanoimidazole **(1)** and 1-methyl-2-vinyl-4,5-dicyanoimidazole **(3)** were prepared using AIBN as an initiator in DMF at 70 °C.[5,6] See Scheme 1.

By comparison, the acetylenic monomer and polymer analogues should have a high degree of conjugation and unique properties due to the dicyanoimidazole electron-withdrawing groups. We focus here on the anionic and transition-metal polymerization of acetylenic dicyanoimidazoles. This work parallels earlier work on the anionic polymerization of cyanoacetylene with butyllithium and triethylamine reported by Gorman and co-workers; however, they did not propose initiation, propagation, or termination mechanisms.[9]

There have also been a number of reports on the polymerization of acetylene derivatives using late-transition-metal catalysts because they are typically more tolerant of a variety of functional groups.[9−25] Catalysts based on molybdenum, tungsten, niobium, and tantulum are generally very air and moisture sensitive,[12] whereas rhodium-, palladium-, and nickel-based catalysts are less sensitive and can be used with a variety of solvents.

Using solid-state NMR, Hirao and co-workers have suggested that polymerization of phenylacetylene with rhodium catalysts proceeds via an insertion mechanism.[16] Poly(phenylacetylene) was made using rhodium(I) complexes with norbornadiene or 1,5-cyclooctadiene by Cataldo.[26] Tang and co-workers have prepared poly(phenylacetylene) using water-soluble rhodium complexes, Rh(nbd)(tos)(H_2O) and Rh(cod)(tos)(H_2O).[12] They also reported that $[Rh(nbd)Cl]_2$ and $[Rh(cod)Cl]_2$ produced stereoregular cis-transoidal polymers of different phenylacetylene derivatives.[10,12] Tabata and co-workers have done extensive work on ortho-, meta-, and para-substituted phenylacetylene derivatives using rhodium catalysis and have achieved unprecedented molecular weights of stereoregular cis-transoidal polyacetylene derivatives.[21−25,27] They have also demonstrated that triethylamine serves as a cocatalyst in the polymerization reaction and promotes catalyst dissociation.[22−24]

Scheme 1. Polymerization of 2-Vinyl-4,5-dicyanoimidazole and Its Alkyl Derivative



Few polyacetylenes reported have contained electron-withdrawing groups. D'Amato and Tabata reported the polymerization of *p*-nitrophenylacetylene using $[Rh(nbd)Cl]_2$ and $[Rh(cod)Cl]_2$, but the polymer's molecular weight was 1200−2100 g/mol.[25] This molecular weight was much lower than other substituted poly(phenylacetylenes) they have reported.

The polymerization of cyanoacetylene illustrates the difficulties with electron-withdrawing substituents, and thus far, a variety of polymerization methods have not produced soluble, high molecular weight polymers. Wallach and Manassen polymerized cyanoacetylene using anionic initiators.[28] Gorman and co-workers have found that nickel and palladium catalysts were effective in the polymerization of cyanoacetylene, giving molecular weights on the order of 10^4 g/mol.[9]

In general, very little has been said about the polyacetylene polymerization mechanism. Kishimoto and co-workers proposed an insertion mechanism for rhodium-catalyzed polymerization of phenylacetylenes.[15] A termi-

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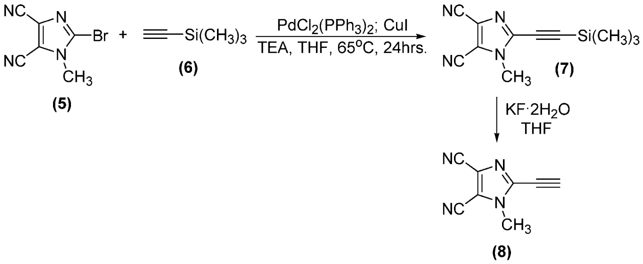
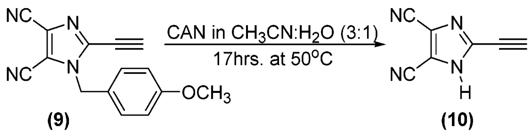
Scheme 2. Successful Sonogashira Coupling To Give 1-Methyl-2-ethynyl-4,5-dicyanoimidazole



Scheme 3. Deprotection of 1-(*p*-Methoxybenzyl)-2-ethynyl-4,5-dicyanoimidazole (9)



nation mechanism was not proposed. Zhan and Yang addressed the polymerization mechanism of acetylenes using palladium and nickel acetylide catalysts.[29] They propose that the initial activation step, and also the rate-determining step, involve coordination of a nickel or palladium acetylide catalyst with an acetylene. Zhan and Yang also discussed polymer termination as a result of particularly acidic acetylenic monomers.[29]

Results and Discussion

Monomer Synthesis. Sonogashira coupling has become widely used in recent syntheses of acetylenic monomers. Tabata and co-workers have prepared a variety of ortho-, meta-, and para-substituted aromatic acetylenes synthesized by Sonogashira coupling.[21−25,27] The successful synthetic approach to 2-ethynyl-4,5-dicyanoimidazole derivatives used palladium-catalyzed Sonogashira coupling of 2-bromo-4,5-dicyanoimidazole derivatives with trimethylsilylacetylene. The reaction is illustrated in Scheme 2. The silyl-protected product was readily deprotected using potassium fluoride dihydrate in THF to give 1-methyl-2-ethynyl-4,5-dicyanoimidazole **(8)** after extensive work-up. Details of our optimized procedures are reported elsewhere.[30] Synthesis of the ethyl and propyl derivatives of 2-ethynyl-4,5-dicyanoimidazole **(10)** can be found in the Supporting Information.

In an effort to produce the unprotected 2-ethynyl-4,5-dicyanoimidazole **(10)**, Sonogashira coupling with 2-bromo-4,5-dicyanoimidazole and trimethylsilylacetylene was attempted. This reaction led to a mixture of products that were extremely difficult to separate. The target product, 2-(trimethylsilylacetylene)-4,5-dicyanoimidazole, could not be isolated from the mixture. Complications with this coupling were largely attributed to the acidity of the 1-position hydrogen. To avoid this problem, protection and deprotection chemistry was investigated,[31−35] although the choice of protecting groups for cyanoimidazoles is limited due the strong electron-withdrawing nature of nitriles.[36−38] Deprotection of 1-(*p*-methoxybenzyl)-2-ethynyl-4,5-dicyanoimidazole **(9)** to give 2-ethynyl-4,5-dicyanoimidazole **(10)** is shown in Scheme 3.

Polymerization. The goal of this work was to prepare acetylenic polymers of dicyanoimidazoles. See Figure 1. With the successful synthesis of monomer our attention turned to the late-transition-metal catalysts, $[Rh(nbd)Cl]_2$ and $[Rh(cod)Cl]_2$. These catalysts have been shown to tolerate functional groups and exhibit increasing catalytic activity in more polar organic solvents.[10,12] We selected nickel- and palladium-based catalysts because Gorman and co-workers found them to be successful in the polymerization of cyanoacetylene.[9] Dimethylformamide was used as a solvent for the initial polymerizations, and the following catalysts were examined: $[Rh(nbd)Cl]_2$, $[Rh(cod)Cl]_2$, $PdCl_2(PPh_3)_2$, $NiCl_2(PPh_3)_2$, and triethylamine.

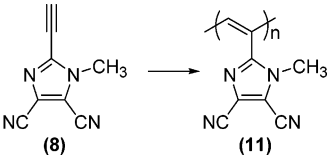


Figure 1. Polymerization of 1-methyl-2-ethynyl-4,5-dicyanoimidazole **(8)**.

Palladium, nickel, and rhodium catalysts were compared using DMF as the solvent and a 100:1 monomer-to-catalyst ratio. Although initial yields were low and high molecular weight polymer was not produced, Table 1 does show that these catalysts produced oligomers. Because the sample sizes and yields were so small in **11-B**, **11-C**, **11-D**, and **11-E**, the M_n was not determined. Oligomer was also produced using rhodium catalysis at both room temperature and 65 °C. Since the rhodium catalyst was much more soluble in common organic solvents, it could be removed easily. For these reasons, additional polymerizations focused largely on $[Rh(nbd)Cl]_2$.

The monomer-to-catalyst ratio, reaction time, and temperature were varied using DMF as a solvent **(11-G**,**A**,**H)**. There was a very slight increase in the polymer yield by increasing the amount of catalyst from a 100:1 to 20:1 monomer-to-catalyst ratio. By extending the reaction time from 24 to 48 h at room temperature, the yield more than doubled. By increasing the temperature to 65 °C, the yield increased to 65% **(11-J)**.

Tabata and co-workers suggest that TEA may serve as a cocatalyst with rhodium complexes because it promotes dissociation of the dimeric rhodium complex.[22−24] The role of TEA alone and with $[Rh(nbd)Cl]_2$ was investigated with 1-methyl-2-ethynyl-4,5-dicyanoimidazole (**8**). It is clear from samples **11-K,L,M,N** that TEA alone leads to polymerization of 1-methyl-2-ethynyl-4,5-dicyanoimidazole (**8**). At room temperature and a reaction time of 18 h, the yield increases with the more polar solvent DMF compared to toluene. Using DMF as a solvent in **11-M**, the yield increased to over 60% when the temperature was increased and the polymerization time was extended. The various yields listed for **11-N** reflect multiple polymerizations using acetonitrile as a solvent, a monomer-to-catalyst ratio of 20:1, and a 24 h reaction time at 65 °C. The properties of the these oligomers (**11-K,L,M,N**) are similar. They are dark brown-black solids and have similar IR and NMR features.

The role of TEA with $[Rh(nbd)Cl]_2$ in the polymerization of 1-methyl-2-ethynyl-4,5-dicyanoimidazole (**8**) was also investigated. Using TEA as a cosolvent in **11-O** resulted in an increase in yield and molecular weight. Whether TEA acts as a cocatalyst with $[Rh(nbd)Cl]_2$ is unclear since TEA alone leads to polymerization. There are perhaps two competing polymerization mechanisms, and if so, it would be very difficult to distinguish

Table 1. Variation of Transition-Metal Catalyst

	catalyst	M:cat	solvent	time (h)	temp	yield (%)	M_n(GPC)
11-A	$[Rh(nbd)Cl]_2$	100:1	DMF	24	r.t.	15	2200[b]
11-B	$Ni(PPh_3)Cl_2$	100:1	DMF	24	r.t.	0	
11-C	$Pd(PPh_3)Cl_2$	100:1	DMF	24	r.t.	0	
11-D	$[Rh(nbd)Cl]_2$	100:1	DMF	24	65 °C	32[a]	
11-E	$Ni(PPh_3)Cl_2$	100:1	DMF	48	65 °C	10[a]	
11-F	$Pd(PPh_3)Cl_2$	100:1	DMF	24	65 °C	21[a]	1100[b]
11-G	$[Rh(nbd)Cl]_2$	20:1	DMF	24	r.t.	20[a]	1800[b]
11-H	$[Rh(nbd)Cl]_2$	250:1	DMF	24	r.t.	0	
11-I	$[Rh(nbd)Cl]_2$	20:1	DMF	48	r.t.	47[a]	1500[b]
11-J	$[Rh(nbd)Cl]_2$	20:1	DMF	48	65 °C	65[a]	1900[b]
11-K	TEA	20:1	toluene	18	r.t.	7	
11-L	TEA	20:1	DMF	18	r.t.	31	
11-M	TEA	20:1	DMF	24	65 °C	63[a]	3100[c]
11-N	TEA	20:1	CH_3CN	24	65 °C	62−79[a]	2000[c]
11-O	$[Rh(nbd)Cl]_2$	20:1	4:1 DMF/TEA	24	r.t.	80[a]	3200[c]
11-P	$[Rh(nbd)Cl]_2$	20:1	TEA	24	r.t.	40	1500[b]

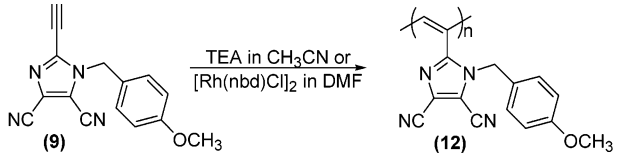
[a] Crude yield. Contains DMF according to ^1H NMR. [b] GPC in THF relative to polystyrene standards. [c] GPC in NMP relative to polystyrene standards.

Table 2. Oligomerization of 1-(*p*-Methoxybenzyl)-4,5-dicyanoimidazole (12)

	catalyst	M:cat	solvent	time (h)	temp	yield (%)	M_n(GPC)
12-A	$[Rh(nbd)Cl]_2$	20:1	DMF	24	r.t.	50	900[a]
12-B	TEA	20:1	CH_3CN	24	r.t.	65	700[a]

[a] GPC in NMP relative to polystyrene standards.

Scheme 4. Oligomerization of 1-(*p*-Methoxybenzyl)-2-ethynyl-4,5-dicyanoimidazole (9)



between the two in this experiment. In **11-P**, TEA was used as the polymerization solvent. It is suspected that the yield decreased compared to **11-O** because TEA is a poor solvent and the oligomer precipitated from solution.

Along with 1-methyl-2-ethynyl-4,5-dicyanoimidazole (**8**), the polymerization of 1-(*p*-methoxybenzyl)-2-ethynyl-4,5-dicyanoimidazole (**9**) was also investigated. The monomer 2-ethynyl-4,5-dicyanoimidazole (**10**) could be produced by deprotecting 1-(*p*-methoxybenzyl)-2-ethynyl-4,5-dicyanoimidazole (**9**) with ceric ammonium nitrate (CAN), and polymerization was avoided. 1-(*p*-Methoxybenzyl)-2-ethynyl-4,5-dicyanoimidazole (**9**) was polymerized using TEA and rhodium-based catalysis. The product consisted largely of dimer and trimer in both cases. The results are illustrated in Table 2.

Following isolation of 1-(*p*-methoxybenzyl)-4,5-dicyanoimidazole oligomers (**12**), the sample was deprotected using CAN in 3:1 (CH_3CN:H_2O) to give 2-ethynyl-4,5-dicyanoimidazole oligomers (**13**). Elements of hydrogen bonding were evident in the FT-IR spectra of (**13**); however, the deprotection byproduct, *p*-anisaldehyde, was difficult to remove from the oligomer.

UV−Vis Characterization. The UV−vis spectrum for 1-methyl-2-vinyl-4,5-dicyanoimidazole (**3**) was compared to the spectra of oligomers of 1-methyl-2-ethynyl-4,5-dicyanoimidazole (**11**). Compared to **3**, the UV absorbance of 1-methyl-2-ethynyl-4,5-dicyanoimidazole oligomers (**11**) “tail off” toward longer wavelengths. The molar absorptivity is considerably higher for the oligomers (**11**) compared to the model compound (**3**). This may be attributed to conjugation and enhanced delocalization of the nonbonded electrons in multiple dicyanoimidazole pendant groups along the oligomer chain. The UV−vis spectra exhibited similar tailing for all oligomers of 1-methyl-2-ethynyl-4,5-dicyanoimidazole (**11**) independent of how they were produced. Such tailing was also observed by Tang and co-workers for poly(phenylacetylene) derivatives.[10] A similar absorption profile was observed by Gorman and co-workers for poly(cyanoacetylene) polymerized using TEA or palladium catalysts.[39] In oligomers of 1-methyl-2-ethynyl-4,5-dicyanoimidazole (**11**), absorption at longer wavelengths clearly represents transitions due to the conjugated backbone.

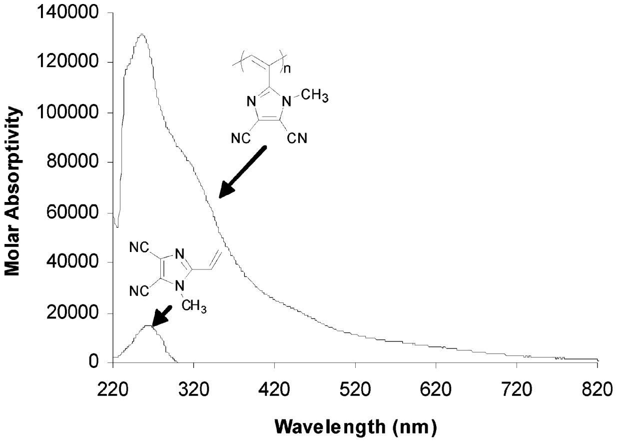
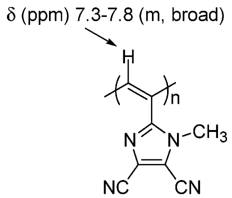


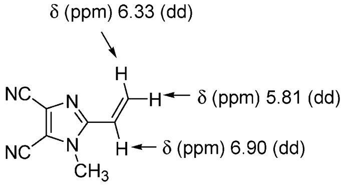
Figure 2. UV−vis spectra of model compound and oligomers.

NMR Characterization. A key element of the characterization was to establish the presence of double bonds in the backbone of 1-methyl-2-ethynyl-4,5-dicyanoimidazole oligomers (**11**). Broad peaks observed in ^1H NMR between 7 and 8 ppm were labeled as the olefinic backbone protons based on comparison to model compounds (Figure 3). The model compound, 1-methyl-2-styryl-4,5-dicyanoimidazole (**15**), was synthesized for NMR comparison. The vinyl derivative, 1-methyl-2-vinyl-4,5-dicyanoimidazole (**14**), was also used as a model compound. The ^1H NMR shifts illustrated in

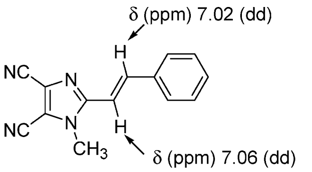


(11)

Figure 3. ^{1}H NMR shifts of oligomers in DMSO-d_6 at 400 MHz.



1-methyl-2-vinyl-4,5-dicyanoimidazole **(14)**



1-methyl-2-styryl-4,5-dicyanoimidazole **(15)**

Figure 4. ^{1}H NMR shifts of model compounds in DMSO-d_6 at 400 MHz.

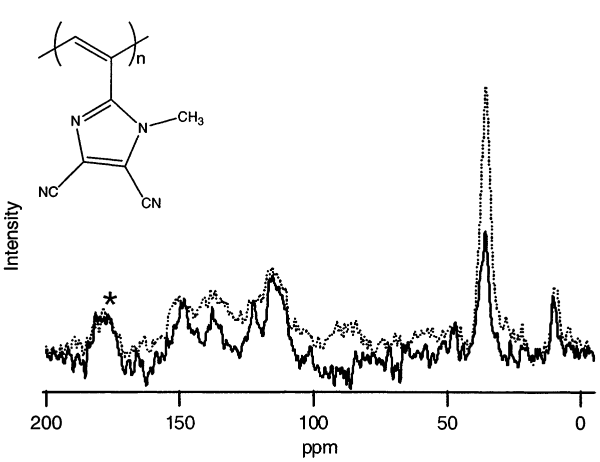


Figure 5. Solid-state NMR of **11-N** with CP and MAS at 5 kHz followed by ^{1}H$-$^{13}C decoupling; *denotes spinning sideband.

Figure 4 support the assignment of olefinic backbone proton shifts in the oligomers (**11**). Oligomers of 1-(*p*-methoxybenzyl)-2-ethynyl-4,5-dicyanoimidazole (**12**) and 2-ethynyl-4,5-dicyanoimidazole (**13**) also show broad, multiple ^{1}H NMR peaks between 7 and 8 ppm.

Solid-state NMR combined with magic angle spinning and decoupling was used to characterize oligomers of 1-methyl-2-ethynyl-4,5-dicyanoimididazole **(11)** and 1-(*p*-methoxybenzyl)-2-ethynyl-4,5-dicyanoimidazole **(12)**. Sample **11-N** was analyzed first with magic angle spinning (MAS) at 5 kHz and cross-polarization (CP).

Following the CP-MAS experiment, a delayed decoupling pulse was applied to probe carbon$-$hydrogen connectivity. The solid-state NMR spectrum is illustrated in Figure 5. A 50 μs delay was introduced following cross-polarization but before decoupling data acquisition began. In Figure 5, the dotted line represents the original CP-MAS spectrum and the bold line represents the spectrum with delayed decoupling. Peaks between 120 and 130 ppm were assigned to the backbone carbons in the oligomer **(11-N)**. The results are summarized in Table 3.

Oligomers of 1-(*p*-methoxybenzyl)-2-ethynyl-4,5-dicyanoimidazole **(12-A)** made with [Rh(nbd)Cl]$_2$ in DMF were also analyzed using solid-state NMR. On the basis of solution NMR of **12-A**, DMF remains in the sample. DMF was also observed in the solid-state NMR. In addition, because the oligomer is largely composed of dimer and trimer, peaks from the possible norbornadiene end group from the rhodium catalyst were also observed.

In Figure 6, peaks at approximately 15$-$20 ppm were assigned to the methylene carbon in the norbornadiene end group. The peaks at 30$-$40 ppm were assigned to the bridgehead carbons in the norbornadiene end group. The broad peaks around 110$-$125 ppm were assigned to the C=C in norbornadiene, backbone carbons in the oligomer chain, and the cyano carbons in the dicyanoimidazole pendant group. After decoupling, a peak remains around 114 ppm that was assigned to the cyano carbons. The results are summarized in Table 4. Additional details about this technique and peak assignments for **11** and **12** can be found in the Supporting Information.

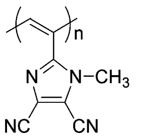
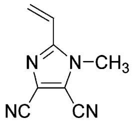
In the solid-state and solution NMR of 1-(*p*-methoxybenzyl)-2-ethynyl-4,5-dicyanoimidazole dimers and trimers **(12-A)**, norbornadiene was easily observed in the short-chain oligomers. The confirmation of norbornadiene in NMR coupled with rhodium analysis supports our proposal that the catalyst remains as an end group on the oligomer chain.

Elemental Analysis. Elemental analysis was used to characterize the 1-methyl-2-ethynyl-4,5-dicyanoimidazole oligomers **(11)** initiated with both triethylamine and rhodium complexes. For **11-N** initiated with TEA, an anionic polymerization is proposed; however, there are few anionic polymerizations that are initiated by neutral nucleophiles such as amines.[40] In the case of the monomer 1-methyl-2-ethynyl-4,5-dicyanoimidazole **(8)**, it seems more likely that triethylamine would act as a base rather than as a nucleophile in the first step of initiation. If this is the case, the oligomer may have the composition shown in Figure 7.

The calculated C, H, N percentages are in good agreement with the experimental data. On the basis of the model illustrated in Figure 7 and the data in Table 5, it is unlikely that TEA is incorporated into the oligomeric product. This would be the case if TEA acted as a nucleophile to initiate the anionic polymerization.

For oligomers made with rhodium catalysis, rhodium analysis was used to confirm its presence in the oligomers of 1-methyl-2-ethynyl-4,5-dicyanoimidazole **(11)** and 1-(*p*-methoxybenzyl)-2-ethynyl-4,5-dicyanoimidazole **(12)**. On the basis of the number-average molecular weight from GPC, ^{1}H NMR, and mechanistic aspects proposed by Kishimoto[15] and Zhan and Yang,[29] an oligomer model was created for the initiation of 2-ethynyl-4,5-dicyanoimidazole derivatives using [Rh(nbd)Cl]$_2$. All oligomer samples were rinsed thoroughly with methylene chloride to remove unreacted monomer and catalysts. However, methylene chloride may displace chlorine as a ligand in the rhodium complex.[21,22,25,27] Combining all these factors, an oligomer model is illustrated in Figures 8.

Table 3. NMR Shift Comparisons

 Solid State NMR shifts for **(11)**:	 Solution ^{13}C NMR shifts (*d*-DMSO) for **(14)**:
-CH_3 = 36 ppm	-CH_3 = 33 ppm
Carbons at positions 4 and 5 and CN in dicyanoimidazole = 108-120 ppm	C at positions 4 and 5 = 108 ppm
	CN = 112 ppm
Backbone carbons = 120-130 ppm	βC = 122 ppm
	αC = 125 ppm
C at position 2 = 150 ppm	C at position 2 = 150 ppm

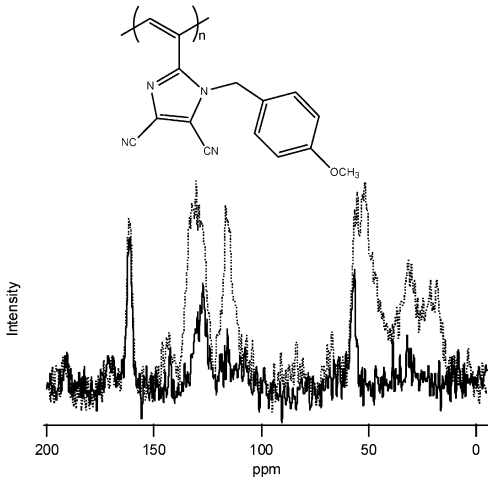


Figure 6. Solid-state NMR of **12-A** with CP and MAS at 5 kHz followed by $^1H-^{13}C$ decoupling.

There is clearly a significant amount of rhodium present in **11-Q** made with $[Rh(nbd)Cl]_2$ in DMF. If the complex is present as an end group, the rhodium percentage corresponds to an average of six monomer repeats per oligomer chain. This agrees reasonably well with the number-average molecular weight of 1400 g/mol determinined by GPC in *N*-methylpyrrolidinone (NMP). See Table 6.

A second sample of 1-methyl-2-ethynyl-4,5-dicyanoimidazole oligomers (**11-R**) made with $[Rh(nbd)Cl]_2$ in CH_3CN was also analyzed, and the rhodium percentage corresponds to an average of three monomer repeats per oligomer chain. This agrees reasonably well with the number-average molecular weight of 1000 g/mol determinined by GPC in *N*-methylpyrrolidinone (NMP). See Table 7.

Oligomers of 1-(*p*-methoxybenzyl)-2-ethynyl-4,5-dicyanoimidazole (**12**) made with $[Rh(nbd)Cl]_2$ in DMF were also analyzed. The rhodium content was 11.21%, roughly corresponding to dimer or trimer with the rhodium complex as an end group. GPC analysis in NMP of the oligomers showed two peaks corresponding to dimer and trimer.

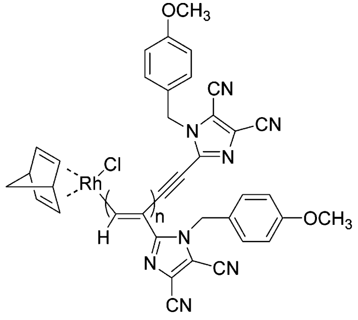
Mechanistic Aspects. As noted above, the anionic polymerization of cyanoacetylene with butyllithium and triethylamine was reported by Gorman and co-workers.[39] In our work, we observed that 1-methyl-2-ethynyl-4,5-dicyanoimidazole (**8**) could be polymerized using triethylamine (TEA). A proposed anionic polymerization mechanism is illustrated in Figure 9. The primary modes of termination are likely to be chain transfer to monomer or a solvent such as methanol (Figure 10). In ionic polymerizations, chain transfer to monomer is one of the most important chain-breaking reactions for most monomers, limiting the molecular weight, especially when the polymerization temperature is higher than approximately 20 °C.[40] It is important to note, however, that the kinetic chain is not terminated since a new propagating species is formed.

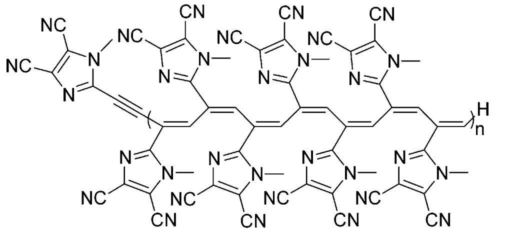
The polymerization 1-methyl-2-ethynyl-4,5-dicyanoimidazole **(8)** was investigated using rhodium-based catalysts, and the presence of the rhodium−norbornadiene end group was verified for the first time. The presence of such end groups was previously suggested by Kishimoto and co-workers but not confirmed.[15] Thus, a more complete mechanistic picture of rhodium-catalyzed acetylene polymerizations can now be proposed (Figure 11).

The dimeric rhodium catalyst $[Rh(nbd)Cl]_2$ dissociates to monomeric form when dissolved in the polymerization solvent (usually DMF or acetonitrile). The acetylene then coordinates with the rhodium center. The resulting vinylic complex is eliminated with the loss of H^+. The polymeric chain begins and grows by insertion of the π-coordinated acetylene monomer with the metal−carbon σ bond in the metal acetylide catalyst. Termination is likely via monomer chain transfer. Transfer may occur when the acidic acetylenic hydrogen is transferred from the π-coordinated monomer to the propagating chain (Figure 12).

Just as in the case of anionic polymerization, chain transfer to monomer limits the polymer molecular weight, especially when the polymerization temperature is increased.[40] The acidic acetylenic hydrogen of 1-methyl-2-ethynyl-4,5-dicyanoimidazole **(8)** implies that monomer chain transfer is very facile. Thus, the molecular weight is more severely limited, and the oligomeric

Table 4. NMR Shift Comparison of 1-(*p*-Methoxybenzyl)-2-ethynyl-4,5-dicyanoimidazole Oligomers

 Solid State NMR shifts for (**12**):
CH_2 (from norbornadiene) = 15-20 ppm
Bridgehead carbons (from norbornadiene) = 30-40 ppm
CH_2 (from p-methoxybenzyl protecting group) = 52-55 ppm
$-OCH_3$ (from p-methoxybenzyl protecting group) = 57 ppm
C≡C (from possible end group)= 70-90 ppm
C=C (from norbornadiene); backbone carbons; CN = 110-125 ppm
Aromatic carbons (from p-methoxybenzyl protecting group); carbons at 2, 4 and 5 position in dicyanoimidazole pendant group = 125-140 ppm
C=O (from residual DMF) = 162 ppm



$C_{64}H_{32}N_{32}$
Exact Mass: 1248.35
Mol. Wt.: 1249.15
C, 61.54; H, 2.58; N, 35.88

Total : 100
C/N : 1.72

Figure 7. Oligomers of 1-methyl-2-ethynyl-4,5-dicyanoimidazole **(11-N)**.

Table 5. Elemental Analysis Data of 11-N

	theoretical	expermental
C	61.54	61.09. 61.20
H	2.58	2.98, 2.87
N	35.88	34.55, 34.78
total	100	98.62, 98.85
C/N	1.72	1.77, 1.76

product results. This is consistent with other poly(phenylacetylene) derivatives reported in the literature. Phenylacetylenes with electron-withdrawing substituents (Cl or NO_2), and consequently more acidic acetylenic hydrogens, have lower molecular weights than other poly(phenylacetylene) derivatives.[23,25]

Table 6. Elemental Analysis Data of 11-Q

	theoretical $n = 6$		
	Rh(nbd)Cl end group	Rh(nbd)CH_2Cl_2 end group	experimental
C	57.22	56.25	53.02, 52.77
H	2.67	2.98	2.85, 2.84
N	29.66	28.26	27.04, 27.01
Rh	7.78	7.41	7.65, 7.65
total	97.33	94.90	90.56, 90.27
C/N	1.93	1.99	1.96, 1.95

Table 7. Elemental Analysis Data of 11-R

	theoretical $n = 3$		
	Rh(nbd)Cl end group	Rh(nbd)CH_2Cl_2 end group	experimental
C	54.85	53.17	51.04, 51.37
H	2.71	2.79	2.93, 2.78
N	26.24	24.80	25.47, 25.82
Rh	12.05	11.39	11.94, 11.94
total	95.85	92.15	91.38, 91.91
C/N	2.09	2.14	2.00, 1.99

EPR Characterization and Quantitation. The presence of unpaired electrons in undoped polyacetylene was detected using EPR over 20 years ago, but exactly how unpaired electrons are generated in undoped samples has been debated since the early 1980s.[41−44] Tabata suggests a radical mechanism for the temperature- and compression-promoted isomerization of the cis-transoidal to trans-transoidal microstructure based on electron spin resonance measurements.[22,25] Tabata asserts that the *g* value can be used to determine the cis or trans geometrical conformation.[27] Tabata has also suggested that the unpaired electrons are generated by "rotational scission of the C═C bond in the cis form during and/or after the polymerization."[21]

EPR quantitation experiments are complicated by a variety of factors such as differences in standards, sample preparation, and sample relaxation times.[45]

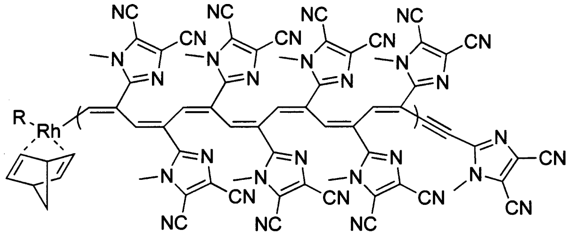


Figure 8. Model of 1-methyl-2-ethynyl-4,5-dicyanoimidazole oligomers **(11-Q**, **11-R)**.

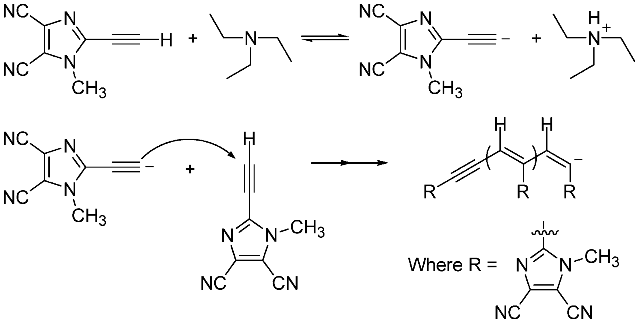


Figure 9. Proposed anionic initiation and propagation for 1-methyl-2-ethynyl-4,5-dicyanoimidazole **(8)**.

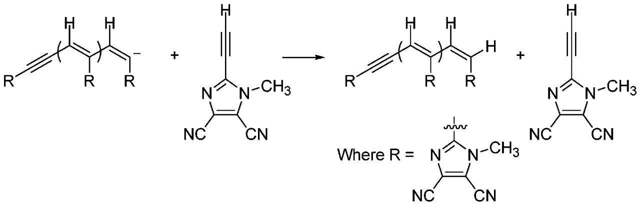


Figure 10. Proposed chain transfer termination.

Despite these difficulties, EPR has been used by Matyjaszewski and Zhu to quantify radical species in atom transfer radical polymerizations using paramagnetic standards such as copper(II) trifluoroacetylacetonate or copper(II) acetylacetonate.[46−50]

Variable temperature EPR and quantitation experiments were carried out on **11.** The temperature was increased from room temperature to 200 °C in 20 °C increments. There was a very slight decrease in the amplitude of the EPR signal upon heating. The decrease in EPR signal with increasing temperature for 1-methyl-2-ethynyl-4,5-dicyanoimidazole oligomers **(11)** can be related to chain length. As the temperature increases, the number of unpaired electrons increases. However, because the chain lengths are short, the unpaired electrons can recombine, thus decreasing the EPR signal with increasing temperature.

For the quantitation of unpaired electrons in **11**, copper(II) acetylacetonate was used as a standard. EPR spectra of the standard and quantitation details can be found in the Supporting Information. Table 8 list oligomers analyzed with EPR. For every unpaired electron in all three 1-methyl-2-ethynyl-4,5-dicyanoimidazole oligomer samples, there are approximately 10^3 repeat units or 10^2 oligomer chains. The concentration of unpaired spins is relatively small but easily observable. On the basis of these observations, we conclude that unpaired electrons are generated from carbon−carbon double bond twisting and possibly localized cis-to-trans isomerization in the chain backbone. Complete chain isomerization seems rather unlikely, especially for long polymer chains.

Cyclic Voltammetry. Cyclic voltammetry was used to investigate trends in reduction potentials for a variety of dicyanoimidazole derivatives. Because of extended conjugation and the electron-withdrawing ability of dicyanoimidazole pendant groups, the reduction of the backbone in 1-methyl-2-ethynyl-4,5-dicyanoimidazole oligomers **(11)** should be observed at more positive potentials compared to other dicyanoimidazole derivatives. For comparison purposes, several dicyanoimidazole derivatives were studied using cyclic voltammetry. The reduction potentials for these dicyanoimidazole derivatives were compared to **11** made using both rhodium-based complexes and amine initiators.

The reduction potential of 1-methyl-2-ethyl-4,5-dicyanoimidazole **(16)** occurs at $E_{1/2} = -3.46$ V (vs ferrocene). The reduction potentials for 1-methyl-2-vinyl-4,5-dicyanoimidazole **(14)** are more positive and can be observed at $E_{1/2} = -1.21$ and -3.06 V (vs ferrocene). The reduction of 1-methyl-2-ethynyl-4,5-dicyanoimidazole oligomers **(11-N)** occurs at even more positive potentials and can be observed $E_{1/2} = 0.41$ and -2.39 V (vs ferrocene). Reduction at a more positive potential reflects the ease of reduction for 1-methyl-2-ethynyl-4,5-dicyanoimidazole oligomers **(11)**.

Trends in reduction potentials for nitrile-substituted ethylenes illustrate the effect of electron-withdrawing substituents on reduction potential. The reduction potential becomes more positive with additional electron-withdrawing nitrile groups. Reduction potential trends are listed in Table 9.

Conclusions

In this work, the synthesis and optimization of the monomer 1-methyl-2-ethynyl-4,5-dicyanoimidazole **(8)** are reported for the first time. The role of catalyst, reaction time, and temperature were investigated. Increasing the amount of catalyst and extending the reaction time generally increased the polymer yield. A more complete mechanistic picture has been proposed for the transition-metal-catalyzed polymerization of acetylenes with electron-withdrawing substituents, and termination modes and end group possibilities are addressed. For the $[Rh(nbd)Cl]_2$ polymerization of 1-methyl-2-ethynyl-4,5-dicyanoimidazole **(8)**, we propose termination occurs via chain transfer to the acidic acetylenic monomer or solvent. We also propose that the rhodium−norbornadiene group serves as an end group on the polymer chain. In addition, we verified and quantified unpaired electrons in 1-methyl-2-ethynyl-4,5-dicyanoimidazole oligomers **(11)** and related their presence to chain length and temperature. Finally, the reduction potentials of 1-methyl-2-ethynyl-4,5-dicyanoimidazole oligomers **(11)** were observed at more positive potentials than the monomeric reference compounds.

Experimental Section

Methods. ^{1}H NMR spectra were collected with Varian 300 and 400 MHz field instruments and referenced to the residual solvent resonance. ^{13}C NMR were collected at 100 MHz and referenced to the residual solvent resonance. All solid-state NMR spectra were collected using a Bruker DSX 300 MHz spectrometer and a 4 mm double-resonance MAS probe. Solid samples were packed in 4 mm o.d. zirconia rotors and spun about the magic angle at 5−6 kHz. FT-IR spectra were collected with a Perkin-Elmer Spectrum BX FT-IR system. Mass spectra were collected with a Micromass V6 70-250-5 magnetic sector mass spectrometer, using electron impact

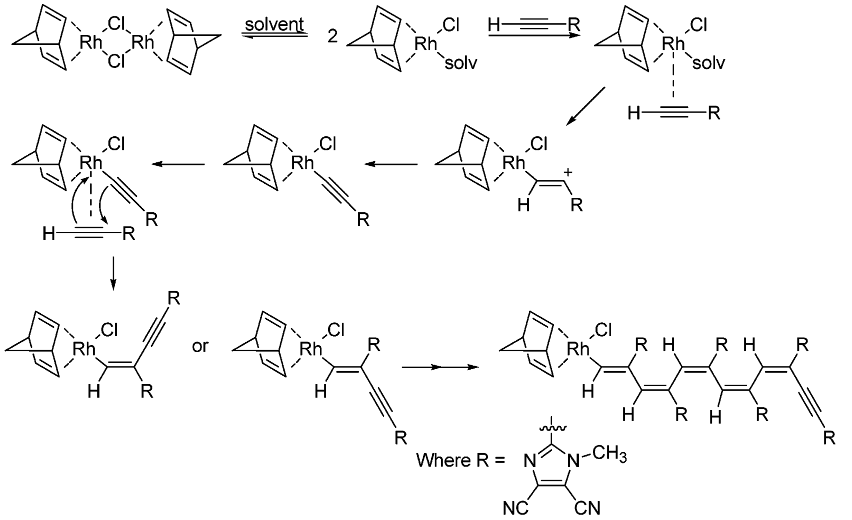


Figure 11. Proposed rhodium-catalyzed polymerization mechanism for 1-methyl-2-ethynyl-4,5-dicyanoimidazole **(8)**.

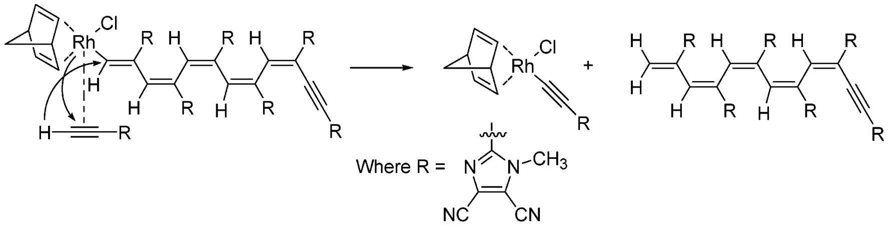
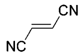
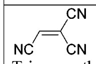
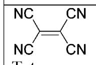


Figure 12. Proposed termination via monomer chain transfer.

Table 8. Oligomers for EPR Study

	catalyst	M:cat	solvent	time (h)	temp (°C)
11-N	TEA	20:1	CH_3CN	24	65
11-Q	$[Rh(nbd)Cl]_2$	20:1	DMF	48	0
11-R	$[Rh(nbd)Cl]_2$	20:1	CH_3CN	48	0

Table 9. Trends in Reduction Potentials for Nitrile-Containing Ethylenes

Compound:	$E_{1/2}$ (V) vs. ferrocene:*
 Dicyanoethylene OR fumaronitrile	-1.23[51]
 Tricyanoethylene	-0.70[52]
 Tetracyanoethylene OR TCNE	0.13[53]; 0.20[52]

[a] The reported potentials were converted to the ferricenium/ferrocene (Fc^+/Fc) = 0 V reference using standard reduction potentials vs NHE: 0.24 V (SCE), 0.40 (Fc^+/Fc), and 0.80 (Ag^+/Ag).[54]

(70 eV), fast atom bombardment, or chemical ionization (ammonia) for ionization. GCMS spectra were collected using a HP 5890 GC system coupled with a Finnigan automated GC/EI-CI mass spectrometer system. EPR spectra were collected using a Varian system with a regulated magnetic power supply, a Varian V-4540 variable temperature controller, and a Bruker ER 041MR microwave bridge controller. CV was done using a Princeton Applied Research potentiostat/galvanostat model PAR 263A interfaced with Powersuite software. The solvent was dry acetonitrile or DMSO, and the supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate ($NBu_4^+PF_6^-$) using a Pt button working electrode, a Pt wire counter electrode, and a Ag/$AgNO_3$ (0.01 M) reference electrode. UV spectra were collected with a Shimadzu UV-160U or UV-1601 spectrometer with baseline correction. GPC was used to determine molecular weights and molecular weight distributions of samples with respect to polystyrene standards. The GPC system uses NMP as a solvent and 100 and 3000 Å PSS GRAM gel columns. Viscosity measurements were made using a Cannon (100-388H) viscometer. Melting points were collected with a Mel-Temp and are uncorrected. Elemental analyses were collected with a Perkin-Elmer CHN 2400. Rhodium analysis was contracted to Galbraith Laboratories. TLC was performed on Whatman silica gel plates with a 250 μm layer and fluorescent indicator. TGA data were collected with a Perkin-Elmer TGA 7. DSC data were collected with a Perkin-Elmer DSC-7.

THF was dried with sodium/benzophenone before use. Acetonitrile was distilled from calcium hydride before use. DMSO-d_6 and DMSO were normally used with residual water present; if dryness was required, the DMSO was frozen, and the unfrozen residual water was decanted. Trimethylsilylacetylene was purchased from GFS Chemicals. All rhodium-, palladium-, and nickel-based transition-metal catalysts were purchased from Strem Chemicals. All other reagents and solvents were purchased from Aldrich or Fisher Scientific.

Characterization. 1-Methyl-2-(trimethylsilylacetylene)-4,5-dicyanoimidazole (7). A three-neck, 500 mL round-bottom flask fitted with a magnetic stir bar and condenser was charged with 9.00 g (42 mmol) of 1-methyl-2-bromo-4,5-dicyanoimidazole **(5)**. Upon addition of 225 mL of freshly distilled THF, the mixture was stirred to dissolve the dicyanoimidazole solid. Via syringe, 9.0 mL (63 mmol) of triethylamine was added to the flask along with 9.45 mL (63 mmol) of trimethylsilylacetylene. To an angled solid addition funnel, 252 mg (1.3 mmol) of copper(I) iodide and 0.900 g (1.3 mmol) of $PdCl_2(PPh_3)_2$ were measured. The solid addition funnel was attached to the round-bottom flask, and a nitrogen/vacuum line was attached to the remaining open neck. The flask was evacuated with reduced pressure and then purged with nitrogen gas for a minimum of 15 min. The flask was immersed in a 65 °C oil bath, and the solids were added. The reaction was allowed to stir under nitrogen for 24 h. The reaction mixture was evaporated down to a dark oil under reduced pressure. To the dark oily residue, 300 mL of 10% acetone in ether was added along with activated charcoal. The mixture was stirred at room temperature for approximately 2 h. The mixture was filtered through a 1.5 in. pad of neutral alumina and rinsed with copious amounts of 10% acetone in ether. The filtrate was evaporated under reduced pressure to give a brown residue. For additional purification, the solid was stirred with warm ethanol and activated charcoal. The mixture was filtered through Celite. The combined yield was approximately 75%. Note: this product cannot be recrystallized by standard means as it will spontaneously deprotect and polymerize.

FW (calcd) 228.3 g/mol; mp 106−110 °C; TLC R_f 0.69 (50/50 hexanes/ethyl acetate). ^{1}H NMR (400 MHz; DMSO-d_6) δ (ppm): 0.29 (s, 9H, $(CH_3)_3$), 3.80 (s, 3H, CH_3). IR (KBr Pellet, cm^{-1}): 2963, 2904, 2239, 1628, 1456, 1391, 1252, 875, 848, 764. CHN Analysis: Anal. Calcd for $C_{11}H_{12}N_4Si$: C, 57.86; H, 5.30; N, 24.54. Found: C, 57.91; H, 5.30; N, 24.85.

1-Methyl-2-ethynyl-4,5-dicyanoimidazole (8). A 250 mL Erlenmeyer flask fitted with a magnetic stir bar was charged with 5.0 g (22 mmol) of 1-methyl-2-(trimethylsilylacetylene)-4,5-dicyanoimidazole **(7)**. To dissolve the solid, 150 mL of distilled tetrahydrofuran was added to the flask. Upon adding 4.13 g (44 mmol) of potassium fluoride dihydrate to the flask, the deprotection process was monitored by TLC. The reaction was stirred at room temperature for no more than 2 h. The mixture was filtered through a pad of neutral alumina, and the filtrate was evaporated down under reduced pressure to give a brown solid consisting of the target product and oligomers. For purification, the crude monomer was rinsed with copious amounts of 20% ethyl acetate in hexanes. The mixture was filtered, and the filtrate was evaporated down to give a 90% combined yield of light yellow solid. Note: this product cannot be recrystallized by standard means as it will polymerize. Very small amounts of monomer can be recrystallized with ether or sublimed carefully. Any heating (>40 °C) appears to polymerize the monomer. In addition, evidence suggests that the monomer may undergo photopolymerization. The product should be stored in an amber vial.

FW (calcd) 156.15 g/mol; mp 97−98 °C; TLC R_f 0.38 (50/50 hexanes/ethyl acetate). ^{1}H NMR (400 MHz; DMSO-d_6) δ (ppm): 3.82 (s, 3H, CH_3), 5.16 (s, 1H, CH). ^{13}C NMR (100 MHz; DMSO-d_6) δ (ppm): 34.33 (CH_3), 70.20 (β), 88.58 (α), 108.25 (C5), 111.90 (C4), 114.04 (CN at C5), 120.01 (CN at C4), 134.99 (C2). IR (KBr pellet, cm^{-1}): 3268, 2953, 2242, 2131, 1469, 1394, 1323, 726, 714, 697, 667. CHN Analysis: Anal. Calcd for $C_8H_4N_4$: C, 61.54; H, 2.58; N, 35.88. Found: C, 61.60; H, 2.91; N, 33.94. UV/vis (CH_3CN) λ_{max} (ϵ) (nm, M^{-1} cm^{-1}): 256.0 (19 200)

2-Ethynyl-4,5-dicyanoimidazole (10). A 100 mL Erlenmeyer flask fitted with a magnetic stir bar was charged with 0.350 g (1.33 mmol) of 1-(*p*-methoxybenzyl)-2-(ethynyl)-4,5-dicyanoimidazole **(9)**. The solid was dissolved in 15 mL of 3:1 acetonitrile/water. In a separate 20 mL glass vial, 2.93 g (5.34 mmol) of ceric ammonium nitrate (CAN) was dissolved in 5 mL of 3:1 acetonitrile/water. The ceric ammonium nitrate solution was added to the Erlenmeyer flask and heated at 50 °C for 17 h. The reaction was monitored with TLC. The presence of *p*-anisaldehyde confirmed the reaction was progressing. After the reaction was complete, the acetonitrile was evaporated off under reduced pressure. The residue was treated with ethyl acetate and water and rinsed with a saturated solution of sodium bicarbonate (3 × 20 mL). The aqueous layer was back-extracted with ethyl acetate (2 × 20 mL). The white ceric hydroxide precipitate was then filtered from the combined aqueous layer. The aqueous filtrate was acidified slowly with hydrochloric acid. The acidified solution was then extracted with ethyl acetate (3 × 20 mL). The combined organics were dried over magnesium sulfate. The drying agent was filtered, and the resulting filtrate was evaporated under reduced pressure to give a 80% yield of yellow waxy solid. Note: *p*-anisaldehyde continues to contaminate the monomer. Additional purification did not completely remove the aldehyde.

FW (calcd) 142.12 g/mol; TLC R_f 0.05 (50/50 hexanes/ethyl acetate). ^{1}H NMR (400 MHz; DMSO-d_6) δ (ppm): 4.72 (s, 1H, CH). IR (KBr pellet, cm^{-1}): 3200−2700 hydrogen-bonding complexity, 2248, 2132, 1383, 1262, 1097, 1022, 800.

1-(*p*-Methoxybenzyl)-2-ethynyl-4,5-dicyanoimidazole (9). A 500 mL Erlenmeyer flask fitted with a magnetic stir bar was charged with 5.00 g (14.9 mmol) of 1-(*p*-methoxybenzyl)-2-(trimethylsilylacetylene)-4,5-dicyanoimidazole. To dissolve the solid, 250 mL of distilled tetrahydrofuran was added to the flask, and the solution was stirred until the solid dissolved. Upon adding 2.80 g (29.8 mmol) of potassium fluoride dihydrate to the flask, the deprotection process was monitored by TLC. The reaction was stirred at room temperature for no more than 2 h. The mixture was gravity filtered through a pad of neutral alumina, and the filtrate was evaporated down under reduced pressure. For purification, the oil was repeatedly rinsed with 10% ethyl acetate in hexanes. The solution was evaporated under reduced pressure to give the first portion of amber oil. The second and third portions were recovered by repeated washings with 20−30% ethyl acetate in hexanes. The combined portions of amber oil gave a 73% yield. Further purification can be achieved by recrystallization with methanol to give a tan yellow solid. This recrystallization proved to be quite difficult and did not work very well on larger scales. The purity of the amber oil is quite good, however, as indicated by NMR. The oil product was used for additional reactions.

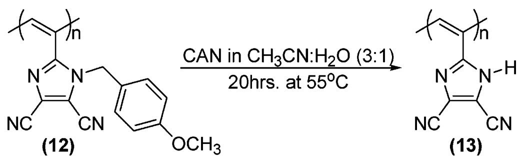
FW (calcd) 262.27 g/mol, generally amber oil; mp 70−74 °C (recrystallized from methanol); TLC R_f 0.48 (50/50 hexanes/ethyl acetate). ^{1}H NMR (400 MHz; acetone-d_6) δ (ppm): 3.73 (s, 3H, CH_3), 5.13, (s, 1H, CH), 5.44 (s, 2H, CH_2), 6.95, 6.98 (d, 2H, aromatic ring), 7.28, 7.31 (d, 2H, aromatic ring). IR (NaCl plate, cm^{-1}): 3267, 2959, 2838, 2241, 2128, 1611, 1585, 1514, 1467, 1407, 1345, 1306,1254, 1179, 1118, 1031, 847, 807.

Typical Oligomerization of Acetylenic Monomers with TEA. A 25 mL three-neck round-bottom flask fitted with a stir bar was charged with 0.67 mmol of acetylenic monomer **(8** or **9)**. To dissolve the monomer, 7.5 mL of distilled acetonitrile was added to the flask. A vacuum/nitrogen line, condenser, and rubber septum were attached to the flask and secured. The flask was evacuated with reduced pressure and purged with nitrogen for 15 min. Via syringe, 0.14 mL (0.96 mmol) of triethylamine was injected through the rubber septum and into the solution. The flask was immersed in a 65 °C oil bath and stirred for 24 h. The apparatus was removed from heat and allowed to cool to room temperature. The acetonitrile was evaporated off under reduced pressure to give a dark residue. The residue was washed with 10% acetone in ether to extract residual monomer in the polymer sample. The dark solid was dried overnight under reduced pressure.

Typical Oligomerization of Acetylenic Monomers with $[Rh(nbd)Cl]_2$. A clean, dry two-neck, 25 mL round-bottom flask was fitted with a stir bar and vacuum/nitrogen line and charged with 0.76 mmol of acetylenic monomer (**8** or **9**). The solid was dissolved in 1.8 mL of DMF, and the open neck was sealed with a rubber septum. The flask was evacuated under reduced pressure and purged with nitrogen several times. A clean, dry vial was charged with 0.017 g (0.038 mmol) of $[Rh(nbd)Cl]_2$, and 2 mL of DMF was added. The mixture was stirred until the catalyst completely dissolved. After 10 min, the catalyst solution was injected into the monomer solution and allowed to stir for 48 h in an ice−water bath. After the 48 h period, the reaction solution was concentrated under reduced pressure. Ether or methylene chloride was added to the residue, and the mixture was centrifuged (or gravity filtered). After decanting off the solution, the solid was again rinsed with ether or methylene chloride and centrifuged. The dark brown/black product was dried under reduced pressure overnight.

Deprotection of Poly[1-(*p*-methoxybenzyl)-2-ethynyl-4,5-dicyanoimidazole] (12). A 50 mL Erlenmeyer flask fitted with a magnetic stir bar was charged with 0.050 g of poly[1-(*p*-methoxybenzyl)-2-(ethynyl)-4,5-dicyanoimidazole] (**12**). The solid was dissolved in 20 mL of 3:1 acetonitrile/water. In a separate 20 mL glass vial, 0.417 g (0.76 mmol) of ceric ammonium nitrate was measured. The ceric ammonium nitrate was added to the Erlenmeyer flask and heated at 55

Scheme 5. Deprotection of Poly[1-(*p*-methoxybenzyl)-2-ethynyl-4,5-dicyanoimidazole] (12)



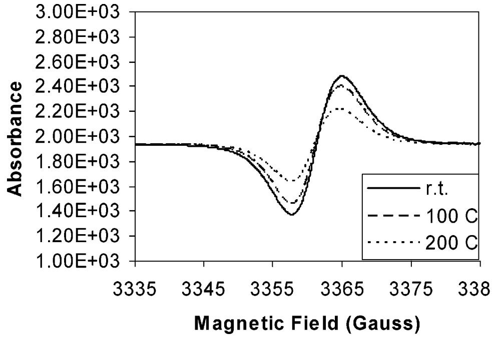
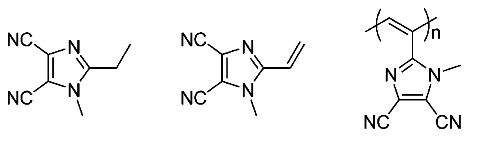


Figure 13. Variable temperature EPR of 1-methyl-2-ethynyl-4,5-dicyanoimidazole oligomers **(11)** at gain = 3.2 × 10^4.



(16) $E_{1/2}$ = -3.46V

(14) $E_{1/2}$ = -1.21V; -3.06

(11) $E_{1/2}$ = 0.41V; -2.39V

Figure 14. Summary of reduction potentials of dicyanoimidazole derivatives and 1-methyl-2-ethynyl-4,5-dicyanoimidazole oligomers; Fc^+/Fc = 0 V.

°C for 19 h. The reaction was monitored with TLC. The presence of *p*-anisaldehyde in TLC confirmed the reaction was progressing as it is a product of oxidative *p*-methoxybenzyl deprotection. After the reaction was complete, the acetonitrile was evaporated off under reduced pressure. The residue was treated with ethyl acetate and water and rinsed with a 10% solution of potassium bicarbonate (3 × 20 mL). The aqueous layer was back-extracted with ethyl acetate (2 × 20 mL). The white ceric hydroxide precipitate was then filtered from the combined aqueous layer. The aqueous filtrate was acidified slowly with hydrochloric acid. The acidified solution was then extracted with ethyl acetate (3 × 20 mL). The combined organics were dried over magnesium sulfate. The drying agent was filtered, and the resulting filtrate was evaporated under reduced pressure, yielding **(13)**.

EPR Parameters. The variable temperature EPR spectra were collected under the following conditions: gain = 2.5 × 10^5, modulation = 2.5 G_{pp}, time constant = 200 ms, center field = 3365 G, sweep width = 50 G, modulation frequency = 100 kHz, phase = 0°, sweep time = 50 s, microwave frequency = 9.41 GHz, microwave power = 208 μW, attenuation = 30 dB, and temperature = r.t. to 200 °C in 20° increments. To quantify the unpaired electron, copper(II) acetylacetonate was used as a standard. The EPR spectrum of solid copper(II) acetylacetonate was collected under the following conditions (the same conditions were used for oligomer samples): gain = 2.5 × 10^5 and 10 × 10^5, modulation = 5 G_{pp}, time constant = 200 ms, center field = 3300 G, sweep width = 1000 G, modulation frequency = 100 kHz, phase = 0°, sweep time = 50 s, microwave frequency = 9.74 GHz, microwave power = 208 μW, attenuation = 30 dB, and temperature = r.t.

Acknowledgment. We are grateful to Joe Gallegos and Prof. Anthony H. Francis for sharing their EPR expertise. We thank Dr. Joel Nemes and Prof. M. D. Curtis for cyclic voltammetry assistance and Erin Wimmers of Prof. Larry Beck's lab for solid-state NMR assistance. We also acknowledge support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and from the General Motors Corp.

Supporting Information Available: Details on the synthesis of additional dicyanoimidazole derivatives, EPR spectra of standards and oligomers, and cyclic voltammagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA035920R