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Preparation of Poly(cyanoacetylene) Using Late-Transition-Metal Catalysts

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ABSTRACT: Poly(cyanoacetylene) has been prepared by polymerization of cyanoacetylene using a variety of late-transition-metal (Pd- and Ni-based) catalysts. The effect of reaction conditions on molecular weight and polymer yield was explored. Significant catalyst residues remain in the polymer samples. However, spectra are consistent with the proposed poly(cyanoacetylene) structure. Notable differences in molecular weight, effective conjugation length, and ability to undergo thermal cyclization to a supposed aromatic ladder polymer were observed between these polymers and those prepared using conventional anionic or radical initiators.

Introduction

Poly(cyanoacetylene) has been an intriguing molecule for two reasons. First, the presence of the strongly electron withdrawing cyano group on alternate carbons should render the conjugated polymer backbone in this molecule extremely easy to reduce (a so-called n-dopable polymer). Although many conjugated polymers are oxidized in a straightforward manner, few are easily and cleanly reduced.[1,2] Second, in the trans-transoidal microstructure (Figure 1), poly(cyanoacetylene) should be poised to cyclize to an aromatic-type ladder structure. Such poly(acene)-type structures have been predicted to be intrinsic conductors (e.g., not requiring oxidation or reduction of the material to become metallic).[3−6] To date, however, although several other aromatic-type ladder polymers have been reported,[7−28] no convincing evidence of this very simple, poly(acene)-type ladder structure has been presented.

Cyanoacetylene has been polymerized using a variety of catalysts including bases/anions, γ-ray initiated radicals, and Ziegler−Natta catalysts.[29−48] The yield and molecular weights of polymer produced with these catalysts have been generally unreported or low. Reports of the appearance of the polymer have varied as well. γ-ray initiated radical polymerization also produced low yields of poly(cyanoacetylene).[38,48] Polymer produced this way was reported to be blue-purple in color, as compared to the black or brown polymers produced by the previously mentioned systems. Although the polymers produced by γ-rays did not exhibit any significant structural differences as determined by infrared or NMR spectroscopy, compared to poly(cyanoacetylene) synthesized via anionic, Ziegler−Natta, or metathesis catalysts, these differences in optical absorption indicate that poly(cyanoacetylene) prepared by most routes has a low effective conjugation length.[49,50] This low effective conjugation length could be due to low molecular weight or due to twisting of the polymer chain. Poly(cyanoacetylene) can, in principle, exist in four microstructural forms (Figure 2). Steric interactions in all but the trans-transoidal structure would probably result in a nonplanar chain that will reduce effective conjugation.

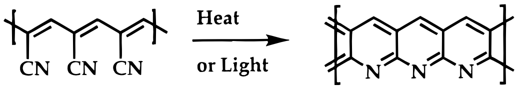

Figure 1. Schematic for the cyclization of *trans*-transoidal poly(cyanoacetylene).

Because substantial structural uncertainty exists in the poly(cyanoacetylene) samples previously reported, and because few good routes exist for the synthesis of this polymer in reasonable yield, we sought to explore other routes for the synthesis of poly(cyanoacetylene).

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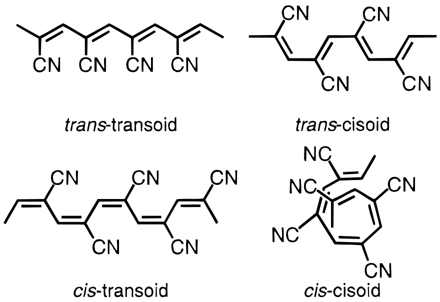

Figure 2. Possible microstructures for poly(cyanoacetylene) assuming a strictly head-to-tail polymerization.

In particular, we sought to explore catalyst systems that might have good functional group tolerance. Several of the catalyst systems previously employed for the polymerization of cyanoacetylene (in particular the Ziegler−Natta catalysts and alkyllithium catalysts) are documented to have poor tolerance of functional groups. The cyano group in the monomer is sufficiently reactive to make this a valid concern.

Nickel salts are well-known to cyclotrimerize, cyclotetramerize, and to polymerize acetylene, producing benzene, cyclooctatetraene, and amorphous presumably low molecular weight poly(acetylene).[51−54] Recently, there have been several reports of the polymerization of acetylene derivatives using late-transition-metal catalysts based on rhodium,[55−72] palladium, and nickel.[73−82] Late-transition-metal catalysts are particularly attractive as they tend to exhibit greater functional group tolerance than the more electron-deficient early-transition-metal catalysts. To our knowledge, these catalysts have not been applied to the synthesis of poly(cyanoacetylene).

Results and Discussion

In this paper, we show that nickel and palladium complexes can initiate the polymerization of cyanoacetylene. The poly(cyanoacetylene) produced has a dramatically different effective conjugation length depending on the catalyst employed. This is ascribed to a difference in molecular weight rather than a difference in polymer microstructure for reasons detailed below. The polymer appears to have substantial residual catalyst incorporated into it, a feature noted previously by others when using late-transition-metal catalysts for acetylene polymerization.[74−80] Nevertheless, the polymers could be characterized as poly(cyanoacetylene), and several distinct influences of the reaction conditions on the polymer yield are noted.

A. General Catalyst Survey. Several common nickel and palladium salts and complexes were reacted with cyanoacetylene, and all were found to produce some amount of polymer. Several catalysts were surveyed and the results are presented in Table 1. For this initial survey, all reactions were run in dimethyl sulfoxide (DMSO) at room temperature for 24 h at a monomer-to-catalyst ratio of 100:1. The resulting poly(cyanoacetylene) samples were sparingly soluble, but were soluble enough to give highly colored solutions. Molecular weights were determined using size exclusion chromatography with UV/vis detection at 350 nm.

Table 1. Polymerization of Cyanoacetylene Utilizing Several Catalysts

catalyst	% yield	M_w	M_n	PDI[a]
rhodium complexes				
$[(nbd)RhCl]_2$[b]	26	9 200	2 500	3.7
nickel complexes				
$Ni(PPh_3)_4$	37	36 000	10 600	3.4
$(PPh_3)_2NiCl_2$	35	14 500	8 800	1.7
$(dppe)NiCl_2$[c]	30	21 900	11 500	1.9
$(dppp)NiCl_2$[d]	46	27 700	7 300	3.8
$(bpy)NiCl_2$[e]	18	18 600	9 000	2.1
$NiCl_2$	16	10 500	6 600	1.6
$NiBr_2$	11	16 300	8 700	1.9
palladium complexes				
$Pd(CH_3CN)_4(BF_4)_2$	60	3 000	1 600	1.9
$(PPh_3)_2PdCl_2$	30	10 400	6 700	1.6
$Pd_2(dba)_3$[f]	21	16 700	7 900	2.1
$(diimine)Pd(CH_3CN)_2$[g]	12	9 600	4 300	2.2
Ni/Pd alkyls				
$(bpy)NiMe_2$[e]	15	9 900	5 400	1.8
(bpy)NiMe(succ)[eh]	5	6 700	5 000	1.3
$(duphos)NiMe_2$	30	6 600	3 800	1.7
$(diimine)PdMe_2$[g]	23	6 600	4 200	1.6
(diimine)PdMeCl[g]	19	7 600	4 700	1.6
anionic/basic				
Et_3N[i]	40	14 000	2 500	5.7
n-BuLi, 0 °C[j]	64	10 800	2 100	5.2
n-BuLi, −78 °C[j]	79	11 400	3 800	3.0
NaCN[k]	79	10 300	2 500	4.1
PPh_3	10	10 500	6 400	1.7
$PPh_3/MeAl(OBHT)_2$[l]	63	6 800	3 900	1.7

[a] PDI = polydispersity index (M_w/M_n). [b] nbd = norbornadiene. [c] dppe = 1,2-bis(diphenylphosphino) ethane. [d] dppp = 1,3-bis(diphenylphosphino)propane. [e] bpy = 2,2′-bipyridine. [f] dba = dibenzylidene acetone. [g] diimine = ArN=C(Me)-C(Me)=NAr, Ar = 2,6-$C_6H_3(i\text{-}Pr)_2$. [h] succ = succinimide. [i] Reaction was run neat. [j] Reaction was run in toluene. [k] Reaction was run in dimethylformamide. [l] OBHT = 2,6-di-*tert*-butyl-4-methyl phenol.

Although rhodium chloro norbornadiene dimer has been used in the polymerization of a number of phenylacetylene derivatives,[55−72] nickel and palladium complexes were found to give generally higher yields and molecular weights. The catalyst $Pd(CH_3CN)_4(BF_4)_2$ has been shown to polymerize phenylacetylene and methyl propiolate.[73] This catalyst produced relatively low molecular weight polymer for cyanoacetylene. Considering the various nickel and palladium catalysts employed, in general, nickel-based catalysts gave higher molecular weight polymer than did palladium-based catalysts. Nickel and palladium complexes can undergo phosphine dissociation,[83,84] and free phosphine might act as an independent initiator. However, this pathway does not appear to be a dominant mode of initiation as polymerization with triphenylphosphine alone as initiator resulted in little polymer. Of the few metal alkyls surveyed, results with these catalysts are not exceptional. This observation suggests that insertion into the metal−methyl bond probably was not the operative initiation step in this polymerization.

The results of several polymerizations conducted using anionic or basic catalysts are also presented in Table 1. In general, these catalysts give comparable or higher yields of polymer than those obtained using nickel and palladium catalysts. These polymers have reasonably high molecular weights. However, polydispersities of these polymers are also high, suggesting sluggish and/or multiple initiation pathways.

B. Effect of Reaction Conditions. Although the results obtained above were intriguing, relatively low reaction yields prompted further exploration of the effect of reaction conditions on the polymerization. First, several variations of solvent and monomer concentration were explored. Poly(acetylenes) are generally not very soluble,[50] and it was suspected that the poly(cyanoacetylene) produced was only sparingly soluble. Table 2

Table 2. Effect of Solvent and Solubilizing Agents on Cyanoacetylene Polymerization

catalyst	solvent	[Monomer][a] (M)	% yield	M_w	M_n	PDI[b]
$Ni(PPh_3)_4$	toluene	1.5	15	4 100	600	6.5
$Ni(PPh_3)_4$	DMSO[c]	1.5	37	36 000	10 600	3.4
$(PPh_3)_2NiCl_2$	DMF[d]	1.5	47	13 300	6 700	2.0
$(PPh_3)_2NiCl_2$	DMSO	1.5	33	14 500	8 800	1.7
$(PPh_3)_2NiCl_2$	DMSO	0.6	51	13 900	9 700	1.4
$(PPh_3)_2NiCl_2$	DMSO	0.3	67	23 700	15 700	1.5
$(PPh_3)_2NiCl_2/ZnCl_2$[e]	DMSO	1.5	22	17 000	8 200	2.1
$(PPh_3)_2NiCl_2/LiBr$[e]	DMSO	1.5	18	11 300	7 200	1.6
$(PPh_3)_2NiCl_2/LiBr$[e]	DMF	1.5	48	20 400	9 200	2.2
$NiCl_2{\cdot}6H_2O$	H_2O	3.0	1	15 600	8 100	1.9
$NiCl_2{\cdot}6H_2O$	H_2O/SDS[f]	3.0	1	17 400	10 700	1.6
$Pd(CH_3CN)_4(BF_4)_2$	H_2O	3.0	6	4 500	1 800	2.5
$Pd(CH_3CN)_4(BF_4)_2$	H_2O/SDS[f]	3.0	7	4 500	1 200	3.8

[a] Monomer concentration at the beginning of the reaction. [b] PDI = polydispersity index (M_w/M_n). [c] DMSO = dimethyl sulfoxide. [d] DMF = dimethylformamide. [e] Monomer:Lewis acid ratio of 10:1. [f] SDS = sodium dodecyl sulfate.

Table 3. Results of Polymerization at Various Temperatures

catalyst	temp (°C)	% yield	M_w	M_n	PDI
$Pd(CH_3CN)_4(BF_4)_2$	−50	34	4 500	1 300	3.4
$Pd(CH_3CN)_4(BF_4)_2$	25	68	7 300	1 500	5.0
$Pd(CH_3CN)_4(BF_4)_2$	75	95	8 300	3 500	2.4
$Ni(PPh_3)_4$	−50	38	28 800	7 400	3.9
$Ni(PPh_3)_4$	25	37	30 900	6 200	5.0
$Ni(PPh_3)_4$	75	67	15 800	11 000	1.4

Table 4. Variation of Monomer/Catalyst Ratio for $(PPh_3)_2NiCl_2$-Catalyzed Polymerizations of Cyanoacetylene

[mon]/[cat]	% yield	M_w	M_n	PDI
25	73	12 400	7 600	1.6
50	46	11 400	7 500	1.5
100	33	14 500	8 800	1.7
150	11	14 700	8 600	1.7
200	12	13 200	9 400	1.4

Table 5. Time Course of the Polymerization for $(PPh_3)_2NiCl_2$-Catalyzed Polymerizations of Cyanoacetylene

time (h)	% conv	M_w	M_n	PDI
1	28	34 800	12 000	2.9
3	34	34 700	11 400	3.0
6	28	51 600	13 300	3.9
12	33	61 500	13 400	4.6
24	36	48 800	9 400	5.2

shows the results of polymerization using a variety of solvents and potential solubilizing agents. Reactions were again conducted at a monomer-to-catalyst ratio of 100:1 at room temperature for 24 h.

When the polymerization reaction was run in toluene, immediate precipitation was observed. Concomitantly, both the yield and molecular weight of this sample were low and the polydispersity was high. This behavior is attributed to poor solubility of the polymer in toluene. Polymer solubility also probably governs the relative yield in other solvents as well. For example, when $(PPh_3)_2NiCl_2$ was used as catalyst in DMSO solution (Table 2), the yield and molecular weight of polymer consistently increased as the concentration of monomer (and polymer) decreased. It was hypothesized that addition of a Lewis acid might increase polymer solubility and improve the reaction yield.[85−87] However, the Lewis acids lithium bromide and zinc bromide did not appear to affect the polymerization. The polymerization was also attempted in an emulsion.[65] These trials were also unsuccessful at producing much polymer (Table 2).

The effect of reaction temperature was also explored. Results of these experiments are shown in Table 3. Reactions were conducted using a monomer-to-catalyst ratio of 100:1 for 24 h in DMSO. In general, it was observed that increased temperature resulted in greater polymer yield with no compromise in molecular weight for the palladium-catalyzed reaction. The nickel-catalyzed reactions did increase in yield when the reaction temperature was raised from 25 to 75 °C. However, this increase in yield was at the expense of a lower molecular weight. From the change in color versus time, it was noted empirically that the nickel-catalyzed reactions proceeded more rapidly than the palladium-catalyzed reactions at all temperatures studied.

These data are consistent with a mechanism for the nickel-catalyzed polymerizations in which the rate of initiation is increased with increasing temperature. Specifically, increased initiation should result in an increased number of polymer chains, reflected by a higher yield, lower molecular weight, and lower polydispersity. This behavior was observed here. The role of autopolymerization in these trials is, admittedly, undefined. However, it is probably low as autopolymerization generally results in sporadic initiation and broad polydispersities. Here, the polydispersity of the molecular weights in these samples is lowest at the highest polymerization temperatures.

The data presented above suggest that, although the nickel-catalyzed polymerizations can give high molecular weight poly(cyanoacetylene), the efficiency of initiation is poor. Recognizing that inefficient initiation will result in poor yield of polymer, particularly at high monomer-to-catalyst ratios, a set of experiments was conducted where the monomer-to-catalyst ratio was varied to optimize the yield of polymer. The results are shown in Table 4. Reactions were conducted as before.

As expected, polymer yield steadily increased with decreasing monomer-to-catalyst ratio. The molecular weight of the polymer was largely unchanged. This behavior is typical in a system where the rate of initiation is slow relative to the rate of propagation.

It was suspected that the polymerization did not require the full 24 h previously allotted to go to completion. To test this hypothesis, polymerizations were run for varying lengths of time. The results are reported in Table 5. Indeed, on the basis of yield and molecular weight, the polymerization is largely complete in approximately 1 h. Broadening of the molecular weight distribution for longer polymerization times suggests that possibly other routes for polymerization (e.g., autopolymerization or polymerization by dissociated phosphine) might take place as the reaction

Table 6. Elemental Analysis Results

conditions	$Pd(CH_3CN)_4(BF_4)_2$ catalyzed reaction C	H	N	$Ni(PPh_3)_4$ catalyzed reaction C	H	N
no Soxhlet	55.73	3.53	18.59	54.62	3.88	13.05
EtOH Soxhlet, 6 h	54.88	3.05	18.85	63.21	3.57	15.14
THF Soxhlet, 6 h	56.58	3.22	18.61	56.73	4.10	12.91
THF Soxhlet, 12 h	57.57	3.24	18.93	58.37	4.18	12.88
THF Soxhlet, 12 h, then 100 °C 24 h	57.22	2.83	19.91	57.54	3.54	13.94
THF Soxhlet, 12 h, then 100 °C 48 h	57.86	2.75	20.23	ND[a]	ND	ND
no Soxhlet, 100 °C 24 h	ND	ND	ND	62.89	3.52	13.29
no Soxhlet, 120 °C 48 h	56.98	2.89	19.87	63.96	3.57	16.04
no Soxhlet, 140 °C 48 h	56.35	2.49	20.51	54.14	3.22	14.13
theoretical	70.59	1.97	27.44	70.59	1.97	27.44

[a] ND = not determined.

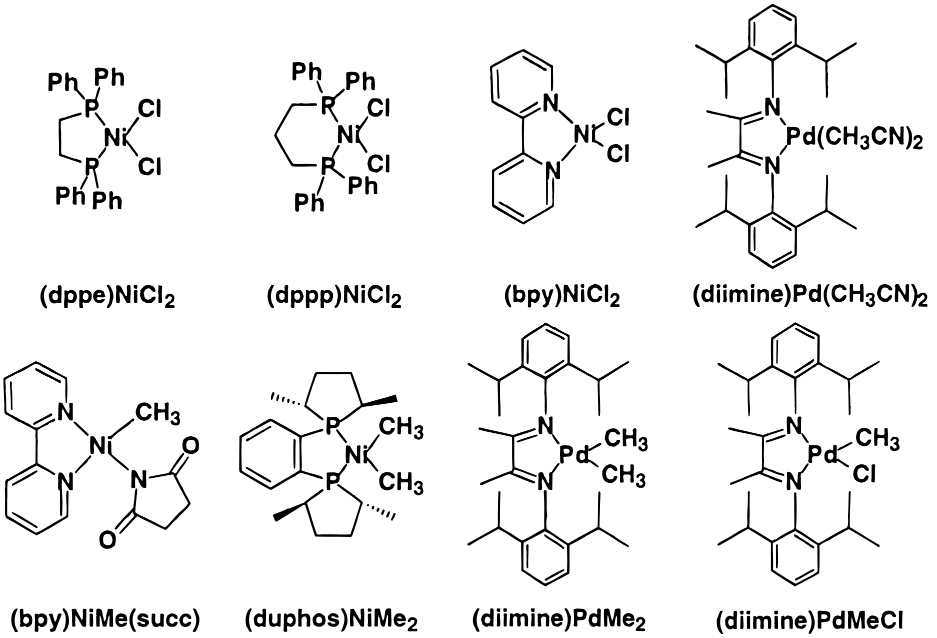

Figure 3. Structures of some of the catalysts employed in this study.

mixture is permitted to stand. Note that these alternate routes of polymerization, if they occur, do not substantially increase the yield of polymer formed.

C. Elemental Analysis of Poly(cyanoacetylene) Samples. When samples of poly(cyanoacetylene) as prepared above were subjected to elemental analysis, significant amounts of impurity were indicated as evidenced by the low values compared to those expected for the formula $(C_3HN)_x$. In an effort to remove these impurities, samples were heated under vacuum (to remove residual solvent) both before and after Soxhlet extraction (to remove catalyst impurities).

From the results shown in Table 6, it is clear that catalyst impurities could not be removed from the polymer samples. This result was not unanticipated as there are several references to metal complexation to polymers produced in other late-transition-metal catalyzed polymerizations of monosubstituted acetylenes containing polar functional groups.[74-80] Figure 4 suggests one possible mode of metal complexation that has been suggested in the literature. To date, this metal complexation hypothesis has been supported only by deviant elemental analyses and upon X-ray photoelectron spectroscopy data. These data do not permit specific structural assignments to be made. The remainder of the polymer characterization data presented here are given with the presence of significant catalyst residues in mind.

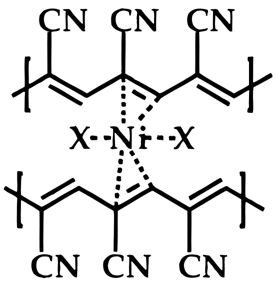

Figure 4. Possible mode of metal complexation in poly(cyanoacetylene).

D. Electronic Absorption Spectroscopy. The effective conjugation length[49,50] of a poly(acetylene) derivative can generally be assessed from its electronic absorption spectrum. More red-shifted (i.e., to lower absorption energy) spectra indicate a higher effective conjugation. Higher conjugation can be due to an increase in molecular length in the case of oligomeric chains. For polymer chains of greater than ca. 20–30 repeat units, a higher effective conjugation length generally results from a more planar polymer chain.

The electronic absorption spectra of three poly(cyanoacetylene) samples are illustrated in Figure 5. In general, poly(cyanoacetylene) samples prepared with various nickel catalysts are similar in color to one another. Poly(cyanoacetylene) samples prepared with

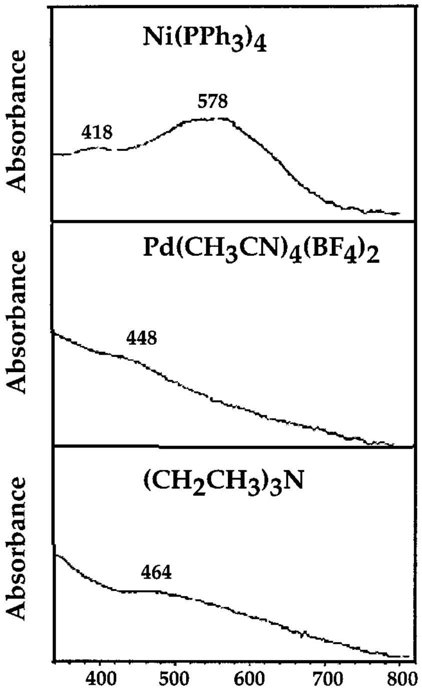

Figure 5. Electronic absorption spectra of poly(cyanoacetylene) samples (as dilute solutions in DMSO).

various palladium catalysts are likewise similar in color to one another. It is particularly notable that the poly(cyanoacetylene) sample prepared with the nickel catalyst exhibited electronic absorptions that were substantially red-shifted compared to those samples prepared with the palladium catalyst or triethylamine. In general, poly(cyanoacetylene) samples prepared with various nickel catalysts were inky purple to blue in color with optical absorption spectra similar to that shown for the $Ni(PPh_3)_4$-catalyzed sample in Figure 5. Likewise, poly(cyanoacetylene) samples prepared with various palladium catalysts were more brown in color with optical absorption spectra similar to that shown for the $Pd(CH_3CN)_4(BF_4)_2$-catalyzed sample in Figure 5.

It was suspected that this difference in effective conjugation length was either due to different microstructures between samples (cf. Figure 2) or that the palladium- and triethylamine-catalyzed samples were oligomeric in nature. In Table 1, it is notable that the palladium catalysts produced poly(cyanoacetylene) with generally lower molecular weights than did the nickel catalysts. Given that these molecular weights are tabulated versus poly(styrene) standards and are expected to have a larger hydrodynamic radius for a given molecular weight, the molecular weights shown in Table 1 are almost certainly higher than the true molecular weights. Thus, it is hypothesized that these color differences are due to differences in polymer molecular weight. In earlier studies of cyanoacetylene polymerizations, a deep blue to purple polymer could be obtained using γ-ray initiation.[48] Furthermore, in that study, the λ_{max} of the electronic absorption also shifted depending upon the solvent used to extract/dissolve the poly(cyanoacetylene). Although this behavior could have been due to a solvatochromic effect, the shift actually appeared to be due to differences in molecular weights between samples. Lower molecular weight portions, soluble in acetone, absorbed at lower wavelengths (approximately 30 nm lower) than the higher molecular weight, dimethyl sulfoxide extracts.[48] This result is consistent with the hypothesis that the colors of the polymers produced in this work were the result of molecular weight differences, rather than for other possible reasons considered below. Intermolecular aggregation of polymer chains could play a role in determining the relative colors of these samples.[49] However, no change in the electronic absorption spectra of these samples was observed as polymer concentration and temperature was varied. Thus, this possibility seems unlikely.

To help to rule out a difference in microstructure as the reason for the different colors of the poly(cyanoacetylene) samples, cuvettes containing dilute solutions of the $Ni(PPh_3)_4$-catalyzed and $Pd(CH_3CN)_4(BF_4)_2$-catalyzed polymers in DMSO were taken and heated under inert atmosphere at temperatures ranging from 40 to 75 °C and times ranging from 1 to 6 h. Dilute solutions of other poly(acetylene) derivatives have been observed to isomerize easily from cis to trans in dilute solution.[50] Despite these thermal treatments, no observable changes in the electronic absorption spectra of these samples were observed, suggesting that these samples were not in a less planar, cis-cisoidal or cis-transoidal microstructure.

An additional explanation for the different colors of the palladium-catalyzed versus nickel-catalyzed poly(cyanoacetylene) samples that cannot be ruled out is the presence of residual metal in the samples. It was shown in section C that complete removal of the catalyst was not possible. The residual nickel or palladium centers could conceivably complex with the polymer chains (Figure 4) and change the optical absorption spectra of the polymers. However, it was noted that increasing nickel concentrations (lower monomer-to-catalyst ratios during polymerization) had no effect on the electronic absorption spectra. There was also no observed color change upon the addition of various nickel catalysts to solutions of palladium-catalyzed polymer. Thus, this possibility seems unlikely.

E. Infrared Spectroscopic Characterization. Infrared spectroscopy indicated the functional groups present in the polymer, and further permitted an estimation of the extent of the delocalization occurring within the polymer backbone. Shown in Figure 6 are the infrared spectra of the polymers initiated by triethylamine, $Pd(CH_3CN)_4(BF_4)_2$, and $Ni(PPh_3)_4$. In all three polymers, a pronounced nitrile stretch at approximately 2190 cm^{-1} was observed, indicating that the polymerization occurred through the acetylenic triple bond and not through the nitrile group.

The position of the carbon−carbon double bond stretch shifted to lower energies going from the triethylamine-catalyzed to the palladium-catalyzed to the nickel-catalyed polymer. A possible rationale for this change was extended delocalization. This interpretation is consistent with that for the electronic absorption spectra detailed previously. The presence of metal complexes may have also affected the observed shifts, although concrete conclusions were difficult to make on the basis of infrared spectra only.

F. NMR Spectroscopic Characterization. Although the poly(cyanoacetylene) samples produced were soluble enough for characterization by size exclusion chromatography and electronic absorption spectroscopy, it was not possible to prepare samples that were concentrated enough to see appreciable ^1H or ^{13}C NMR signals in solution. Poly(cyanoacetylene) prepared with

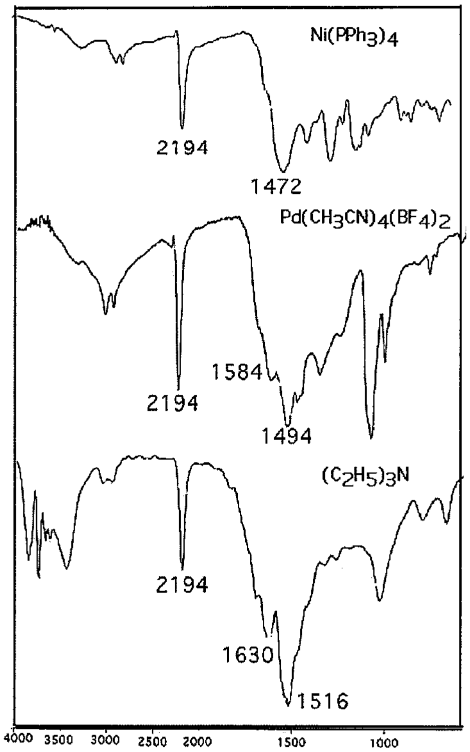

Figure 6. Infrared transmission spectra of poly(cyanoacetylene) samples.

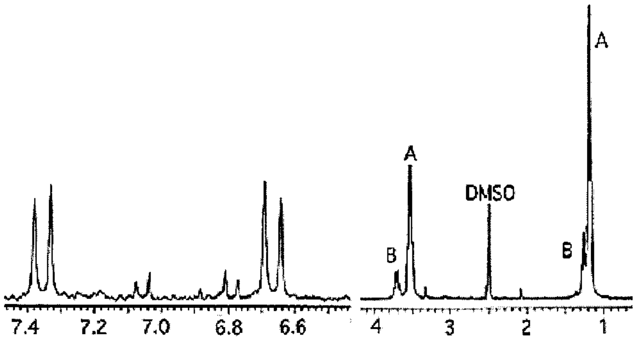

Figure 7. NMR spectra of poly(cyanoacetylene) prepared with triethylamine catalyst. A and B denote two ethyl groups indicating probable incorporation of catalyst as end groups.

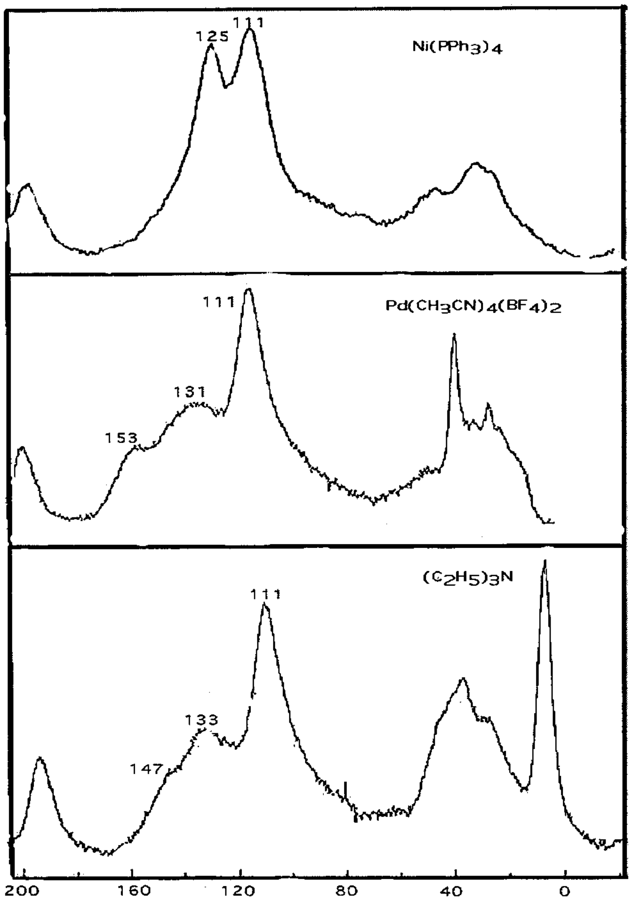

Figure 8. Solid-state ^{13}C NMR spectra of poly(cyanoacetylene) samples.

triethylamine as catalyst did show several distinct NMR signals (Figure 7). These, however, were not assigned to polymer but rather to short oligomers and/or cyclotrimerized or cyclo-tetramerized acetylenes.[51−54,88,89] It was notable that the poly(cyanoacetylene) samples prepared with nickel or palladium catalysts generally did not show these NMR signatures, despite the fact that nickel complexes are precedented acetylene cyclotrimerization and cyclo-tetramerization catalysts.[51]

Since solution NMR spectroscopy yielded little information, solid-state ^{13}C NMR spectra were collected of several poly(cyanoacetylene) samples (Figure 8). Unfortunately, these spectra were so broad that few conclusions could be made. All samples showed a pronounced nitrile signal at 111 ppm. Signals upfield of ca. 80 ppm are probably due to solvent, sidebands, and catalyst residues which have been acknowledged previously (cf. section C). Notably, each sample had a different conjugated olefin region with the nickel-catalyzed polymer being most different in character. In section D, it was argued that the nickel-catalyzed polymers were more conjugated than the palladium- or triethylamine-catalyzed polymers by virtue of their red-shifted electronic absorption spectra. It was expected that perhaps this extended conjugation would be manifest by a downfield shift of olefin carbon resonances in the nickel-catalyzed polymer. This, however, was not observed. Again, it is possible that metal complexation is more significant in the nickel-catalyzed polymer, and this complexation could result in upfield shifts of olefin carbon resonances. However, this interpretation is completely speculative.

G. High-Temperature Behavior. It was stated previously and illustrated in Figure 1 that poly(cyanoacetylene) should be a good candidate for thermal cyclization to an aromatic ladder structure. Although there are few ways to directly probe this cyclization reaction, thermal analysis including differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) was performed on several samples. TGA of samples heated to 500 °C showed approximately 40% weight loss for polymers prepared using $Ni(PPh_3)_4$, $Pd(CH_3CN)_4(BF_4)_2$, and $(C_2H_5)_3N$ as catalysts. These results indicate loss of solvent from the samples, but probably also represent loss of small molecules due to partial degradation of polymer chains. DSC, unfortunately, failed to show any transitions indicative of any reactivity in these samples.

Infrared spectroscopy however indicated reactivity consistent with the scheme shown in Figure 1. Figure 9 shows infrared spectra of poly(cyanoacetylene) samples prepared using $Ni(PPh_3)_4$, $Pd(CH_3CN)_4(BF_4)_2$, and *n*-butyllithium as catalysts, respectively. The former two samples showed a loss of the nitrile stretch at 2194 cm^{-1}

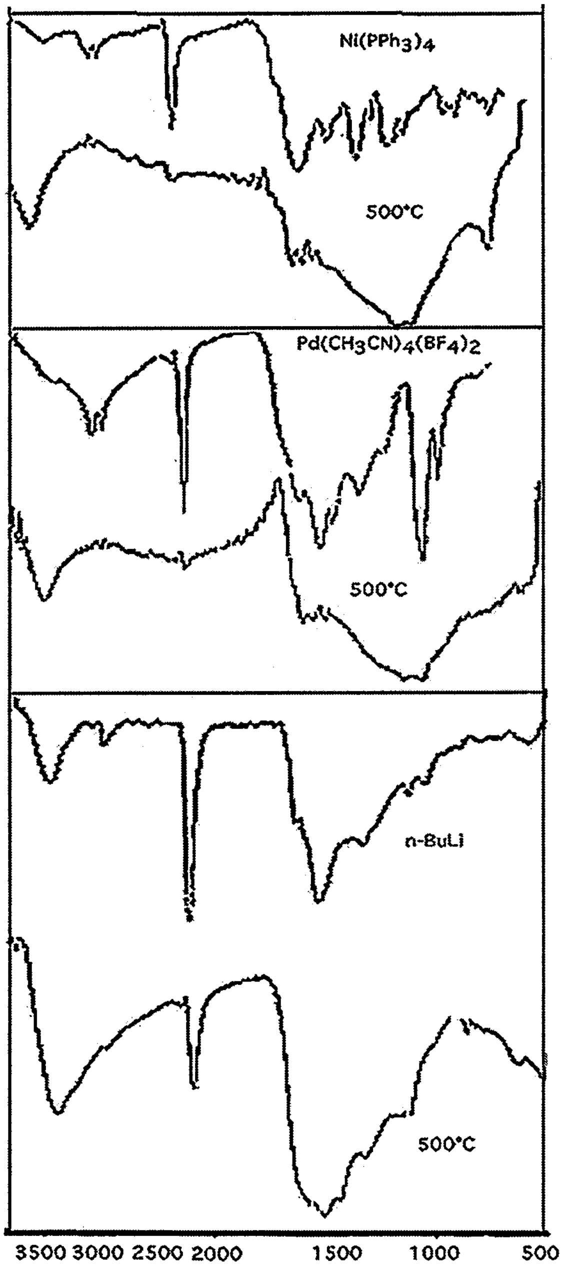

Figure 9. Infrared spectra of poly(cyanoacetylene) samples before and after heating to 500 °C.

consistent with thermally induced cyclization. It is notable that the nitrile groups in the *n*-butyllithium catalyzed sample had not completely reacted at this temperature. Thus, these thermal data suggest that cyclization of poly(cyanoacetylene) to an aromatic ladder-type structure probably occurs upon heating, but that significant weight loss consistent with some polymer degradation occurs as well.

Summary

Cyanoacetylene can be polymerized through its acetylinic linkages to form poly(cyanoacetylene) using nickel- and palladium-based catalysts. In an effort to better define the polymerization, variations of reaction conditions such as solvent, temperature, and reaction time were explored. From size exclusion chromatography and electronic absorption spectroscopy, it appears that nickel-based catalysts can produce polymer of a higher molecular weight than the palladium-based catalysts. These catalysts do have the disadvantage that they are apparently very difficult to impossible to remove from the polymer. The possible complexation of catalyst residue to the polymer backbone and/or side groups has been acknowledged.

Several spectroscopic techniques were employed in an effort to illustrate differences between the palladium- and nickel-catalyzed polymers. Infrared spectroscopy showed identical nitrile stretches, while the ($-C=C-$) stretches were shifted to lower energies for the nickel polymers. Solid-state ^{13}C NMR spectroscopy also showed significant structural differences, although the broadness of the peaks did not allow for concrete conclusions.

Experimental Section

Instrumentation. All syntheses that were air and/or moisture sensitive were performed either using standard Schlenk techniques under argon or in a nitrogen-filled Vacuum Atmospheres drybox. ^{1}H NMR were obtained with either a Gemini spectrometer operated at 300 MHz or a Varian spectrometer operating at 300 MHz. ^{13}C NMR spectra were obtained on a Gemini spectrometer operating at 75 MHz or on a Varian spectrometer operating at 75 MHz. Chemical shifts were referenced to the chemical shifts of the residual protons of the NMR solvents. UV/vis spectra were recorded on a HP 8452A diode array spectrometer. Thermogravimetric analysis and differential scanning calorimetry were performed on a Perkin-Elmer Series 7 thermogravimetric analyzer or differential scanning calorimeter. Size exclusion chromatography was performed on a mixed-bead cross-linked DVB (divinylbenzene) column purchased from Jordi, heated to 40 °C. An ERC-7515A refractive index detector, or a UV/vis detector set at 350 nm, was used with 0.05 M lithium bromide/dimethyl formamide as eluent, at a flow rate of 1.5 mL/min. Sample concentrations varied from 3 to 8 mg/mL, and all samples were filtered through a Whatman 0.2 μm filter, in the drybox, prior to injection. Molecular weights were calculated against a series of known poly(styrene) standards.

Materials. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl. Dimethyl sulfoxide and dimethyl sulfoxide-d_6 were distilled from calcium hydride. Dimethylformamide was distilled over Linde 4 Å molecular sieves. Ethanol (100%) was sparged with argon prior to use. All solvents used in the drybox went through several freeze–pump–thaw cycles before use. DUPHOS was purchased from STREM and used without further purification. Lithium bromide was purchased from Alfa Aesar and used as such. All other compounds were purchased from Aldrich and used without purification unless otherwise noted. The following compounds were synthesized from known literature methods: MeAl(OBHT)$_2$,[90] (bpy)NiCl$_2$,[91] (bpy)NiMe(succ),[92,93] (diimine)PdMeCl,[94] (diimine)PdMe$_2$,[94] (diimine)NiBr$_2$,[94] and (bpy)NiMe$_2$.[95] The compounds (duphos)NiMe$_2$,[96] and (diimine)Pd(CH$_3$CN)$_2$[97] were generated in situ according to known literature methods.

Synthesis of Propiolamide. This compound was synthesized according to a modified literature procedure. Into an oven-dried, two-necked 500 mL round-bottom flask was added 22 mL (0.2 mol) of methyl propiolate. The flask was then cooled to −45 °C, whereupon 200 mL of ammonia was condensed into the flask. After stirring overnight, 100 mL of freshly distilled diethyl ether was added to prevent polymerization of the product by residual ammonia. The flask was removed from the bath and warmed to room temperature, allowing the excess ammonia to evaporate. The solid was dried under vacuum overnight and isolated. Yield: 17 g, 93%. ^{1}H NMR (DMSO-d_6): δ 7.83(d, 2H, $J = 13.8$ Hz), 4.00(s, 1H). ^{13}C NMR (DMSO-d_6): δ 153.33, 78.52, 75.44. IR (KBr): 3327, 3168, 2109, 1669, 1568, 1387, 1135, 805, 772, 660 cm^{-1}.

Synthesis of Cyanoacetylene. This compound was synthesized according to a modified literature procedure.[98,99] Into an oven-dried three-necked round-bottom flask was added excess phosphorus pentoxide. Then 15 g (0.22 mol) of propiolamide was ground with a mortar and pestle, added to the phosphorus pentoxide, and mixed thoroughly. The reaction flask was then heated to 180 °C for 1 h, and the resulting cyanoacetylene was collected in a sidearm flask submerged in liquid nitrogen. The collected cyanoacetylene was then vacuum transferred into a flame-dried sidearm flask, wrapped in aluminum foil, and stored at −10 °C. Yield: 9.43 g (11.5 mL), 85%. ^1H NMR ($CDCl_3$): δ 2.54(s, 1H). ^{13}C NMR (DMSO-d_6): δ 104.75, 79.35, 56.40.

General Polymerization Procedures. In a drybox, 0.03 mmol of catalyst was weighed into an oven-dried scintillation vial, which was stoppered with a self-sealing rubber septum. Then 2 mL of dry, degassed dimethyl sulfoxide was added, and the solution was allowed to stir for approximately 30 min. Then 200 μL of cyanoacetylene (3 mmol) was added dropwise into the catalyst solution, which was then allowed to stir for 24 h. The polymer solution was then dripped into 8 mL of 100% ethanol in a poly(propylene) centrifuge tube. The vial was then washed with 2 × 2 mL of 100% ethanol, which was also added to the centrifuge tube. The polymer was then separated by repeated centrifugation for up to 2 h, followed by cannulation. The precipitated polymer was then dried under vacuum overnight. Variations of the drying procedure were done using a vacuum oven, and various Soxhlet extractions were also attempted as well, using tetrahydrofuran and ethanol as extraction solvents.

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