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Living CO/Olefin Alternating Copolymerizations of Electron-Poor Bicyclic Olefins Initiated by Neutral Palladium(II) Alkyl Complexes: A Route to the Perfectly Alternating Copolymer of CO and Acetylene

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Abstract: The alternating copolymerizations of carbon monoxide with the electron-poor bicyclic olefins, diethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**1**) and diethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**2**), is achieved with neutral palladium(II) initiators. These Pd(II) complexes utilize a σ,π-alkyl ligand, a halide anion, and 1 equiv of a stabilizing donor ligand (pyridine or triphenylphosphine). The preferred catalyst, due to reactivity and stability, is iodo(*endo*-6-phenyl-2-norbornene-*endo*-5σ,2π)(triphenylphosphine)-palladium(II) (**6**). This initiator produces living copolymerizations of **1** with CO in the presence of H_2O and O_2. The polymer isolated, poly(**1**-*alt*-**CO**), retains the Pd as the endgroup, and can be used to reinitiate copolymerization leading to chain extension or diblock copolymer formation. Both of the copolymers poly-(**1**-*alt*-**CO**) and poly-(**2**-*alt*-**CO**) undergo retro Diels−Alder reaction to produce furan derivative **7** and a new cross-conjugated material, poly(ketovinylene) (PKV). While the temperature for complete conversion of poly-(**1**-*alt*-**CO**) is ca. 280 °C, poly(**2**-*alt*-**CO**) goes to completion at room temperature and above. During this thermal conversion, the polymer undergoes melt flow that is assisted by the ejected furan solvent, allowing for the fabrication of wires and free-standing films of the conjugated material.

Introduction

Polymers with ketone functionality in the backbone have been receiving increasing notice over the last few decades. Research has mostly been published in the area of saturated polyketones. This work has largely focused on the perfectly alternating carbon monoxide/olefin copolymers formed using late transition metal complexes.[1−22] However, some of the earlier work looked at the formation of random copolymers of ethylene and CO initiated by radicals[23,24] or γ-irradiation.[25] In addition, conjugated polyketones have been formed by either the random copolymerization of CO with acetylene using a Ziegler−Natta catalyst system[26] or the polycondensation of aldehydes with ketones.[27,28]

For the transition metal catalyzed systems, palladium(II) cationic complexes are the most commonly used and have been shown to mediate the most controlled polymerizations. High molecular weight copolymers can be formed from the polymerization of CO with a variety of olefins, although the majority of research has focused on ethylene,[1−3,11−13,18] propylene,[6,14,15,17,29] or styrene.[4,9,11] The original work in the transition metal catalyzed systems (disclosed in a 1950 patent) utilized nickel cyanide complexes in an aqueous medium with carbon monoxide pressures as high as 200 atm, and temperatures up to 250 °C, to form “high molecular weight polyketones”.[22] The subsequent advances made using a variety of nickel and palladium complexes were outlined in a review by Sen, one of the major contributors to this field over the past decade.[7] A significant improvement, first reported by researchers in The

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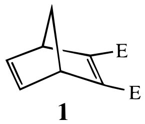
Netherlands, was the use of chelating diphosphine or dinitrogen ligands to stabilize the metal center and fix the proper cis geometry for propagation.[18,19,30] These chelating ligands were subsequently used by a number of researchers with preformed dicationic Pd(II) complexes; however, with these catalytic systems, an alcohol solvent or cosolvent was necessary to initiate copolymerization.[6,11,14] Most recently, Brookhart and coworkers reported monocationic palladium−methyl complexes which initiate the living copolymerization of *tert*-butylstyrene and CO in aprotic solvents at room temperature under 1 atm of CO.[9]

Although there have been numerous advancements in the area of palladium-initiated alternating copolymerizations of olefins with carbon monoxide, these have been successful with a limited class of olefins: ethylene, α-olefins, and styrene. No CO copolymers have been formed using electron-poor olefins such as acrylates or vinyl ketones, but these types of monomers have been shown to insert into palladium−acyl bonds[31] which is a key step in CO/olefin copolymerizations. The vast majority of reported polymerizations are catalyzed by cationic palladium(II) rather than neutral palladium(II) complexes. This is most likely due to the evidence that has been put forth in insertion studies which shows that cationic acyl complexes undergo olefin insertion more rapidly and with a larger variety of olefins than do the neutral acyl species.[31−34] These findings have largely been attributed to two factors: the stronger electropositive character of the palladium cation over the neutral palladium analogue which would cause weaker coordination and thus more facile insertion, and the fact that the neutral palladium(II) complexes must undergo dissociation of a ligand (either neutral or a halide) for insertion to occur (vide infra).

Our focus in the area of palladium-initiated olefin polymerizations has been the polymerization of electron-poor[35] bicyclic olefins typified by **1** and **2**.



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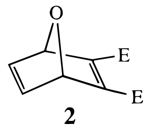
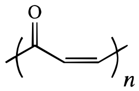


2

E = $-CO_2Et$

Our motivations transcend the incorporation of functional groups into polyolefin materials and include the use of these units as “protecting groups” for latent polymeric double bonds.[36] This latter application will be illustrated herein by forming an illusive cross-conjugated polymer with a vinyl ketone repeat unit, poly(ketovinylene) (PKV).



PKV

The work described here focuses on developing a living, alternating copolymerization of the same electron-poor bicyclic olefins with carbon monoxide and the use of these polymers as precursors to PKV.

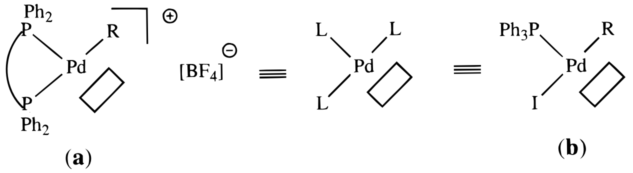
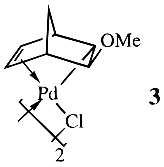


Figure 1. Desired coordination sphere for CO/olefin copolymerization initiators: (a) cationic Pd complex with one empty site for monomer association; (b) neutral Pd complex with one empty site for monomer association. R represents the growing polymer chain in either the alkyl or acyl form.

Results and Discussion

Polymerization Using the Two-Component Catalyst System. Initial test copolymerization of **1** with CO were conducted under an atmosphere of CO using complex **3**, the same initiator as was used in our previous work on the living homopolymerization of **1** and **2**.[36]



3

The chloride bridged dimer of **3** splits into the monometallic form upon treatment with monomer or other donor ligands. We found that complex **3** would initiate the copolymerization of **1** with CO, but it was less than desirable for a number of reasons. First, under polymerization conditions, complex **3** was highly sensitive in polar solvents and prone to reduction to Pd(0). This could be seen in the yields associated with the copolymerizations conducted in methylene chloride, THF, and toluene which gave yields of 10, 50, and 90%, respectively. Also, the fact that **3** was known to allow multiple insertions of **1** and **2** suggested that the copolymerization of **1** with CO might be less than perfectly alternating.[36]

The studies that have looked at CO/olefin copolymerization,[1,2,18,32] or the analogous insertion reactions,[21,31,33,34] by neutral Pd(II) have focused on complexes which utilize the same ligands as the active Pd(II) monocationic systems (i.e., $Pd(L)_2(R)(X)$ or $Pd(L-L)(R)(X)$ with $X =$ anion, $L =$ phosphine, and $L-L =$ chelating diphosphine). They have found that for olefin coordination and insertion to occur, a vacant coordination site must be present. If an additional phosphine is added to the system ($[PdL_3]^+X^-$) to fill all available coordination sites, the catalytic activity is shut down,[20] similar to the neutral Pd systems with filled coordination spheres. Translating these facts into our neutral complex suggests using a single monophosphine (Figure 1).

To test this paradigm, two-component catalysts consisting of complex **3** and 1 equiv of added donor ligand (pyridine or PPh_3) per palladium center (**3**·py and **3**·PPh_3, respectively) were investigated. Both of these systems afforded poly(**1**-*alt*-**CO**) in quantitative yields (eq 1).

The alternating structure of poly(**1**-*alt*-**CO**) was confirmed by ^{13}C NMR spectroscopy, IR, and elemental analysis. Molecular weights were controllable and determined by the monomer-to-initiator ratio, and typically polydispersity indices (PDIs) were found to be near 1.1 as determined by GPC/light scattering (vide infra). The **3**·py system was more reactive (relative rate: **3**·py/**3**·PPh_3 = 16), but **3**·PPh_3 proved to be more

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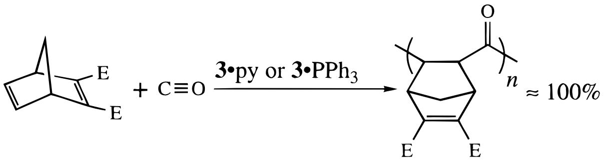


(1)

poly(**1**-*alt*-**CO**)

stable. Instability of **3**·py in the absence of monomer could be seen by decomposition to Pd(0) at the end of the copolymerization. This instability showed solvent dependencies identical with the "ligandless" system of **3** alone. Rates of polymerization showed a modest increase with increasing solvent polarity. The relative rates for the toluene, THF, nitromethane, and acetonitrile systems were found to be 1.0, 1.5, 1.5, and 1.2, respectively.

Copolymerization Kinetics. The kinetics associated with CO/olefin copolymerizations have not been fully studied for cationic palladium complexes. In their report on the kinetics and energetics of CO insertion into a Pd^+-alkyl bond versus ethylene insertion into a Pd^+-acyl bond, Brookhart and coworkers showed that the activation barrier for the CO insertion is 1.1 kcal/mol lower in energy than for the ethylene insertion.[37] This is in accord with their earlier observation that the stable intermediate in the alternating copolymerization of CO with *tert*-butylstyrene is the Pd−acyl bond suggesting that olefin insertion is the slow step.[9] This has also been suggested by other researchers for the ethylene/CO system.[2,18] However, a preliminary kinetic study by Chien and co-workers suggest that the rate law for CO/olefin copolymerization is dependent on the concentration of both ethylene and CO.[15]

The kinetics of the copolymerization of **1** and CO were studied in order to understand the polymerization mechanism and compare it with the previously reported CO copolymerizations initiated by cationic palladium. Catalyst **3**·py in toluene was chosen because of its higher activity. A series of copolymerizations were set up with constant initiator and olefin concentration. The reactions were found to follow linear first-order kinetic in terms of carbon monoxide consumption (see the Supporting Information for linearized first-order plots). Plotting the observed rate constants as a function of P(initial) confirmed that the alternating copolymerization of **1** and CO is first order in carbon monoxide pressure. Similarly, a series of polymerizations were set up with varying initiator, or olefin, concentrations, and the observed rate constants obtained from the linear first-order kinetics were plotted versus [**3**·py] or [**1**], respectively (Supporting Information). We thus found the copolymerization to have a first-order dependence on palladium initiator concentration and a zero-order dependence on olefin concentration.

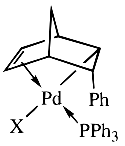
We have thus shown that the alternating copolymerization of **1** with CO initiated by the neutral palladium(II) complex **3** with added donor ligand is first order in [Pd], first order in P_{CO}, and zero order in [olefin].

$$-\frac{dP_{CO}}{dt} = k[Pd]P_{CO} \qquad (2)$$

This suggests that CO association to the palladium complex is rate determining. Although this is counterintuitive due to the strong binding affinity of CO as compared to olefins, it makes sense when considering the relative concentrations of the two monomers in solution. Our polymerizations are conducted with olefin concentrations from 0.75 to 1.75 M and with P_{CO} between 16 and 29 psi. The solubility of CO in organic solvents is low, around 10^{-2} M per atm,[13] which implies by Henry's law a CO concentration of ca. 10^{-2} M. Thus, in our system the concentration of olefin is 2 orders of magnitude greater than the concentration of CO. We believe that under these conditions the system is flooded with olefin and thus the kinetics steps in which olefin plays a role become pseudo zero order.

From the study of initiator concentration dependence, the true rate constant k can be determined. The observed rate constant from a first-order plot in terms of CO consumption is a product of the true rate constant k times the catalyst concentration ($k_{obs} = k[Pd]$). Thus, the slope of the plot of k_{obs} as a function of [Pd] gives the absolute rate constant for polymerization, $k = 8.2 \times 10^{-3}\ M^{-1}\ s^{-1}$.

Copolymerization Using the One-Component Catalyst System. Although the two-component initiator system worked well to give us a quantitative yield of poly(**1**-*alt*-**CO**), a one-component initiator system would avoid the possibility of having less than exactly a 1:1 ratio of Pd to donor ligand. This is desirable because having lower than a 1:1 ratio means that some Pd complexes are without any donor ligand (and thus prone to decomposition) and greater than a 1:1 ratio means that some Pd complexes potentially have two donor ligands (which we have shown to be inactive to polymerization). Unfortunately, we were not able to isolate adducts of **3** with 1 equivalent of donor ligand per Pd center due to the facile rearrangement reactions that the σ,π ligand are known to undergo.[38−42] When the *endo*-phenyl substituent was used in place of the *exo*-methoxy substituent, however, isolation of the complexes **4**−**6** with one triphenylphosphine ligand became possible.[43,44] A study of the effect on polymerization rate of the halide ligand used showed that the iodide complex **6** was the most reactive with the relative rates for **4**, **5,** and **6** of 1.0, 3.3, and 10, respectively.



X = Cl; (**4**)
= Br; (**5**)
= I; (**6**)

Using complex **6** as initiator, under inert/dry conditions, we obtained poly(**1**-*alt*-**CO**) in quantitative yield with a PDI of 1.04. In addition, we observed that the palladium(II) endgroup did not decompose at the end of the polymerization even after workup in humid air. These polymers could be isolated as stable, light pink solids. Redisolved in monomer solutions, these active polymers would reinitiate polymerization.

These Pd endgroups were found to be surprisingly difficult to remove from the polymer. Treating the polymer with aqueous or alcoholic HCl proved futile. Successful cleavage was finally achieved by forming the palladium cation in the presence of methanol. Although the neutral Pd−acyl endgroup formed from

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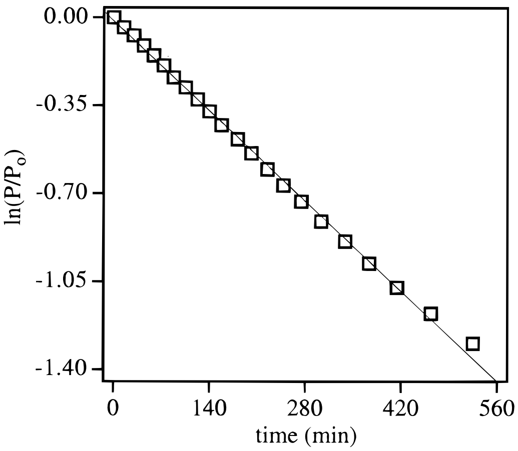
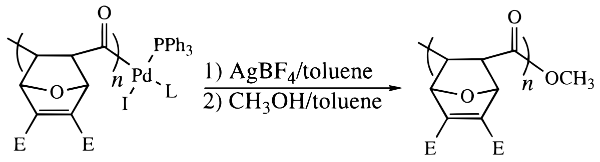


Figure 2. Kinetics of copolymerization of **1** and CO using initiator **6** (monitored by the disappearance of CO) showing the absence of chain termination. Time axis correlates to 3.5 half-lives in olefin consumption.

6 is stable in the presence of protic sources, it is well-known that methanolysis of cationic Pd−acyl complexes occurs readily.[45] Thus, we found we could cleave the Pd endgroup by first transforming it into the palladium cation, followed by methanolysis to yield snow-white polymers (eq 3).



(3)

L = monomer

In addition to the spectroscopic evidence, the removal the Pd endgroup was also confirmed by a change in the d*n*/d*c* value (variance in refractive index as a function of concentration) for the polymer. The d*n*/d*c* for poly[(**1**-*alt*-**CO**)-PdL$_n$] was determined to be 0.117 mL/g, whereas the purified material gave a value of 0.107 mL/g, within experimental error of the value measured for poly(**1**-*alt*-**CO**) from the **3**·py system (0.106 mL/g) in which the Pd decomposes at the end of the polymerization.

Living polymerizations are polymerizations that lack any kinetically significant chain termination or chain transfer processes.[46,47] Translated into practical terms, living polymerizations provide unparalleled control over molecular architecture. Due to the unusual stability of the active polymers derived from **6**, as well as their narrow PDIs, a study of the living nature of the copolymerization was warranted. The absence of termination can be shown by a linear plot of the first-order consumption of monomer, which exhibits no change in the number of active chains throughout the lifetime of the polymerization. Following the procedure above for preforming the active palladium complex under atmospheric conditions, addition of olefin **1** started the copolymerization for which linear kinetics were observed to greater than 3.5 half-lives (in terms of olefin) showing the absence of any chain termination processes (Figure 2).

The second criterion for a living polymerization, the absence of chain transfer, can be shown by a linear correlation between molecular weight and the monomer-to-initiator ratio. Calculation of the absolute molecular weights via online GPC/LS led to a linear relationship of M_n vs M/I (Figure 3) showing the absence of chain transfer.

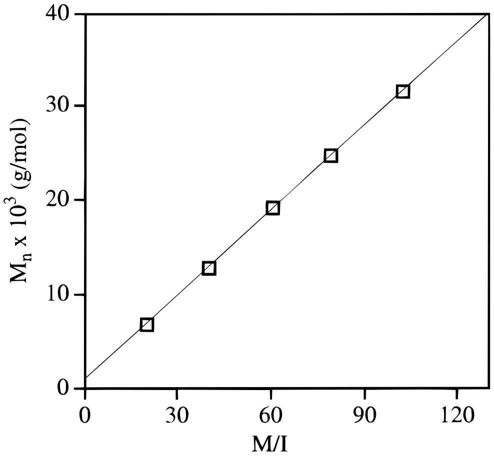


Figure 3. Linear correlation of molecular weight (as determined by GPC/LS) versus monomer:initiator ratio (for CO/**1** copolymerization with initiator **6**) demonstrating the absence of chain transfer.

These two observations (lack of termination and transfer) prove that the alternating copolymerization of CO and **1** initiated by complex **6** under atmospheric conditions (O_2/H_2O) is living. This observation suggests that protonolysis of the Pd−alkyl bond or hydrolysis of the Pd−acyl bond by H_2O is kinetically insignificant. Since our kinetics suggests that the resting state should be the Pd−alkyl species, the protonolysis reaction would be expected to be the major contributor to chain transfer. This observed aqueous stability is in agreement with our earlier work showing that Pd−alkyl bonds formed in homopolymerizations of **2** using initiator **3** are not only stable under atmospheric conditions, but are actually difficult to cleave, even under acidic conditions.[36,48]

The combination of living nature and atmospheric stability of these CO/olefin copolymerizations is an important point for consideration. Rarely are these two desirable traits observed together because protic sources and O_2 usually promote chain termination or transfer reactions. Recently, water-soluble Pd(II) cationic complexes have been synthesized which initiate the alternating copolymerization of CO with ethylene and propylene in an aqueous medium.[49] Although the productivity of this systems is lower than in organic solvents, and it is not living, it still yields reasonable molecular weight polymer (M_n = 14 000), which shows that transfer and termination do not completely dominate this aqueous system.

Copolymerization of 2 with CO. Alternating copolymerization of **2** with CO could be achieved with all of the above-mentioned initiators: **3**·py, **3**·PPh$_3$, and **4**−**6**. With any of these systems, quantitative consumption of **2** occurred yielding orange polymers with a PDI value of 1.06 (for **4**−**6**). However, only 60−65 wt % of polymer was isolated. The remaining mass was recovered as diethyl furan-3,4-dicarboxylate (**7**), the product of a retro Diels−Alder reaction of inserted **2**. We have previously reported that the homopolymers of **1** and **2** will undergo retro Diels−Alder reactions to produce polyacetylene.[48] For 100% of the inserted **2** to undergo a retro Diels−Alder reaction, a theoretical mass loss of 79.9% is expected. Thus, from our mass balance we can conclude that approximately half of the inserted units are undergoing a retro Diels−Alder reaction at room temperature during polymerization (eq 4).

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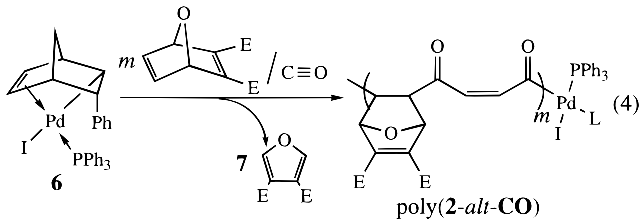
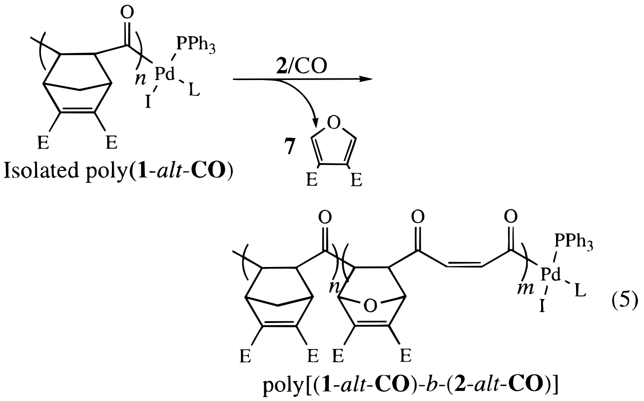


(4)

Chain Extension Reactions and Diblock Copolymer Formation. Utilizing the atmospherically stable initiator **6**, chain extension reactions with poly(**1**-*alt*-**CO**), as well as diblock and triblock copolymerizations of poly(**1**-*alt*-**CO**) and poly(**2**-*alt*-**CO**), were examined. All of these reactions were conducted using two techniques: (1) in situ addition of a second aliquot of monomer to the stirring polymer solution and (2) isolation of the macromolecules possessing the active catalyst endgroups by precipitation followed by their redissolution and addition of a second aliquot of monomer.

Chain extension reaction for poly(**1**-*alt*-**CO**) were conducted in three steps using both the "in situ" and "isolated" methods described. We found using the "isolated" method that when three subsequent additions of **1** at $M/I = 50$ for each addition were used, the molecular weight at each step increased by 20 000, from 21 100 to 41 600 to 63 600, and the PDI for each sample was constant at 1.02 for every step. With the "in situ" method, nearly identical results were obtained. These chain extension reactions show that the living Pd endgroup remains active toward copolymerization of **1** even after precipitation and isolation of the solid polymer.

The diblock copolymer poly[(**1**-*alt*-**CO**)-*b*-(**2**-*alt*-**CO**)] was formed by adding **2** to a solution of poly(**1**-*alt*-**CO**) with an active Pd endgroup (eq 5). Starting with a poly(**1**-*alt*-**CO**) block having $M_n = 20\,300$ and PDI = 1.02, addition of 90 equiv of **1** led to formation of the copolymer with $M_n = 58\,100$ and PDI = 1.06. (The molecular weight is approximate as the d*n*/d*c* for poly(**1**-*alt*-**CO**) was used.)



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Thermal Formation of PKV. In principle, both poly(**1**-*alt*-**CO**) and poly(**2**-*alt*-**CO**) are thermal precursors to the new conjugated polymer PKV. Using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), the thermal conversion reactions were studied. Looking first at poly(**1**-*alt*-**CO**), TGA showed the onset of mass loss around 165 °C. However, the polymer appeared to degrade by a three-step process as evidenced by different mass loss rates in three temperature regimes: 165−210 °C; 220−270 °C; above 280 °C. In addition, complete conversion of poly(**1**-*alt*-**CO**) to PKV was not occurring at temperatures below 270 °C. These temperatures are too high to be useful for the processing of a conjugated polymer due to possible thermal cross-linking and chain scission reactions.[41,42] We thus turned our attention to the poly(**2**-*alt*-**CO**) copolymer.

In contrast to the polymers derived from **1**, it was found that PKV could be cleanly formed by the thermolysis of poly(**2**-*alt*-**CO**) at temperatures considerably under 100 °C. Interestingly, it was observed that at 70 °C, poly(**2**-*alt*-**CO**) underwent melt flow during this conversion process to form black continuous films of the conjugated polymer (Figure 4). The retro Diels−Alder product **7** is ultimately excluded from the polymer matrix and could be removed at lower temperatures under vacuum.

This flow behavior is directly linked to the retro Diels−Alder reaction and the formation of **7**. When the thermal reaction was conducted under vacuum to remove **7** as it forms, no flow was observed. This suggested that as **7** is formed it acts as a solvent/plasticizer for the mutating polymer. This unexpected benefit is atypical. Normally, precursor routes to conjugated polymers have the problem of undergoing mass loss during the conversion which can create voids in the morphology thus decreasing conductivity.[50] In contrast, PKV produced in the presence of **7** is obtained in continuous, defect-free films. To our knowledge, the flow observed during the transformation of poly(**2**-*alt*-**CO**) to PKV is the first example of an noncatalyzed thermal transition associated with the formation of a conjugated polymer.

The final polymer, PKV, is a conjugated material with the highest possible incorporation of CO into the backbone. The polar nature of the carbonyl may allow for facile doping using Lewis acid or other p-dopants as well as n-dopants. The backbone carbonyl is observed in the ^{13}C NMR spectrum as a broad signal over the region from 180 to 210 ppm. In addition, four olefin signals are observed (110, 117, 128, 149 ppm). We believe that the presence of four signals is due to the multiple environments that would occur if both cis and trans units were randomly present in the backbone. Two bands in the IR spectrum at 1024 and 800 cm^{-1} correlate well to the *trans*- and *cis*-C−H out-of-plane wags, respectively, associated with polyacetylene.[51]

Conclusion

We have found that the electron-poor bicyclic olefins (e.g., **1** and **2**) and CO can be copolymerized in a living fashion using neutral Pd(II) initiators possessing σ,π-alkyl chelating initiators and a monodentate donor (e.g., pyridine and phosphine). The advantage of using neutral complexes over their more common cationic counterparts is that they yield polymers with remarkably stable and controlled propagating endgroups. In addition to displaying living polymerization behavior in the presence of oxygen and water, the stability of the resultant endgroups can be exemplified by the fact that the polymer chains can be isolated with these endgroups intact. Dissolved latter in solvent and monomer, these endgroups continue to propagate. Di- and triblocks prepared by either this isolation method or a more standard sequential addition of monomers to the growing chain are essentially indistinguishable from one another.

Why develop methods of (co)polymerizing monomers such as **1** and **2**? Because they can act as protecting groups for latent olefins in the backbone. This in turn allows for the formation of polymers hitherto unobtainable through other routes. In the context of this CO copolymerization work, the copolymers produced from **2** and CO undergo retro Diels−Alder reactions

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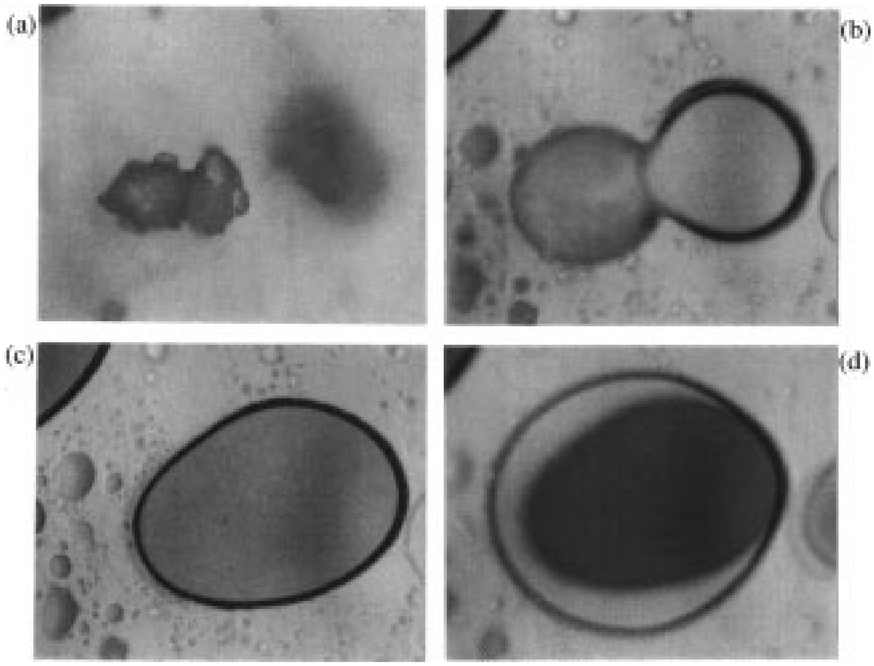

Figure 4. Transformation of poly(**2**-*alt*-**CO**) to PKV showing thermal flow under an optical microscope: (a) poly(**2**-*alt*-**CO**) at 75 °C after 2 min; (b) *flow* at 75 °C after 5 min; (c) *coalescence* at 75 °C after 10 min; (d) *ejection of substituted furan* at 130 °C.

at mild temperatures (25−75 °C) to yield perfectly alternating vinylene−CO copolymer. As an unexpected bonus, the furan produced from this process acts as a solvent/plasticizer to this forming polymer facilitating melt flow behavior.

Experimental Section

General. Procedures, Materials, and Characterization. IR spectra were determined with a Perkin-Elmer 1600 series FTIR spectrometer from KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker AC-200, ASX-300, or AMX-500 spectrometer. ^{1}H NMR spectra were measured at 200 MHz. Proton-decoupled ^{13}C NMR solution spectra were recorded at 125 MHz. Proton-decoupled ^{13}C NMR solid spectra were recorded at 75 MHz. ^{1}H and ^{13}C chemical shifts (δ) are referenced to a selected resonance of residual protons in the solvent employed. Elemental analyses were performed on a Control Equipment model 240XA elemental analyzer at the Microanalytical Laboratory Research Services, operated by the Graduate School, University of Massachusetts. UV−vis spectra were obtained with a Hitachi U-2000 Spectrophotometer. Solutions were contained in a 0.5 cm path length quartz cell. Thermogravimetric analysis was performed on a DuPont Instruments TGA-2950. Temperature ramping rates ranging from 1 to 10 °C/min were used over the temperature range from 25 to 600 °C. Differential scanning calorimetry was performed on a DuPont Instruments DSC-2910 at a rate of 10 °C/min. DSC and TGA were analyzed on a DuPont Instruments thermal analyst 2000. Gel-permeation chromatography/light scattering (GPC/LS) was performed using a Hewlett-Packard 1050 series liquid chromatography pump equipped with a Wyatt Dawn DSP-F laser photometer, a Wyatt/Optilab interferometric refractometer, and a Waters 746 data module integrator. Separations were effected by 10^5, 10^4, 10^3, and 5×10^2 Å Permagel columns (purchased from Pacific Column Co.) run in series. Samples were prepared as 1−2% polymer (w/v) and were passed through 0.45 μm filters prior to injection. THF was used as the mobile phase. Measurements of d*n*/d*c* were made using an Otsuka Electronics Photal model RM-102 differential refractometer, thermostated at 25 °C with a VWR model 1155 constant temperature circulator. Samples were prepared as 1−5% polymer (w/v) in THF. An Olympus model BH-2 optical microscope equipped with a Linkam THMS-600 hot stage was used to observe the thermal conversion reactions. Fischer-Porter bottles with a maximum pressure capability of 10 atm were built from Andrews Glass Company 3 oz. aerosol reaction vessels and stainless steel fittings purchased from Oakland Valve and Fitting. Glass inserts used to reduce the system volume in kinetics experiments were made by the Glass shop, operated by the Graduate School, University of Massachusetts.

Air- and moisture-sensitive experiments were conducted using standard Schlenk line and drybox techniques. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. 1,2,4-Trichlorobenzene was distilled under N_2 from CaH_2, degassed by 3 freeze−pump−thaw cycles, and stored under an atmosphere of argon. THF and toluene were distilled under N_2 from sodium/benzophenone. Nitromethane and acetonitrile were distilled under N_2 from CaH_2 and degassed with three freeze−pump−thaw cycles prior to use. Chloroform was purified by washing with H_2SO_4 and subsequently H_2O and then dried over CaH_2 and degassed with three freeze−pump−thaw cycles prior to use.[52] Unless otherwise noted, solvents were removed with the assistance of a rotary evaporator. Palladium complexes **3**[53] and **6**[54] were synthesized according to literature. Complexes **4** and **5** were synthesized in a manor analogous to **6**. Monomers **1** and **2** were synthesized by the Diels−Alder reaction of diethyl acetylenedicarboxylate with cyclopentadiene and furan, respectively,[55] and purified, dried, and degassed by Kügelröhr distillation under high vacuum at 65 °C.

Polymerizations. Alternating Copolymerization of 1 and CO with Initiator 3 and Pyridine (Poly(1-*alt*-CO)). Method A. In a typical polymerization a 50 mL Schlenk tube was charged with 2.8 mg (0.0106 mmol) of **3**, evacuated, and pumped into a drybox under argon. To the tube were then added 765 μL of dry/degassed toluene (for other solvents used the procedure is identical), 81 μL (0.0106 mmol) of a 0.13 M solution of pyridine in toluene, and 250 mg (1.06 mmol) of **1**. The tube was then sealed, removed form the drybox, and attached to a Schlenk line. The yellow solution was then frozen with LN_2, the argon atmosphere was evacuated and replaced with an atmosphere of CO, and the solution was allowed to warm to room temperature and stir under a constant atmosphere of CO for 12 h. The tube was then opened to air, and CH_2Cl_2 (5 mL) was added. The solution was filtered through a 0.45 μm filter to remove Pd metal and then precipitated to hexanes (100 mL). Filtration and drying under vacuum yielded 273 mg (1.03 mmol, 97%) of poly(**1**-*alt*-**CO**) as an off-white powder. d*c*/d*c*: 0.107 g/mL. M_n (GPC/LS): 35 200. PDI (GPC/LS): 1.11. IR

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(KBr): 2983 (m), 1718 (s), 1624 (m), 1458 (w), 1269 (s), 1098 (s), 1022 (m) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.26 (6H), 1.4−2.4 (2H), 2.8−3.8 (4H), 4.18 (4H). ^{13}C NMR (100 MHz, C_6D_6): δ 14.2 (CH_3), 44.5 (CH_2), 50.0 (CH), 57.6 (CH), 61.0 (CH_2), 145.3 (C), 164.2 (C), 208.4 (C). Anal. Calcd. for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10. Found: C, 63.24; H, 6.14.

Method B. To a 50 mL Fischer-Porter bottle was added 2.8 mg (0.0106 mmol) of **3**. The bottle was then pumped into a drybox under argon where dry/degassed toluene (765 mL), 81 μL (0.0106 mmol) of a 0.13 M solution of pyridine in toluene, and 250 mg (1.06 mmol) of **1** were added. The bottle was then sealed using a stainless steel adapter equipped with a 0−200 psi pressure gauge, removed from the drybox, and pressurized with CO (positive pressures between 15 and 120 psi were used and all give similar results). After 12 h, the pressure was released from the system, CH_2Cl_2 (5 mL) was added, and polymer was isolated as described above to yield quantitative poly(**1**-*alt*-**CO**).

Alternating Copolymerization of 1 and CO with Initiators 4−6 (Poly(1-*alt*-CO)). Method A (under argon). In a typical polymerization a 50 mL Fischer-Porter bottle was charged with 7.0 mg (0.0106 mmol) of **6** (or the equivalent amount of **4** or **5**) and pumped into a drybox under argon. To the bottle were then added dry/degassed toluene (845 μL) and 250 mg (1.06 mmol) of **1**. The bottle was then sealed using a stainless steel adapter equipped with a 0−200 psi pressure gauge and removed from the drybox. The solution was frozen with LN_2 and degassed with three freeze−pump−thaw cycles prior to being pressurized with CO. Over the first hour, the solution changed in color from yellow to orange (only in the case of **6**). After 1 day of stirring (2 days for **5**, and 3 days for **4**), the pressure was released from the system, CH_2Cl_2 (5 mL) was added, and polymer was isolated as described above to yield 279 mg (1.05 mmol, 99%) of poly(**1**-*alt*-**CO**) as a pink powder. Following cleavage of the Pd from the polymer (vide infra), 269 mg (1.01 mmol; 96% recovery) of poly(**1**-*alt*-**CO**) was isolated as a white powder. M_n (GPC/LS): 36 800. PDI (GPC/LS): 1.04.

Method B (under air). To a 50 mL Fischer-Porter bottle were added 7.0 mg (0.0106 mmol) of **6**, toluene (845 μL), and 250 mg (1.06 mmol) of **1** on the benchtop. The bottle was then sealed and pressurized with CO. Over the first hour the solution changed in color from yellow through orange to a deep red color (turned to orange for **5**, and stayed yellow for **4**). After 1 day of stirring, the pressure was released for the system, CH_2Cl_2 (5 mL) was added, and the polymer was isolated as described above to yield 281 mg (1.06 mmol, 100%) of poly(**1**-*alt*-**CO**) as a pink powder. Following cleavage of the Pd form the polymer (vide infra), poly(**1**-*alt*-**CO**) was isolated as a white powder. M_n (GPC/LS): 38 700. PDI (GPC/LS): 1.10.

Method C (preformed propagating species under air). To a 50 mL Fischer-Porter bottle were added 7.0 mg (0.0106 mmol) of **6** and toluene (845 μL) on the benchtop. The bottle was then sealed, pressurized with CO, and stirred for 1 h during which the color of the solution changed from yellow through orange to a deep red (turned to orange for **5**, and stayed yellow for **4**). The pressure was then released, 250 mg (1.06 mmol) of **1** was added, and the system was repressurized with CO. The red solution was then allowed to stir for a day after which the pressure was released, CH_2Cl_2 (5 mL) was added, and polymer was isolated as described above to yield 281 mg (1.06 mmol; 100%) of poly-(**1**-*alt*-**CO**) as a pink powder. Following cleavage of the Pd from the polymer (vide infra), poly(**1**-*alt*-**CO**) was isolated as a white powder. M_n (GPC/LS): 31 200. PDI (GPC/LS): 1.02.

Alternating Copolymerization of 2 and CO with Initiators 6 (Poly(2-*alt*-CO)). (All of the catalyst systems and methodologies above for the formation of poly(**1**-*alt*-**CO**) can be used here.) To a 50 mL Fischer-Porter bottle were added 7.0 mg (0.0106 mmol) of **6** and toluene (845 μL) on the benchtop. The bottle was then sealed and pressurized with CO, and the solution was stirred for 1 h during which the color of the solution changed from yellow through orange to a deep red. The pressure was then released, 250 mg (1.06 mmol) of **2** was added causing the color to immediately change to yellow, and the system was repressurized with CO. The solution was then allowed to stir for a day over which time the color darkened. The pressure was released, CH_2Cl_2 (5 mL) was added, and polymer solution was precipitated to hexanes (100 mL). Following filtration and vacuum-drying, 175 mg (1.06 mmol, 100%) of poly(**2**-*alt*-**CO**) was isolated as a tan powder. M_n (GPC/LS, using d*n*/d*c* = 0.107 g/mL): 52 600. PDI (GPC/LS): 1.06. IR (KBr): 2983 (m), 1718 (s), 1636 (m), 1560 (w), 1465 (w), 1448 (w), 1280 (s), 1101 (s), 1018 (m) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.27, 1.8−3.6, 4.22, 4.9−5.9. ^{13}C NMR (100 MHz, C_6D_6): δ 14.1, 42.1, 55.1, 61.6, 83.4, 138.1, 145.3, 162.1, 196.8, 204.4. Anal. Calcd. for $C_{14}H_{16}O_5$: C, 60.00; H, 5.04. Found: C, 59.30; H, 5.36. Solvent was removed from the filtration supernatant to yield diethyl furan-3,4-dicarboxylate (**7**). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.27 (t, J = 7.2 Hz, 3H), 4.25 (q, J = 7.2 Hz, 2H), 7.86 (s, 1H).

Chain Extension Experiments with Poly(1-*alt*-CO). Method A (in situ addition of second aliquot of monomer). To a 50 mL Fischer-Porter bottle were added 9.7 mg (0.0146 mmol) of **6** and toluene (1.5 mL) on the benchtop. The bottle was then sealed, pressurized with CO (30 psi), and stirred for 1 h during which the color of the solution changed form yellow through orange to a deep red. The pressure was then released, 181 mg (0.767 mmol) of **1** was added, and the system was repressurized with CO (30 psi). The red solution was then allowed to stir for a day after which the pressure was released and an aliquot (0.15 mL) was taken and precipitated into hexanes for GPC/LS analysis. (M_n (GPC/LS): 19 900. PDI (GPC/LS): 1.02.) To the Fischer-Porter bottle was then added 185 mg (0.784 mmol) of **1**, and the purple solution was repressurized with CO (30 psi). The solution was allowed to stir for 1 day at which point the pressure was released and an aliquot was taken and precipitated to hexanes for GPC/LS. (M_n (GPC/LS): 39 000. PDI (GPC/LS): 1.02.) To the Fischer-Porter bottle was then added 180 mg (0.763 mmol) of **1**, and the bottle was pressurized with CO (30 psi). After 1 day of stirring, the pressure was released, THF was added (4 mL) and the polymer was precipitated to hexanes. Following filtration and vacuum-drying, 557 mg (2.09 mmol) of poly-(**1**-*alt*-**CO**) was isolated. M_n (GPC/LS): 61 500. PDI (GPC/LS): 1.02.

Method B (isolation of poly(1-*alt*-CO) at each step). To a 50 mL Fischer-Porter bottle were added 9.8 mg (0.0147 mmol) of **6** and toluene (1.5 mL) on the benchtop. The bottle was then sealed, pressurized with CO (30 psi), and stirred for 1 h during which the color of the solution changed from yellow through orange to a deep red. The pressure was then released, 179 mg (0.758 mmol) of **1** was added, and the system was repressurized with CO (30 psi). The red solution was then allowed to stir for a day, after which the pressure was released, THF was added (3 mL), and the polymer was precipitated to hexanes. Following filtration and vacuum-drying, 202 mg (0.759 mmol) of poly-(**1**-*alt*-**CO**) was isolated. (M_n (GPC/LS): 21 100. PDI (GPC/LS): 1.02.) To another 50 mL Fischer-Porter bottle were then added 93 mg (0.350 mmol) of this poly(**1**-*alt*-**CO**) and toluene (1.0 mL). The bottle was then sealed and pressurized with CO (30 psi), and the solution was stirred for 1 h. The pressure was then released, 93 mg (0.394 mmol) of **1** was added, and the system was repressurized with CO (30 psi). The red solution was then allowed to stir for a day after which the pressure was released, THF was added (4 mL), and the polymer was precipitated to hexanes. Following filtration and vacuum-drying, 200 mg (0.752 mmol) of poly-(**1**-*alt*-**CO**) was isolated. (M_n (GPC/LS): 21 100. PDI (GPC/LS): 1.02.) To another 50 mL Fischer-Porter bottle were then added 97 mg (0.365 mmol) of this poly(**1**-*alt*-**CO**), toluene (2.0 mL), and 58 mg (0.246 mmol) of **1**, and the system was pressurized with CO (30 psi). The solution was then allowed to stir for a day, after which the pressure was released, THF was added (2 mL), and the polymer was precipitated to hexanes. Following filtration and vacuum-drying, 152 mg (0.571 mmol) of poly(**1**-*alt*-**CO**) was isolated. (M_n (GPC/LS): 63 600. PDI (GPC/LS): 1.02.)

Block Copolymer Formation (Poly[(1-*alt*-CO)-*b*-(2-*alt*-CO)]). Method A (in situ addition of second aliquot of monomer). To a 50 mL Fischer-Porter bottle were added 9.8 mg (0.0148 mmol) of **6** and toluene (1.5 mL) on the benchtop. The bottle was then sealed and pressurized with CO (30 psi), and the solution was stirred for 1 h during which the color of the solution changed from yellow through orange to a deep red. The pressure was then released, 179 mg (0.758 mmol) of **1** was added, and the system was repressurized with CO (30 psi). The red solution was then allowed to stir for a day, after which the pressure was released and an aliquot (0.15 mL) was taken and precipitated into hexanes for GPC/LS analysis. (M_n (GPC/LS): 20 300. PDI (GPC/LS): 1.02.) To the Fischer-Porter bottle was then added

285 mg (1.20 mmol) of **2** causing the color to immediately change to yellow, and the system was then repressurized with CO (30 psi). After 1 day of stirring, the pressure was released, THF was added (4 mL), and the polymer was precipitated to hexanes. Following filtration and vacuum-drying, 402 mg of poly[(**1**-*alt*-**CO**)-*b*-(**2**-*alt*-**CO**)] was isolated as an tan powder. M_n (GPC/LS, using dn/dc = 0.107 g/mL): 58 100. PDI (GPC/LS): 1.06.

Method B (isolation of poly(1-*alt*-CO)). To a 50 mL Fischer-Porter bottle were added 9.8 mg (0.0147 mmol) of **6** and toluene (1.5 mL) on the benchtop. The bottle was then sealed and pressurized with CO (30 psi), and the solution was stirred for 1 h during which the color of the solution changed from yellow through orange to a deep red. The pressure was then released, 179 mg (0.758 mmol) of **1** was added, and the system was repressurized with CO (30 psi). The red solution was then allowed to stir for a day, after which the pressure was released, THF was added (3 mL), and the polymer was precipitated to hexanes. Following filtration and vacuum-drying, 202 mg (0.759 mmol) of poly(**1**-*alt*-**CO**) was isolated. (M_n (GPC/LS): 21 100. PDI (GPC/LS): 1.02.) To another 50 mL Fischer-Porter bottle were then added 93 mg (0.350 mmol) of this poly(**1**-*alt*-**CO**) and toluene (1.0 mL) to make a red solution. The bottle was then sealed and pressurized with CO (30 psi), and the solution was stirred for 1 h. The pressure was then released, 145 mg (0.609 mmol) of **2** was added causing the color to immediately change to yellow, and the system was repressurized with CO (30 psi). The solution was then allowed to stir for a day, after which the pressure was released, THF was added (4 mL) and the polymer was precipitated to hexanes. Following filtration and vacuum-drying 228 mg of poly[(**1**-*alt*-**CO**)-*b*-(**2**-*alt*-**CO**)] was isolated. (M_n (GPC/LS, using dn/dc = 0.107 g/mL): 59 000. PDI (GPC/LS): 1.06.)

Thermal Conversion of Poly(2-*alt*-CO) to PKV. Method A (under vacuum). To a 100 mL round-bottom flask was added 1.33 g of poly(**2**-*alt*-**CO**). The flask was attacked to a vacuum source and placed in a Kügelröhr distillation oven. The system was evacuated to below 10 mbar and then heated to 150 °C. After 24 h, the oven was allowed to cool to room temperature and 468 mg (75% mass loss) of PKV was isolated as a rust-brown insoluble powder. IR (KBr): 2980 (w), 1718 (s), 1610 (m), 1227 (m), 1094 (m), 1020 (m), 800 (w) cm^{-1}. ^{13}C NMR (70 MHz, solids): δ 48 (cross-linking), 109 (olefin), 117 (olefin), 128 (olefin), 149 (olefin), 195 (carbonyl) (plus unconverted repeat units at 14, 61, 82, 168). Anal. Calcd. for $C_{14}H_{16}O_5$: C, 66.67; H, 3.73. Found: C, 66.35; H, 4.82.

Method B (under nitrogen). To a 50 mL Kügelröhr bulb suspended in an oven was added 342 mg of poly(**2**-*alt*-**CO**). The bulb was then attached to a nitrogen source at one end and an oil bubbler at the other. After the system was purged with dry/O_2-free nitrogen for 2 h, the nitrogen flow was reduced to a slow rate and the oven was turned on to 65 °C. After 4 h, the temperature was then increased to 130 °C for the next 20 h. After cooling to room temperature, the bulb was reweighed and 314 mg (8% mass loss) of a black solid covered in a clear oil was isolated. The bulb was then attached to a LN_2 trap, placed under vacuum, and heated at 130 °C. After 1 day the system was cooled to room temperature and 120 mg (65% mass loss) of PKV was isolated as a semi-continuous black solid. In the LN_2 trap was isolated diethyl furan-3,4-dicarboxylate (**7**) as a colorless liquid.

Method C (in solution). To a 500 mL Schlenk flask was added 660 mg of poly(**2**-*alt*-**CO**). The flask was then evacuated and placed under an argon atmosphere. Dry/degassed 1,2,4-trichlorobenzene (150 mL) was then added to the flask via cannulation to make an orange solution. The flask was then placed in an oil bath at 65 °C and stirred for 4 h during which the solution darkened. The temperature was then increased to 110 °C, and the solution was allowed to stir overnight. After cooling to room temperature, the flask was opened to air and Et_2O (350 mL) was added causing coagulation of the insoluble polymer. The solvent mixture was then decanted, and the solid polymer was washed (3 × 350 mL) with Et_2O. Following filtration and vacuum-drying, 175 mg of PKV was recovered as a rust-brown insoluble powder.

Removal of Pd Endgroup from Poly(1-*alt*-CO). To a 50 mL round-bottomed flask were added 100 mg of pink poly(**1**-*alt*-**CO**) (formed using initiator **6**) and toluene (5 mL) to make a red solution. To this solution was added a solution of $AgBF_4$ (25 mg) in THF (1 mL) causing the solution to turn light yellow immediately. The solution was then allowed to stir in the dark overnight. The solvent was removed, $CHCl_3$ (5 mL) was added, and the silver salts were removed by filtration through Celite and washing with additional $CHCl_3$. The solution was then reduced to 6 mL, MeOH was added (3 mL), and the yellow solution was placed in a Fischer-Porter bottle. After pressurizing with CO (80 psi), the system was allowed to stir overnight leading to the formation of a black precipitate. Filtration through a 0.45 μm filter afforded a colorless solution which was precipitated to hexanes (100 mL). Filtration and vacuum-drying afforded 96 mg (96% recovery) of poly(**1**-*alt*-**CO**) as a white powder.

Kinetics of Polymerization. Formation of Poly(1-*alt*-CO) Using 3·py as Initiator. Method B above for the formation of poly(**1**-*alt*-**CO**) was followed using **3**·py as the initiator (0.75 M (0.75 mmol) < [**1**] < 1.75 M (1.75 mmol); 5 × 10^{-3} M (5 × 10^{-3} mmol) < [**I**/pyridine] < 1.5 × 10^{-2} M (1.5 × 10^{-2} mmol); 16 psi (1.2 mmol) < P_{CO} < 29 (2.2 mmol) psi). The stainless steel adapter was now equipped with a 0−30 psi pressure gauge, and prior to sealing the Fischer-Porter bottle and removing it from the drybox, a glass insert was added which reduced the system volume to 27 mL. The system was then sealed, removed from the drybox, and thermostated at 25.3 ± 0.3 °C prior to being pressurized with CO. Reaction times were then recorded for each psi of CO consumed.

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Supporting Information Available: Linearized first-order kinetic plots for the copolymerization of 1 and CO (2 pages). See any current masthead page for ordering and Internet access instructions.

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