A New Polymerization Reaction for the Synthesis of Aromatic Polyketones

Gary A. Deeter and Jeffrey S. Moore*

The Willard H. Dow Laboratories, Department of Chemistry and the Macromolecular Research Center, The University of Michigan, Ann Arbor, Michigan 48109-1055

Received May 28, 1992; Revised Manuscript Received January 11, 1993

ABSTRACT: A new polymerization reaction for aromatic polyketones is described based on palladium-catalyzed cross-coupling of aromatic diacid chlorides and bis(trimethylstannane) monomers. This method addresses some of the shortcomings of current synthetic approaches to this valuable class of thermoplastics. Most importantly, the polymerization can be carried out under mild conditions and polymer backbones free of ether linkages can be realized. Several high molecular weight, soluble polyketones having good thermal stability are synthesized using this polymerization reaction. An improved synthesis of aromatic bis(trimethylstannane) monomers is also described that provides monomers in high yield.

Introduction

The organic and organometallic chemistry of transition-metal-catalyzed cross-coupling reactions has matured to a very high level in recent years.[1] These developments open many possibilities for using this chemistry to construct organic molecules that are interesting from a materials standpoint, including polymers. In fact, several polymerization reactions based on palladium-catalyzed coupling chemistry have recently been demonstrated, including the preparation of poly(arylene alkyne)s,[2] polynaphthylenes,[3] poly(arylenevinylene)s,[3] polyamides,[4] polyesters,[5,6] polyphenylenes,[7] and polyimides.[8] From these examples the advantages of palladium-catalyzed step-growth polymerizations are clearly illustrated. First, polymerizations may be based on carbon–carbon bond-forming reactions. Therefore, monomers do not have to be linked together using heteroatom functional group chemistry, making it possible to prepare polymers that have wholly carbon backbones. Second, metal-mediated coupling chemistry is well suited for AB monomers that are difficult or impossible to polymerize using traditional functional group chemistry. Third, monomers bearing a variety of pendant functional groups can be polymerized owing to the mildness of cross-coupling reactions.

Typical substrates employed in small-molecule cross-coupling chemistry are organic electrophiles (halides or triflates) and organometallic nucleophiles. The most successful organometallic substrates are based on boron,[9] zinc,[10] and tin.[11] Of these, we have found that organotin reagents show particular promise for development of new step-growth polymerizations because of their high yields, monomer stability, and ease of monomer purification. To date, however, the use of aromatic bis(trialkylstannanes) in polymer synthesis has been very limited.[2a] In light of these facts we are investigating the use of these monomers in polymer synthesis, and our emphasis thus far has been on wholly aromatic polyketones.

Poly(aryl ketone)s are an important class of high-performance polymers displaying excellent thermal and chemical stability and good mechanical properties.[12] Electrophilic aromatic substitution of isophthaloyl chloride and diphenyl ether has been used in the synthesis of poly(aryl ether ether ketone) (PEEK), but low molecular weights and chain irregularities were often encountered.[13] High molecular weight PEEK has been synthesized by Rose et al.[14] using nucleophilic aromatic substitution of 4,4′-difluorobenzophenone and hydroquinone. This procedure remains the method of choice. Despite the success of these methods, some limitations still remain. For example, these methods must always incorporate the diphenyl ether linkage into the polymer backbone, harsh reaction conditions are usually required, and poor solubility is commonplace. To circumvent the solubility problem McGrath[15] and Sogah[16] independently reported the use of pendent *tert*-butyl groups that were later removed through a retro-Friedel–Crafts reaction, and Hay et al.[17] used the kinked 1,2-bis(4-fluorobenzoyl)benzene monomer. Each of these routes has proven to be quite successful in addressing the poor-solubility issue.

We believe a new approach to this very valuable class of thermoplastics is important and will enable the full potential of these materials to be explored. We have developed a palladium-catalyzed step-growth polymerization that is very mild and eliminates some of the above-stated inadequacies. Most importantly, the backbone ether linkage is no longer a required part of the polymerization chemistry, and thus wholly aromatic polyketones can be prepared.[18] Our method is based on the synthesis of aromatic ketones developed by Stille in which aromatic acid chlorides and aryltrialkylstannane compounds are coupled in the presence of a palladium catalyst.[11d,i] This paper will provide full details of this polymerization, including methods of aromatic bis(trialkylstannane) monomer synthesis.[19] A variety of new aromatic polyketones have been prepared, and their chemical and physical characterization is also described.

Results and Discussion

Monomer Synthesis. To prepare the desired aromatic bis(trialkylstannane) monomers a variety of methods for synthesizing trialkyltin arenes were evaluated. Unfortunately, few of these approaches were found to be suitable for monomer synthesis. For example, transmetalation of aryl di-Grignard or aryl dilithio compounds with the desired trialkyltin chlorides[20] was not pursued, because these methods produce a substantial amount of monostannylated arene and do not tolerate many organic functional groups. Palladium-catalyzed coupling of aromatic halides and hexaalkyldistannanes is a useful method for the synthesis of highly functionalized aromatic trialkylstannanes.[21] Unfortunately, the prohibitively expensive distannane only transfers 1 equiv of tin and must be used in excess to prevent biaryl coupling. Kuivila and Wursthorn used the reaction of an alkali trialkylstannate with aromatic dihalides to prepare several functionalized trialkyltin arenes that could not be prepared using Grignard

0024-9297/93/2226-2535$04.00/0

or lithium chemistry.[22] However, their procedure has the disadvantage that the alkali stannate is synthesized from hexaalkyldistannane. Owing to the expense of hexaalkyldistannanes and the shortcomings of the transmetalation approach, we have developed an improved synthesis of sodium trialkylstannate that is simple and more economical than previous methods. Furthermore, we demonstrate that sodium trialkylstannate reacts cleanly with aromatic dihalides to give bistin monomers in high purity and reasonable yield.

Several routes to sodium trimethylstannate were examined to eliminate the need for hexamethyldistannane. We found that the reaction of trimethyltin chloride with excess sodium in tetraethylene glycol dimethyl ether (tetraglyme) gave a clean, near-quantitative yield of sodium trimethylstannate. Rapid stirring of the reaction mixture for 72 h at room temperature under an inert atmosphere yields a dark green suspension, which upon filtration leaves a homogeneous, pale green sodium trimethylstannate solution. Concentrations, typically in the range of 0.6–1.0 M, can easily be determined using ^{1}H NMR[23] and appear to remain constant over time when solutions are stored under a nitrogen atmosphere at 0 °C.

Sodium trimethystannate prepared in this manner was reacted with several aromatic dihalides to provide the monomers 1–6 listed in Chart I. Although this method proved to be effective in the synthesis of aromatic bis(trimethylstannanes), some amount of reductive dehalogenation was often observed. To address this problem and Kuivila's[24] report on the reactions extreme sensitivity to slight changes in reaction conditions, we investigated the effects of solvent, order of addition, concentration, and temperature on the monotin:ditin ratio. Careful choice of reaction medium has had the greatest effect on decreasing the amount of monostannylated side product. For example, we found that the reaction of *m*-diiodobenzene and sodium trimethylstannate when run in tetraglyme, diethyl ether, and benzene furnished ratios of bis(trialkyltin) to mono(trialkyltin) at 15:1, 62:1, and 150:1, respectively. Although less critical, we have determined addition of sodium trimethylstannate to dilute dihalide solutions to be most optimal with concentration in the range of 0.05–0.1 M in aromatic dihalide. Low monotin:ditin ratios were maintained when reactions were run at 0.1 M, with the exception of monomer 5. This particular monomer was synthesized at 0.05 M, because at this concentration a 10:1 ditin:monotin ratio was obtained where at greater concentrations this ratio approached 1:1. Low reaction temperature was also found to favor aromatic bis(trimethylstannane) monomers, and all reactions gave best results when run at −78 °C. When applied under these carefully controlled conditions, this reaction consistently provided bis(trimethylstannane) monomers in high purity and in reasonable yield. Final purity greater than 99.8% was obtained for all monomers by recrystallization from petroleum ether, yielding white crystalline compounds.[25] High stability is demonstrated in these monomers by the absence of carbon–tin bond hydrolysis during aqueous workup and their ability to stand unchanged in air for extended periods of time. Because of their stability, ease of purification, and their high yields in cross-coupling reactions, aromatic bis(trimethylstannane) monomers have proven to be very useful in the synthesis of wholly aromatic polyketones, as discussed below.

Polymer Synthesis and Characterization. Aromatic diacid chlorides and aromatic bis(trimethylstannane) monomers were coupled in the presence of a palladium catalyst to synthesize the aromatic polyketones listed in Chart I. As previously reported[19] we found that Pd(II) catalysts were more successful in polymerizations than Pd(0) catalysts, with dichlorobis(triphenylarsine)palladium(II) providing the best results.[26] A 1.0 mol % catalyst stoichiometry with respect to aromatic diacid chloride was typically employed. We also observed the need to use an excess of aromatic bis(trimethylstannane) monomer equal

Chart I. Wholly Aromatic Polyketones and Their Respective Aromatic Bis(trimethylstannane) and Diacid Chloride Monomers

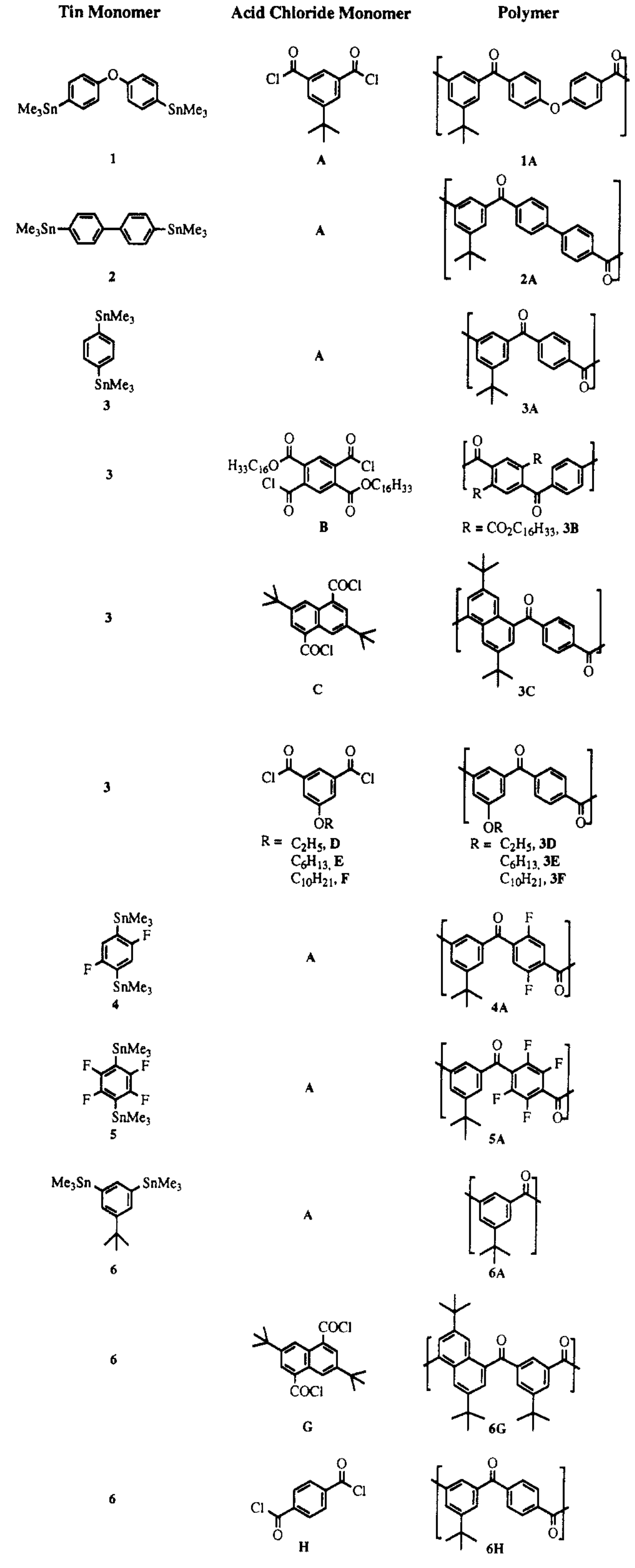


Table I. Size Exclusion Chromatography Molecular Weight Data[a] for Wholly Aromatic Polyketones

polymer	M_n[b]	M_w[c]	PDI[d]	yield (%)	DP[e]
1A	52700	67900	1.3	90	148
2A	37000	59000	1.6	90	109
3A	29000	51000	1.7	60	110
4A	4000	5600	1.3	82	13
5A	400	560	1.5	60	1
3B	7100	11000	1.6	60	9
3D	900	1300	1.4	82	4
3E	1000	1800	1.7	<10	3
3F	4600	5900	1.5	<10	13
6H	13000	18500	1.4	76	49

[a] Molecular weight data are relative to polystyrene standards. [b] Number-average molecular weight. [c] Weight-average molecular weight. [d] Polydispersity index. [e] Degree of polymerization determined from number-average molecular weight.

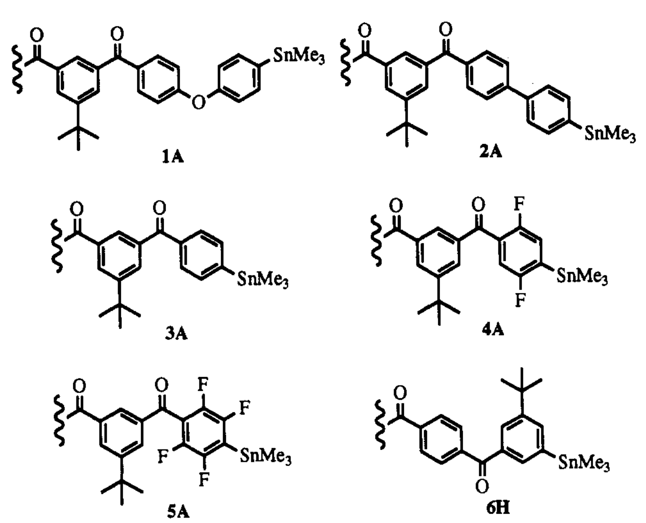


Figure 1. Tin end groups at an intermediate point in the polymer synthesis.

to that of catalyst used, and this is discussed further below. We have gained a firm understanding of this reaction, and through the synthesis and characterization of the wholly aromatic polyketones listed in Chart I, we have begun to test the scope of this polymerization reaction.

Most polymers were soluble in common organic solvents, and the higher molecular weight products formed clear flexible films when cast from these solutions. Polymer molecular weights were obtained using size exclusion chromatography (SEC) in THF at 23 °C and are relative to polystyrene standards. Table I summarizes these data. It can be seen that number-average molecular weights varied substantially from 400 to 50 000 with polydispersity indices (PDI) of approximately 1.5. The narrow PDI's of these polymers are surprising for condensation polymerizations and may be due to inadvertent fractionation of low molecular weight polymer during precipitation. Nonetheless, yields remain reasonably high, suggesting that these losses are minimal.

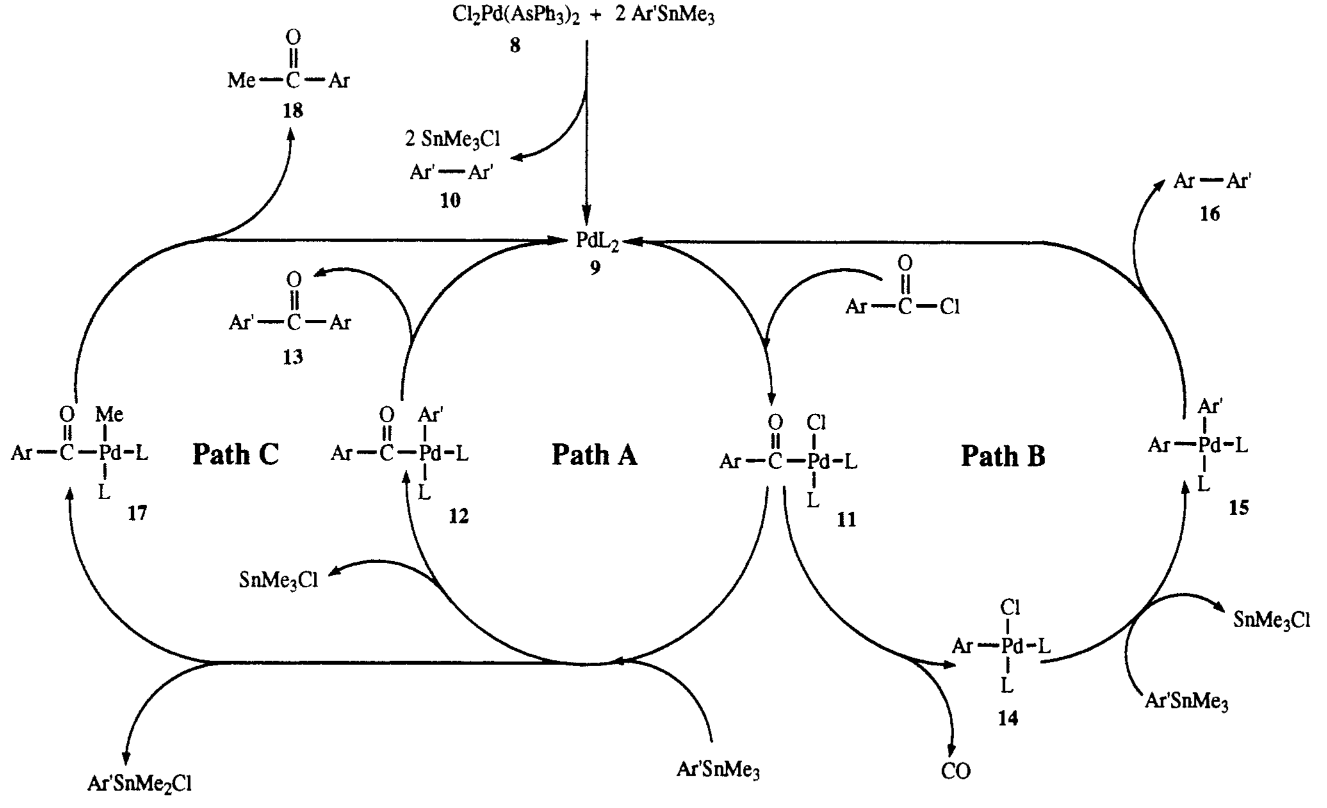
The wide range of molecular weights seen in these polymers was also surprising and can be attributed to differences in monomer reactivity in some cases and poor polymer solubility in others. For example, some of the data in Table I can clearly be attributed to the reactivity differences among the various aromatic bis(trimethylstannane) monomers. This is apparent upon considering the chemical structure of the tin end groups at an intermediate stage of polymer growth as shown in Figure 1 for polymers **1A**, **2A**, **3A**, **4A**, **5A**, and **6H**. These aromatic end groups possess a range of functionality from the electron-donating phenyl ether linkage in **1A** to the electron-withdrawing carbonyl groups in polymers **2A** and **3A** and fluoride groups in **4A** and **5A**. Correlation of these structural characteristics with the molecular weights in Table I indicates that the electron-donating phenyl ether linkage in **1A** provides the highest molecular weight polymer. A single para ketone group (e.g., **2A** and **3A**) does not affect the molecular weight significantly, but the added electron-withdrawing groups in **4A** and **5A** result only in low molecular weight polymer. This trend is consistent with the rate-limiting step of the catalytic cycle being transmetalation of an acylpalladium chloride electrophile by an aromatic trialkyltin moiety.[11a,j] Another possibility is that the rate of the reductive elimination step becomes rate determining as the aryl unit becomes electron deficient. Thus, the phenyl ether linkage in **1A** may be enhancing the reactivity of its tin end group or acylpalladium aryl complex, resulting in a higher polymer molecular weight. Based on this apparent trend, one would expect polymer **6H** to be formed in higher molecular weight than **3A**. These polymers have an identical repeat unit but the end groups at intermediate stages of growth are different (see Figure 1). Instead of the expected behavior, we have reproducibly found **3A** to be higher in molecular weight than **6H**. The molecular weight discrepancy in **6H** versus **3A** may be due to an adventitious impurity in **6H**, and further work is in progress to elucidate this point.

The low molecular weights of polymers **3B** and **3D** can be attributed to their poor solubility in most organic solvents. The alkyl side chains in diacid chlorides **B** and **D** are apparently insufficient to maintain solubility during polymerization. Solubility problems were also encountered in polymers **3C**, **6A**, and **6G**, demonstrating that *tert*-butyl groups are not always sufficient to maintain polymer solubility. Interestingly, these low molecular weight polymers were found to be semicrystalline materials by wide-angle X-ray scattering and DSC analysis.

End groups and chain termination reactions in these polymers were examined using ^{1}H NMR.[27] For example, polymer **3A** can be compared to oligomers containing tin and acid end groups. These oligomers were obtained by deliberately using excess tin or acid chloride monomer, respectively. To aid in assignments, 4-(trimethylstannyl)benzophenone was prepared as a model compound for tin end groups of polymer **3A**. The trimethyltin protons of this model compound were found to have a chemical shift of 0.32 ppm, similar to that of the tin end capped oligomer. Moreover, the aromatic ring bound to trimethyltin is seen as a pair of doublets at 7.59 and 7.71 ppm. Unfortunately, we were unable to identify resonances in the spectrum of the acid end capped oligomer which could clearly be associated with acid end groups. An additional resonance at 2.63 ppm was seen in the spectrum of **3A** and was determined to be from methyl ketone. The origin of this resonance is discussed below. Most importantly, the spectrum of polymer **3A** shows virtually no evidence of identifiable end groups. Furthermore, no end groups were observed in the spectra of polymers **1A** and **2A**, supporting the high molecular weight nature of these polymers.

Scheme I summarizes the relevant reaction pathways for this polymerization reaction. As discussed elsewhere,[19] the catalytic cycle is entered through reduction of the initial divalent palladium species **8** to the active zerovalent catalyst **9**. This is accomplished by coupling two aryl trimethylstannane monomers, yielding trimethyltin chloride and dimer **10**. Thus, a stoichiometric imbalance is created during initiation, causing low molecular weight polymers. An excess of aromatic stannane monomer equal to that of catalyst is routinely used to compensate for the

Scheme I. Relative Reaction Pathways in the Palladium-Catalyzed Polymerization of Poly(aromatic ketone)s



Ar = polymer or acid chloride monomer. Ar' = polymer of tin monomer.

stoichiometry of initiation, leading to the generation of high molecular weight polymer. The activated palladium catalyst **9** can then undergo oxidative addition to an acid chloride monomer to produce acylpalladium chloride complex **11**. Typically, **11** continues through path A to generate polymer **13** and the active zerovalent catalyst **9**. However, two alternative pathways are possible, one of which leads to chain termination and the other to decarbonylated polymers. First, **11** can follow path B and undergo decarbonylation (**14**), transmetalation (**15**), and reductive elimination to yield decarbonylated growing polymer **16** and active catalyst **9**. Evidence for this side reaction has been observed in the aromatic region of the ^{1}H NMR spectrum of polymer **6G**. Resonances at 7.95, 7.85, 7.70, and 7.56 ppm are present and have been assigned to decarbonylation product. Furthermore, in model reactions of monomer **G** and trimethylphenylstannane we observed decarbonylated product in greater than 10%. Performing this reaction under a CO atmosphere should stop this side reaction and is currently being investigated. Path C can also occur and leads to chain termination. In path C, **17** is generated when one methyl group from the aromatic trimethylstannane monomer is transmetalated to palladium rather than the desired aryl group. Reductive elimination yields end group **18** and zerovalent species **9**. Support for this side reaction is provided by the appearance of methyl phenyl ketone protons at 2.63 ppm in the ^{1}H NMR spectrum of **3A**. The detection of resonances associated with decarbonylation and methyl group transfer defects suggests these other pathways do participate, but based on the intensity of these resonances they only occur to a very small extent. Although we believe that the SEC molecular weight values may be somewhat higher than the true molecular weights, the NMR results and the film-forming tendencies of these polymers support their high molecular weight.

Table II. Thermal Gravimetric Analysis and Differential Scanning Calorimetry Data for Wholly Aromatic Polyketones

polymer	T_g[a] (°C)	T_m[b] (°C)	DOT N$_2$[c] (°C)	DOT air[d] (°C)	% wt loss[e]	DOT air[f] (°C)
1A	153	NO[g]	506	517	26	589
2A	220	NO	522	523	38	646
3A	186	NO	541	511	28	613
4A	NO	164	474	340	26	534
6A	177	299	538	541	41	604
3B	13	NO	391	387	70	607
3C	NO	375	532	524	42	601
3D	NO	NO	438	440	23	581
6G	205	NO	508	501	48	570

[a] Glass transition temperature obtained at a heating rate of 20 °C min^{-1}. [b] Polymer melt temperature obtained at a heating rate of 20 °C min^{-1}. [c] Inert-atmosphere decomposition onset temperature obtained at a heating rate of 20 °C min^{-1}. [d] Initial decomposition onset temperature in air atmosphere obtained at a heating rate of 20 °C min^{-1}. [e] Percent weight loss at completion of initial decomposition in air atmosphere. [f] Secondary decomposition temperature in air atmosphere. [g] NO = no transition was observed.

High thermal stability was anticipated for these polymers and is borne out by the thermal gravimetric analysis data (TGA) found in Table II. All polymers have decomposition onset temperatures above ca. 375 °C, which can be attributed to the thermal oxidative resistant aromatic backbone. Heating in nitrogen leaves char residues in the range of 30–55%, but in air all polymers decompose bimodally to 100% weight loss. Initial mass losses are consistent with decomposition that first involves loss of substituents followed by backbone decomposition. Table II also includes glass transition temperatures of these polymers. We observed low glass transition temperatures for polymer **1A** and polymer **3B** due to the flexible phenyl ether linkage and hexadecyl side chains, respectively. Incorporation of aromatic rings into the polymer increases backbone rigidity as demonstrated by the increased glass transition temperatures of polymers **3A**, **6A**, **2A**, and **6G**.

Conclusions. We have presented a new polymerization reaction leading to aromatic polyketones based on palladium-catalyzed coupling of aromatic bis(trimethylstannane) monomers and diacid chlorides. We have also developed an improved synthesis of aromatic bis(trimethylstannane) monomers, which provides monomers in high purity and reasonable yield based on the reaction of aromatic dihalides and sodium trimethylstannate. Also, a new method of synthesizing sodium trimethylstannate was presented which is simple and more economical than previous approaches. Several poly(aryl ketone)s that have high molecular weight and good thermal stability were synthesized using this new polymerization reaction. However, polymer molecular weight was found to be dependent on the nature of the monomer structure. For example, aromatic tin monomers containing electron-donating groups provided very high molecular weight polymer (polymer **1A**) but electron-withdrawing substituents (polymers **4A**, **5A**, and **6H**) gave low molecular weight materials. Poor polymer solubility was encountered in the case of polymers **3B**, **3C**, **3D**, **6A**, and **6G**.

This new polymerization reaction has successfully addressed some of the problems associated with conventional polyketone synthesis. Most notable are mild reaction conditions and the absence of ether linkage in the backbone. However, at least two side reactions that can interfere with the polymerization were identified, leading to chain decarbonylation sites and chain termination through methyl group transfer. However, under favorable conditions these pathways can be minimized, leading to high molecular weight polymers.

Experimental Section

CAUTION: Trimethyltin chloride is volatile and highly toxic.

Instrumentation. Synthetic manipulations involving air- and/or moisture-sensitive compounds were carried out on a Schlenk link or in a nitrogen-filled Vacuum Atmospheres drybox. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 GC using a split/splitless injector and flame ionization detector. A fused-silica capillary column (0.31 mm × 25 m) was employed (0.52-μm methylsilicone stationary phase). Melting points were recorded on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Size exclusion chromatography was performed using a Waters 6000A solvent delivery system and Model 440 absorbance detector at 254 nm. A series of three μStyragel columns of pore sizes 500, 10^3, and 10^4 Å were utilized and calibrated with narrow molecular weight polystyrene standards. SEC analyses were performed in THF at 23 °C. DSC and TGA were performed using a Perkin-Elmer 7 apparatus and at a rate of 20 °C/min. Decomposition onset temperatures (DOT) were determined from TGA as the temperature of initial mass loss. NMR spectra were recorded on a Bruker AM-300 spectrometer (300-MHz ^{1}H; 75-MHz ^{13}C) and referenced to the residual proton solvent resonance. ^{1}H NMR data are presented in a condensed format as follows: chemical shift (ppm), multiplicity, scalar coupling constant (hertz), integrated intensity. Multiplicities are abbreviated by s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet) and broad signals are indicated by br. Carbon NMR shifts are given in ppm and referenced to the solvent ^{13}C signal. Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded on a Finnigan 4021 mass spectrometer and a VG 70-S mass spectrometer, respectively.

Materials. 1,2-Dichloroethane and methylene chloride were vacuum transferred off calcium hydride. Tetra(ethylene glycol) dimethyl ether (tetraglyme) was vacuum distilled from calcium hydride. Benzene and toluene were vacuum transferred from sodium benzophenone ketyl. *tert*-Butylisophthalic acid was obtained as a gift from the Amoco Chemical Corp. The palladium catalyst, $Pd[AsPh_3]_2Cl_2$, was prepared as previously described.[28] Other reagents were purchased from Aldrich Chemical Co. and used as received.

Sodium Trimethylstannate. A 500-mL round-bottom flask was charge with trimethyltin chloride (101 mmol, 20 g) and dissolved in 100 mL of tetra(ethylene glycol) dimethyl ether in a drybox. The solution was rapidly stirred, and sodium shot (303 mmol, 7.0 g) was added. The reaction mixture was allowed to stir for 72 h and vacuum filtered through dried Celite 545 (from Aldrich Chemical Co.). The solution concentration was determined by ^{1}H NMR using pentamethylbenzene as an internal standard; ^{1}H NMR (300 MHz, benzene-d_6) δ 0.41 (s, 9 H).

General Synthetic Procedure for Aromatic Bis(trimethylstannane) Monomers. A mechanically stirred solution of 1,4-diiodobenzene (21 mmol, 6.96 g) in 200 mL of toluene was maintained at −78 °C under a nitrogen atmosphere. A sodium trimethylstannate solution (46 mmol, 1.08 M, 43 mL) was added dropwise over 30 min and stirred for an additional 30 min. An aliquot taken from the reaction mixture was analyzed using gas chromatography (GC), and all starting material was found to be consumed. The reaction mixture was quenched with ice water (400 mL), extracted with petroleum ether (400 mL), washed with water (3 × 300 mL), and dried over molecular sieves. The solvent was evaporated, leaving a white crystalline solid, which was recrystallized from petroleum ether at −54 °C, yielding colorless needles of **1,4-bis(trimethylstannyl)benzene (3)** in 85% yield: mp 122–124 °C; ^{1}H NMR (360 MHz, benzene-d_6) δ 7.49 (s, 4 H), 0.24 (s, 18 H); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (s, 4 H), 0.32 (s, 18 H); ^{13}C NMR (90 MHz, benzene-d_6) δ 142.1, 136.0, −2.0. Anal. Calcd for $C_{12}H_{22}Sn_2$: C, 35.82; H, 5.51. Found: C, 35.83; H, 5.78. MS (EI, 70 eV) Calcd for $C_{12}H_{22}SnCH_3$: 388.9525. Found: 388.9525.

4,4′-Bis(trimethylstannyl)phenyl Ether (1). The yield was 85% after recrystallization from petroleum ether: mp 57–59 °C; ^{1}H NMR (300 MHz, benzene-d_6) δ 7.34 (d, 4 H), 7.09 (d, 4 H), 0.19 (s, 18 H); ^{13}C NMR (75 MHz, benzene-d_6) δ 158.0, 137.0, 135.8, 119.3, −9.7. Anal. Calcd for $C_{18}H_{26}Sn_2$: C, 43.73; H, 5.30. Found: C, 43.78; H, 5.21.

4,4′-Bis(trimethylstannyl)biphenyl (2). The yield was 45% after recrystallization from petroleum ether: mp 124–126 °C; ^{1}H NMR (300 MHz, benzene-d_6) δ 7.60 (d, 4 H), 7.53 (d, 4 H), 0.25 (s, 18 H); ^{13}C NMR (75 MHz, benzene-d_6) δ 141.8, 140.9, 136.7, 127.2, −9.7. Anal. Calcd for $C_{18}H_{26}Sn_2$: C, 45.06; H, 5.46. Found: C, 45.11; H, 5.61.

1,4-Bis(trimethylstannyl)-2,5-difluorobenzene (4). The yield was 64% after recrystallization from petroleum ether: mp 156–158 °C; ^{1}H NMR (300 MHz, benzene-d_6) δ 7.05 (s, 2 H), 0.24 (s, 18 H); ^{13}C NMR (75 MHz, benzene-d_6) δ 121.6, −9.4. Anal. Calcd for $C_{12}H_{20}F_2Sn_2$: C, 32.78; H, 4.58. Found: C, 32.82; H, 4.81.

1,4-Bis(trimethylstannyl)-2,3,5,6-tetrafluorobenzene (5). The yield was 40% after recrystallization from petroleum ether: mp 111–112 °C; ^{1}H NMR (300 MHz, benzene-d_6) δ 0.32 (s, 18 H); ^{13}C NMR (75 MHz, benzene-d_6) δ 1.3, −8.2. Anal. Calcd for $C_{12}H_{18}F_2Sn_2$: C, 32.29; H, 3.81. Found: C, 30.02; H, 3.87.

1,3-Bis(trimethylstannyl)-5-*tert*-butylbenzene (6). The yield was 36% after recrystallization from petroleum ether: mp 47–48 °C; ^{1}H NMR (300 MHz, benzene-d_6) δ 7.69 (s, 3 H), 1.38 (s, 9 H), 0.31 (s, 18 H); ^{13}C NMR (75 MHz, benzene-d_6) δ 149.9, 141.4, 140.4, 132.6, 34.8, 31.5, −9.5. Anal. Calcd for $C_{16}H_{30}Sn_2$: C, 41.92; H, 6.60. Found: C, 41.89; H, 6.94.

4-(Trimethylstannyl)benzophenone (7). Due to monomer instability, this compound could only be isolated in 80% purity. Impurities identified by gas chromatography were found to be 4-bromobenzophenone and benzophenone. ^{1}H NMR (300 MHz, $CDCl_3$) δ (d, 3 H), 7.74 (d, 2 H), 7.62 (d, 2 H), 7.46 (d, 2 H), 0.34 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8, 149.0, 137.6, 137.2, 135.6, 132.3, 130.0, 129.0, 128.2, −9.5.

Diacid Chloride of the 1,4-Di(1-hexadecyl ester) of 1,2,4,5-Benzenetetracarboxylic Acid (B). Using standard literature methods,[29] compound **B** was prepared in 20% overall yield: mp 62–63 °C; ^{1}H NMR (360 MHz, benzene-d_6) δ 7.86 (s, 2 H), 4.18 (t, 4 H), 1.51 (s, 6 H), 1.38 (m, 50 H), 0.97 (t, 6 H); ^{13}C NMR (90

MHz, benzene-d_6) δ 163.5, 139.6, 132.5, 129.2, 67.1, 32.3, 30.2, 30.1, 30.0, 29.9, 29.8, 29.5, 28.5, 26.1, 23.1, 14.4 Anal. Calcd for $C_{42}H_{68}O_6Cl_2$: C, 68.26; H, 9.27. Found: C, 68.31; H, 9.16. MS (CI, NH_3) Calcd for $C_{42}H_{68}O_6Cl_2 + NH_4^+$: 756.4737. Found: 756.4697.

3,7-Di-*tert*-butyl-1,5-naphthalenedicarboxylic Acid Chloride (C). Compound **C** was prepared by reacting 3,7-di-*tert*-butyl-1,5-naphthalenedicarboxylic acid with oxaloyl chloride and a catalytic amount of dimethylformamide in methylene dichloride. ^1H NMR (300 MHz, $CDCl_3$) δ 9.00 (d, 2 H), 8.62 (d, 2 H), 1.20 (s, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.0, 150.5, 134.0, 131.0, 130.0, 35.3, 30.9. Anal. Calcd for $C_{20}H_{22}O_2Cl_2$: C, 65.92; H, 6.09. Found: C, 66.05; H, 6.19.

Isophthaloyl Chloride 5-Ethyl Ether (D). Compound **D** was synthesized from 5-hydroxyisophthalic acid using standard literature procedures. 5-Hydroxyisophthaloyl ethanoate was O-alkylated using K_2CO_3 and ethyl bromide in dimethylformamide.[30] Subsequent to deesterification,[31] the acid was reacted with oxaloyl chloride using a catalytic amount of dimethylformamide in methylene dichloride. Following recrystallization from diethyl ether, compound **D** was obtained in 53% overall yield: mp 74–76 °C; ^1H NMR (300 MHz, benzene-d_6) δ 8.22 (s, 1 H), 7.42 (s, 1 H), 3.16 (q, 2 H), 0.95 (t, 3 H); ^{13}C NMR (75 MHz, benzene-d_6) δ 166.6, 159.2, 134.9, 125.7, 122.1, 63.9, 13.9. Anal. Calcd for $C_{10}H_8O_3Cl_2$: C, 48.79; H, 3.28. Found: C, 48.88; H, 3.38. MS (EI, 70 eV) Calcd for $C_{10}H_8O_3Cl_2$: 245.9850. Found: 245.9862.

Isophthaloyl Chloride 5-Hexyl Ether (E). The synthesis of compound **E** was performed in a manner similar to that of compound **D**. The yield was 32% following recrystallization from diethyl ether: mp 40–41 °C; ^1H NMR (300 MHz, benzene-d_6) δ 8.25 (t, 1 H), 7.49 (d, 2 H), 3.28 (t, 2 H), 1.45 (m, 2 H), 1.22 (m, 6 H), 0.90 (t, 3 H); ^{13}C NMR (75 MHz, benzene-d_6) δ 166.8, 159.9, 135.6, 126.0, 122.5, 69.1, 31.8, 29.1, 25.8, 22.8, 14.1.

Isophthaloyl Chloride 5-Decyl Ether (F). The synthesis of compound **F** was performed in a manner similar to that of compound **D**. The yield was 64% following recrystallization from diethyl ether: mp 36–37 °C; ^1H NMR (300 MHz, benzene-d_6) δ 8.82 (t, 1 H), 8.06 (d, 2 H), 3.87 (t, 2 H), 2.05 (m, 3 H), 1.85 (m, 15 H), 1.5 (t, 3 H); ^{13}C NMR (75 MHz, benzene-d_6) δ 166.9, 159.7, 135.2, 126.0, 122.4, 68.7, 32.3, 30.0, 29.7, 29.6, 29.1, 26.2, 23.1, 14.3. Anal. Calcd for $C_{18}H_{24}O_3Cl_2$: C, 60.32; H, 6.75. Found: C, 60.35; H, 6.68. MS (EI, 70 eV) Calcd for $C_{18}H_{24}O_3Cl_2$: 358.1103. Found: 358.1096.

General Polymer Synthesis. Diacid chloride A (0.3858 mmol) and $Pd(AsPh_3)_2Cl_2$ (0.0039 mmol) were weighed into a polymerization tube in a drybox. Aromatic stannane monomer (0.3898 mmol) was added to the polymerization tube, which was sealed, removed from the drybox, and rapidly stirred at 70 °C for 24 h. The polymerization mixture was poured into rapidly stirred methanol. Following centrifugation, the solid was dried and analyzed using size exclusion chromatography.

Polymer 1A: ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, 2 H), 7.91 (t, 1 H), 7.87 (d, 4 H), 7.13 (d, 4 H), 1.38 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.5, 160.0, 152.0, 137.7, 133.0, 132.6, 130.2, 128.2, 118.7, 35.2, 31.2; T_g = 150 °C; DOT = 506 °C in N_2, 517 °C in air; M_n = 52700; M_w = 67900; PDI = 1.3.

Polymer 2A: ^1H NMR (300 MHz, $CDCl_3$) δ 8.08 (s, 2 H), 8.01 (s, 1 H), 7.93 (d, 4 H), 7.75 (d, 4 H), 1.39 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) 195.0, 152.3, 144.1, 137.8, 136.8, 130.8, 130.6, 128.5, 127.4, 35.2, 31.3; T_g = 221 °C; DOT = 522 °C in N_2, 523 °C in air; M_n = 37000; M_w = 59000; PDI = 1.6.

Polymer 3A: ^1H NMR (300 MHz, $CDCl_3$) δ 8.07 (s, 2 H), 8.01 (s, 1 H), 7.91 (s, 4 H), 1.36 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.0, 152.6, 140.6, 137.4, 131.0, 129.9, 128.1, 35.0, 31.2; T_g = 188 °C; DOT = 541 °C in N_2, 511 °C in air; M_n = 29700; M_w = 51500; PDI = 1.7.

Polymer 4A: ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 (s, 2 H), 8.08 (s, 1 H), 7.43 (t, 2 H), 1.37 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.6, 160.0, 152.2, 137.7, 133.0, 132.5, 130.2, 128.2, 118.7, 35.0, 31.2; T_m = 164 °C; M_n = 4400; M_w = 5600; PDI = 1.3.

Polymer 5A: M_n = 400; M_w = 560; PDI = 1.5.

Polymer 6A: T_g = 177 °C; T_m = 299 °C; DOT = 538 °C in N_2, 541 °C in air.

Polymer 3B: ^1H NMR (300 MHz, $CDCl_3$) δ 7.88 [s (br), 2], 7.44 [s (br), 4 H], 4.11 [s (br), 4 H], 1.48 (s (br), 4 H], 1.21 [s (br), 52 H], 0.87 [t (br), 6 H]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.7, 140.5, 139.7, 133.9, 132.0, 128.4, 65.7, 32.0, 29.7, 29.4, 29.3, 28.5, 25.9, 22.7, 14.0; T_g = 13 °C; DOT = 391 °C in N_2, 387 °C in air. Anal. Calcd for $C_{48}H_{72}O_6$: C, 77.37; H, 9.74. Found: C, 78.00; H, 9.66.

Polymer 3C: T_m = 375 °C; DOT = 532 °C in N_2, 524 °C in air.

Polymer 3D: ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 (s, 4 H), 7.76 (s, 1 H), 7.53 (s, 2 H), 4.12 (q, 2 H), 1.42 (t, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.7, 159.1, 140.3, 138.5, 129.9, 123.4, 119.9, 64.4, 14.6; DOT = 438 °C in N_2, 440 °C in air.

Polymer 3E: M_n = 1000; M_w = 5900.

Polymer 3F: (300 MHz, $CDCl_3$) δ 7.90 (s, 4 H), 7.76 (s, 1 H), 7.54 (s, 2 H), 4.04 (t, 2 H), 1.79 (m, 2 H), 1.44 (m, 2 H), 1.24 (m, 12 H), 0.84 (t, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.5, 159.4, 140.4, 138.6, 129.8, 123.3, 119.9, 68.0, 31.9, 29.5, 29.3, 29.1, 26.0, 22.6, 14.0.

Polymer 6G: ^1H NMR (300 MHz, $CDCl_3$) δ 8.42 (s, 1 H), 8.39 (s, 2 H), 8.15 (s, 2 H), 7.95 (m), 7.85 (m), 7.75 (s, 2 H), 7.70 (m), 7.56 (m), 1.31 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) 197.0, 152.3, 147.8, 139.3, 135.5, 131.7, 130.1, 129.5, 128.4, 124.4, 31.3, 31.1; T_g = 205 °C; DOT = 508 °C in N_2, 501 °C in air. Anal. Calcd for $C_{30}H_{34}O_2$: C, 84.46; H, 8.03. Found: C, 84.46; H, 8.17.

Acknowledgment. This work was supported in part by the U.S. Army under Grant DAAK60-92-K-0005. A generous gift of 5-*tert*-butylisophthalic acid from the Amoco Chemical Corp. is gratefully acknowledged. J.S.M. would like to thank the 3M Co. for financial support through their nontenured faculty awards program.

References and Notes

(1) (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340.

(2) (a) Bochmann, M.; Kelly, K. *J. Chem. Soc., Chem. Commun.* **1989**, 532. (b) Havens, S. J.; Hergenrother, P. M. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 587. (c) Trumbo, D. L.; Marvel, C. S. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 2311. (d) Pugh, C.; Percec, V. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31* (1), 512.

(3) (a) Weitzel, H. P.; Mullen, K. *Makromol. Chem.* **1990**, *191*, 2837. (b) Fahnenstich, U.; Koch, K. H.; Mullen, K. *Makromol. Chem., Rapid Commun.* **1989**, *10*, 563. (c) Heitz, W.; Brugging, W.; Freind, L.; Gailberfer, M.; Greiner, A.; Jung, H.; Kampschulte, U.; Niessner, N.; Osan, F.; Schmidt, H. W.; Wicher, M. *Makromol. Chem.* **1989**, *189*, 119.

(4) (a) Yoneyama, M.; Kakimoto, M.; Imai, Y. *Macromolecules* **1988**, *21*, 1908. (b) Yoneyama, M.; Kakimoto, M.; Imai, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 1985. (c) Perry, R. J.; Turner, S.; Blevins, R. W. Eur. Pat. Appl. EP 459,386. (d) Turner, S. R.; Perry, R. J.; Blevins, R. W. *Macromolecules* **1992**, *25*, 4819.

(5) Yoneyama, M.; Kakimoto, M.; Imai, Y. *Macromolecules* **1989**, *22*, 2593.

(6) Suzuki, M.; Lim, J. C.; Saegusa, T. *Macromolecules* **1990**, *23*, 1574.

(7) (a) Rehahn, M.; Schluter, A. D.; Wegner, G.; Feast, W. J. *Polymer* **1989**, *30*, 1054. (b) Rehahn, M.; Schluter, A. D.; Wegner, G.; Feast, W. J. *Polymer* **1989**, *30*, 1060. (c) Rehahn, M.; Schluter, A. D.; Wegner, G. *Makromol. Chem.* **1990**, *191*, 1991. (d) Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 7411. (e) Cramer, E.; Percec, V. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 3029. (f) Suzuki, M.; Lim, J. C.; Oguni, M.; Eberhardt, A.; Saegusa, T. *Polym. J.* **1990**, *22*, 815.

(8) (a) Perry, R. J.; Turner, R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (1), 335. (b) Perry, R. J.; Turner, R. *Makromol. Chem., Macromol. Symp.* **1992**, *54/55*, 159.

(9) (a) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513. (b) Miller, R. B.; Dugar, S. *Organometallics* **1984**, *3*, 1261. (c) Sharp, M. J.; Cheng, W.; Snieckus, V. *Tetrahedron Lett.* **1987**, 5093. (d) Cheng, W.; Snieckus, V. *Tetrahedron Lett.* **1987**, 5097. (e) Thompson, W. J.; Guadino, J. *J. Org. Chem.* **1984**, *49*, 5237. (f) Miyaura, N.; Suzuki, A. *J. Chem. Soc., Chem. Commun.* **1979**, 596.

(10) (a) Negishi, E.; King, A. O.; Okukado, N. J. *J. Org. Chem.* **1977**, *42*, 1821. (b) Negishi, E.; Okukado, N. J.; King, A. O.; Van Horn, D. E.; Spiegel, B. I. *J. Am. Chem. Soc.* **1978**, *100*, 2254. (c) King, D. E.; Negishi, E.; Villani, F. J., Jr.; Silveira, A. *J. Org. Chem.* **1978**, *43*, 358. (d) Negishi, E.; Bagheri, W.; Chatterjee, S.; Luo, F.; Miller, J. A.; Stoll, A. T. *Tetrahedron Lett.* **1983**,

5181. (e) Sato, T.; Naruse, K.; Euokiya, M.; Fujisowa, T. *Chem. Lett.* **1981**, 1135. (f) Al-Hassan, M. *Synth. Commun.* **1987**, *28*, 701. (g) McCague, R. *Tetrahedron Lett.* **1987**, *28*, 701. (h) Keenan, R. M.; Kruse, L. I. *Synth. Commun.* **1989**, *19*, 793. (i) Negishi, E.; Matsushita, H.; Okukado, N. *Tetrahedron Lett.* **1981**, 2715.

(11) (a) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4992. (b) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478. (c) Bailey, T. R. *Tetrahedron Lett.* **1986**, 4407. (d) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 3636. (e) Kosugi, M.; Migita, Y. S. *Chem. Lett.* **1977**, 1423. (f) Bumagin, N. A.; Bumagina, I. O.; Kashin, A. N.; Beletskaya, I. P. *Zh. Org. Khim.* **1982**, 1131. (g) Soderquist, J. A.; Leong, W. H. *Tetrahedron Lett.* **1983**, 2361. (h) Logue, M. W.; Teng, K. J. *J. Org. Chem.* **1982**, *47*, 2549. (i) Milstein, D.; Stille, J. K. *J. Org. Chem.* **1979**, *44*, 1613. (j) Labadie, J. W.; Stille, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6129. (k) Bumagin, N. A.; Bumagina, I. O.; Kashin, A. N.; Beletskaya, I. P. *Dokl. Akad. Nauk SSSR* **1981**, *261*, 1141. (l) Stille, J. K.; Groh, B. L. *J. Am. Chem. Soc.* **1987**, *109*, 813. (m) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033.

(12) May, R. Poly(ether ether ketones). *Encyclopedia of Polymer Science and Engineering*; Wiley: New York, 1988; Vol. 12, p 313.

(13) (a) Bonner, W. H. U.S. Patent 3 065 205, 1962. (b) Marks, B. M. U.S. Patent 3 442 857, 1969. (c) Dahl, K. J. Br. Pat. Appl. 1387 303, 1975.

(14) (a) Rose, J. B.; Staniland, P. A. U.S. Patent 4 320 224, 1982. (b) Attwood, T. E.; Dawson, P. C.; Freeman, J. L.; Hoy, R. J.; Rose, J. B.; Staniland, P. A. *Polymer* **1981**, *22*, 1096.

(15) Mohanty, D. K.; Lin, T. S.; Ward, T. C.; McGrath, J. E. *Int. SAMPE Symp. Exp.* **1986**, *31*, 945.

(16) Risse, W.; Sogah, D. Y. *Macromolecules* **1990**, *23*, 4029.

(17) (a) Singh, R.; Hay, A. S. *Macromolecules* **1992**, *25*, 1017. (b) Singh, R.; Hay, A. S. *Macromolecules* **1992**, *25*, 1025. (c) Singh, R.; Hay, A. S. *Macromolecules* **1992**, *25*, 1033.

(18) For interesting structure–property correlations related to the percent of ether linkage in poly(aromatic ether ketones)s, see: Herold, F.; Schneller, A. *Adv. Mater.* **1992**, *4*, 143.

(19) For preliminary accounts of this work, see: (a) Moore, J. S. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 91. (b) Moore, J. S.; Deeter, G. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (3), 213.

(20) (a) Chivers, T. *J. Organomet. Chem.* **1969**, *19*, 75. (b) Shiina, K.; Brennan, T.; Gilman, H. *J. Organomet. Chem.* **1968**, *11*, 471. (c) Jaura, K. L.; Sharma, K. K. *J. Indian Chem. Soc.* **1969**, *46*, 835. (d) Jaura, K. L.; Hundal, H. S.; Handa, R. D. *Indian J. Chem.* **1967**, *5*, 211.

(21) Azizian, H.; Earborn, C.; Pidcock, A. *J. Organomet. Chem.* **1981**, *215*, 49.

(22) Wursthorn, K. R.; Kuivila, H. G. *J. Organomet. Chem.* **1977**, *140*, 29.

(23) The concentration of Me_3SnNa was determined in the following manner. A benzene-d_6 solution of a known amount of pentamethylbenzene (internal standard) and a known volume of Me_3SnNa in tetraglyme was prepared. The following equation was used to determine the concentration:

$$[\mathrm{Me_3SnNa}] = \frac{\left(\frac{6}{9}\right)\frac{I_{\mathrm{Sn}}}{I_{\mathrm{IS}}}M_{\mathrm{IS}}}{V_{\mathrm{Sn}}}$$

where I_{Sn}/I_{IS} is the ratio of integral protons at 0.34 and 2.2 ppm, respectively, and V_{Sn} is the volume of sodium trimethylstannate tetraglyme solution used.

(24) Alnajjar, M. S.; Kuivila, H. G. *J. Am. Chem. Soc.* **1985**, *107*, 416.

(25) (a) Monomer purity was determined by gas chromatography. (b) One advantage of trimethyltin derivatives as opposed to other trialkyltin monomers is their ability to be purified by recrystallization.

(26) While this work was in progress, Farina et al. reported on the large rate accelerations in coupling with triphenylarsine as palladium catalyst ligand: Farina, V.; Krisnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585.

(27) No additional end group information could be found in the ^{13}C NMR spectrum.

(28) Tayim, H. A.; Bouldoukian, A.; Awad, F. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3799.

(29) Harkness, B. R.; Watanabe, J. *Macromolecules* **1991**, *24*, 6759.

(30) *Org. Synth. Collect. Vol. 3.* **1950**, 140.

(31) *Org. Synth. Collect. Vol. 3.* **1955**, 267.