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A New Polymerization Reaction: Synthesis of Soluble Polyketones and Poly(arylenevinylene)s

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Introduction

Palladium-catalyzed cross-coupling reactions have received intensive research attention. A number of important carbon−carbon bond formation processes have been realized.[1] Palladium-catalyzed coupling reactions are also of growing importance in the synthesis of macromolecules.[2−5] Compared to many other metal complexes, palladium catalysts are reactive, stable, and tolerant to a wide variety of functionalities during the course of the reaction, which make them ideal candidates for construction of functionalized molecules. The reactivities of the complexes can also be tuned through the variation of ligands. Development of new palladium-mediated polymerization processes provides new synthetic routes to functionalized polymers, which are both fundamentally interesting and practically important.

Polyketones are high-performance materials and have several attractive properties including high glass transition temperature (T_g) and thermal stability because of the incorporation of carbonyl and/or aromatic groups in the polymer backbones, as well as the ease of modification to other functionalized polymers.[6] Moreover, aliphatic polyketones have been used as photodegradable polymers.[7] Aromatic polyketones are typically synthesized by Friedel−Crafts or nucleophilic aromatic substitution reactions.[8] These materials are usually insoluble and intractable. Aliphatic polyketones have been prepared through the copolymerization of CO with ethylene or α-olefins.[9] Aromatic aliphatic polyketones have, however, not been reported. We describe herein a new polymerization strategy for the generation of poly(arylene methylene ketone), which can be readily converted to poly(*p*-arylenevinylene) (PAV), a material that has many significant applications.[10−12]

Results and Discussion

Coupling reaction of a ketone and an aryl halide to form an alkyl aryl ketone using Pd(0) phosphine complexes has been reported.[13] We envision that this reaction might be useful for polymer synthesis, which will provide new approaches to novel materials. We have found that 1,4-dihaloarenes and 1,4-diacetylbenzene readily undergo condensation polymerization in the presence of a catalytic amount of Pd(0) or Pd(II) complexes, base, and phosphine ligands (Scheme 1). Long alkyl substituents on the phenyl ring are introduced to enhance the solubility of the polymers.

Table 1. Effect of Phosphines and Substrates on Pd(0)-Catalyzed Polymerizations[a]

entry	X	R	phosphine	yield (%)	M_n[b]	M_w
1	I	$C_{12}H_{25}$	DPPF	44	12 800	14 000
2[c]	I	$C_{12}H_{25}$	PPh_3	61		
3	I	$C_{12}H_{25}$	$P(Bu^t)_3$	96	14 800	23 200
4	I	$C_{12}H_{25}$	$P(o\text{-}MeC_6H_5)_3$	77	3 900	8 700
5	I	$C_{12}H_{25}$	BINAP	83	8 900	12 800
6	I	$C_{16}H_{33}$	BINAP	66	12 300	15 600
7	Br	$C_{16}H_{33}$	BINAP	70	7 100	13 000

[a] Pd_2dba_3 is used in the reactions. [b] Molecular weights were determined by GPC using polystyrene standards. [c] Only oligomers are formed, and molecular weights are not determined.

Table 2. Effect of Phosphines and Substrates on Yield and Molecular Weight[a]

entry	X	R	phosphine	yield (%)	M_n	M_w
1	I	$C_{12}H_{25}$	DPPF	93	13 800	18 700
2	I	$C_{16}H_{33}$	PCy_3	90	14 300	18 300
3	Br	$C_{16}H_{33}$	$P(Bu^t)_3$	93	6 700	10 700
4	I	$C_{16}H_{33}$	$P(Bu^t)_3$	95	13 400	16 500
5	Br	$C_{12}H_{25}$	BINAP	75	5 300	9 800
6	I	$C_{16}H_{33}$	BINAP	88	13 800	18 200
7	Br	C_8H_{17}	BINAP	70	4 200	7 200
8	I	C_8H_{17}	BINAP	82	4 700	11 000

[a] $Pd(OAc)_2$ is used.

We have examined both mono- and bis-phosphines and found that both were effective ligands for the polymerization reactions in the presence of Pd(0) complexes (Table 1). Rigid and steric bulky bis-phosphines are efficient ligands for catalyzing the polymerizations. As for monophosphines, both electron donating and steric bulkiness are required to achieve a good polymerization activity. For example, both molecular weights and yields of the polymers were improved when electron donating and steric hindered $P(t\text{-}Bu)_3$ (Table 1, entry 3) was used. We have also found that aryl diiodes are more reactive substrates than aryl dibromides.

Palladium(II) complexes, such as $Pd(OAc)_2$, were also active in catalyzing the condensation polymerization of diketones and dihalide in the presence of both mono- and bis-phosphine ligands (Table 2). Similar to Pd(0) complexes, electron donating and steric bulky phosphines favor the polymerizations.

The polymerization was also studied in the presence of different solvents. Polar solvents enhance the polymerization. For example, polymers prepared using a catalytic amount $Pd(OAc)_2$/ligand exhibit higher molecular weights in THF than in other solvents. Better yields of polymers were also obtained in solvents such as $o\text{-}C_6H_4Cl_2$ and diphenyl ether. However, no polymerization was observed when DMAc was used as a solvent.

The polymers were isolated by precipitation, and structures of the polymers were determined by spectroscopic techniques. For example, polymer **1c** shows a peak at δ 3.8 ppm in the ^1H NMR spectrum corresponding to the CH_2 resonance. The carbonyl resonance was observed at δ 200.3 ppm and was further confirmed by IR spectroscopy ($\nu = 1690.8$ cm^{-1}). The molecular weight was determined by gel permeation chromatography (GPC) using polystyrene as standards. The molecular weights (M_n) of the polymers obtained range from 5000 to 23 000 depending on the reaction conditions, such as catalysts, ligands, and solvents used. The stability of the polymers were studied using thermal gravimetric analysis (TGA), suggesting a initial decomposition temperature of 357 °C under nitrogen.

The carbonyl groups in the polymers can be quantitatively reduced to hydroxyl groups using $LiAlH_4$

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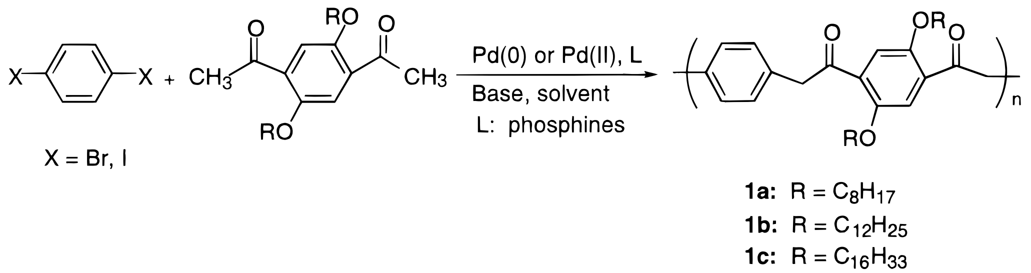
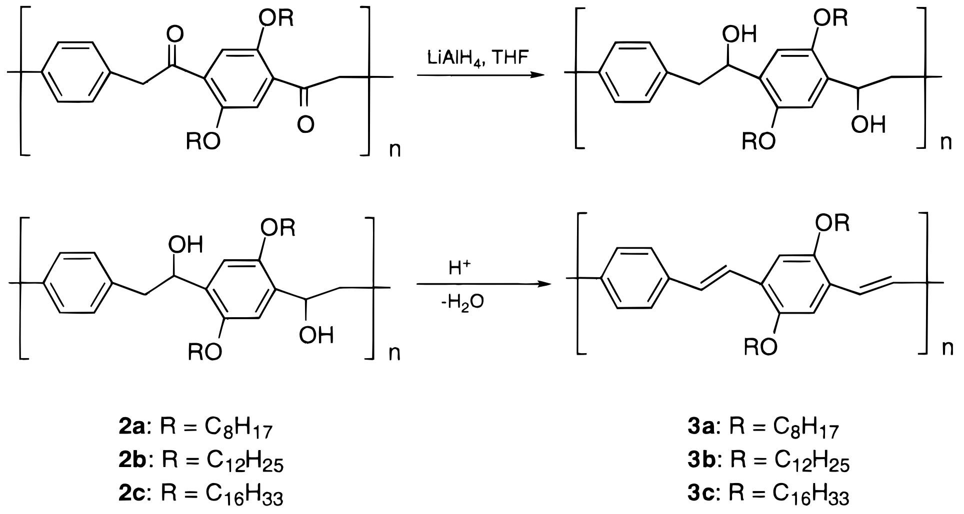
Scheme 1



Scheme 2. Conversion to Conjugated Polymers



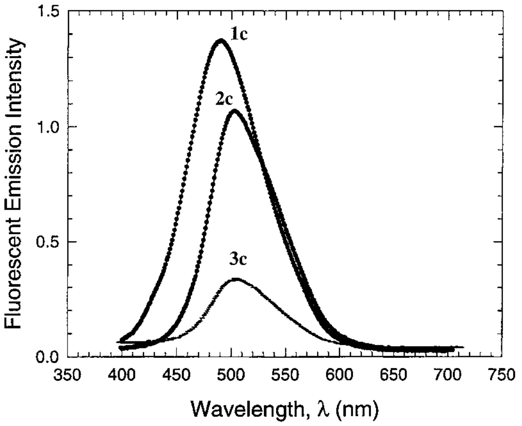


Figure 1. Fluorescence emission spectra of conjugated polymers.

(Scheme 2). Both ^{13}C NMR and IR spectra indicated the complete reduction of the carbonyl groups. Polymer **2c** was obtained as a white solid and was insoluble in hexane. To obtain conjugated polymer, polymer **2c** was further treated with catalytic amount of TsOH in toluene. Rapid elimination of H_2O was observed to yield polymer **3c** (Scheme 1). The polymer is soluble in common organic solvent, such as THF, CH_2Cl_2, and hexane. Both IR and ^{1}H NMR spectra indicate the complete elimination. Comparison of the UV spectra of the polymers with a calculated spectrum of *trans*-poly(phenylenevinylene) suggests that the double bonds formed in the polymer backbone are predominantly trans.[14] The polymer has an UV absorption peak around 380 nm and exhibits strong green emissions ($\lambda_{\max} =$ 490−507 nm) (Figure 1) when an excitation at 380 nm is applied. The position of the emission peak shifts slightly toward longer wavelength with the increasing of alkyl chain length.

Conclusion

Palladium-catalyzed coupling reactions of aryl dihalide and diketones are useful for polyketones synthesis. These polymers can be easily converted to poly(arylenevinylene)s through a reduction and elimination sequence. Both steric and electronic properties of the ligands as well as solvents have significant effects on the success of the polymerization. The conjugated polymers synthesized are soluble and exhibit photoluminescence properties. Synthesis of other polyketones and electro- and/or photoluminescence polymers using this new methodology is being explored.

Experimental Section

Typical Procedure for the Synthesis of Polymers 1a−c. To a suspension of Pd_2dba_3 (1.5 mol %), BINAP (3.6 mol %), and $NaOBu^t$ (2.1 mmol) in THF (10 mL) were added 1,4-aryl dihalide (1 mmol) and 1,4-diacetylbenzene (1 mmol). The mixture was heated under N_2 for 12−20 h at 75 °C and then cooled to room temperature and quenched with H_2O (5 mL). The product was extracted with CH_2Cl_2, and the organic layer was washed with brine and H_2O and dried over Na_2SO_4. The resulting product was further purified by flash chromatography on silica gel using CH_2Cl_2 as eluent and reprecipitated into methanol. **1a**: ^{1}H NMR (CD_2Cl_2): δ 8.30 (2H), 6.70 (4H), 3.80 (4H), 2.50−1.00 (28H), 0.87 (6H). ^{13}C NMR (CD_2Cl_2): δ 198.5, 152.5, 141.3, 129.1, 117.6, 71.3, 41.5, 32.6, 30.0, 26.6, 23.3, 14.5. **1b**: ^{1}H NMR ($CDCl_3$): δ 8.05 (4H), 6.75 (2H), 3.80 (4H),2.61 (4H), 1.80−1.00 (40H), 0.91 (6H). ^{13}C NMR ($CDCl_3$): δ 198.7, 150.3, 150.2, 140.2, 128.9, 128.8, 69.0, 32.1, 29.9, 29.6, 29.3, 26.3, 22.9, 14.3. **1c**: ^{1}H NMR ($CDCl_3$): δ 8.13 (2H), 7.94 (2H), 6.68 (s, 2H), 3.72 (4H), 2.60 (4H), 1.55−1.04 (56H), 0.88 (6H).

Reduction of Polyketone 1c. To a suspension of $LiAlH_4$ (4 mmol) in THF (20 mL) was added dropwise a solution of polymer **1c** (0.5 mmol) in THF (15 mL) to maintain a gentle reflux. After addition, the mixture was refluxed for 4 h and cooled to room temperature. The product (86%) was isolated by precipitation in methanol. ^{1}H NMR ($CDCl_3$): δ 7.43 (br, 4H), 6.74 (2H), 4.97 (2H), 3.95 (br, 8H), 3.09 (br, 2H), 2.90 (4H), 1.80 (4H), 1.28 (52H), and 0.89 (6H).

General Procedure for Dehydration. The polymer was dissolved in dry benzene in the presence of a catalytic amount of *p*-toluenesulfonic acid and molecular sieves. The mixture was heated to reflux for 10 h, and the color of the solution changed to bright green. The solution was cooled to room temperature, washed with water, and precipitated into methanol to yield the desired product (yield 98%). **3c:** ^{1}H NMR ($CDCl_3$): δ 7.22 (br, 10H), 3.81 (4H), 1.75 (4H), 1.28 (52H), and 0.88 (t, $J = 7.5$ Hz, 6H). ^{13}CNMR ($CDCl_3$): δ 151.8, 145.8, 143.1, 129.1, 127.2, 125.6, 125.3, 70.4, 69.4, 32.5, 30.4, 30.0, 27.0, 23.3, and 14.5.

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