

New polymerization catalyzed by palladium complexes: synthesis of poly(*p*-phenylenevinylene) derivatives

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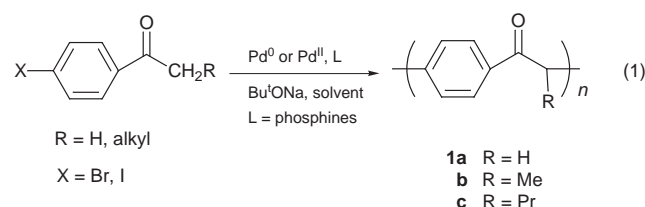
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Palladium complexes are found to catalyze the condensation polymerization of halophenyl alkyl ketones to form polyketones, which can be readily converted to poly(phenylenevinylene) and its derivatives.

Recently, palladium-catalyzed cross-coupling reactions have received a great deal of 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. Several important coupling reactions catalyzed by palladium complexes, such as the Stille coupling reaction,² the Suzuki coupling reaction,³ and the Heck reaction,⁴ as well as the reaction of a diyne or bisallene with an aryl dihalide,⁵ have been successfully applied in the synthesis of macromolecules. In our ongoing program, we are interested in developing other palladium-catalyzed polymerization reactions and utilizing these reactions to synthesize important materials.

Poly(*p*-phenylenevinylene) (PPV) and its derivatives have attractive properties, such as electrical conductivity,⁶ large third-order nonlinear optical response⁷ and photo- and electroluminescence in the visible region.⁸ However, the extended planar topology of the PPV backbone, which renders it infusible and insoluble in non-reactive media, limits its capacity for subsequent synthesis and fabrication. The problem can be overcome by synthesis of an intermediate soluble polymer, which is typically synthesized from the precursor route first developed by Wessling and Zimmerman,⁹ in which the soluble precursor polymer is synthesized through a Wittig or nucleophilic displacement reaction. Thermal induced elimination to PPV can then be accomplished under mild conditions. Other routes to PPV based on this strategy were also reported.¹⁰ We describe here our efforts in developing new polymerization methodology using aryl and ketone coupling reactions, and the application of these reactions to the synthesis of soluble poly(phenylenevinylene) derivatives.

It was reported recently by Buchwald *et al.* that Pd⁰ complexes catalyzed the coupling reaction of a ketone and an aryl halide to form an alkyl aryl ketone.¹¹ We envision that this reaction might be useful for polymer synthesis, providing new approaches to novel materials. We found that halophenyl alkyl ketones readily underwent condensation polymerization in the presence of a catalytic amount of Pd⁰ or Pd^{II} complex, base and phosphine ligand [eqn. (1)].



We find that both mono- and bis-phosphines are effective ligands for the polymerization reactions. The influence of α -alkyl substituent R on the polymerization (Table 1) was also

Table 1 Polymerization of 4-halophenyl alkyl ketones^a

Entry	X	R	Yield (%)	M_n	M_w
1	Br	H	60	1800 ^b	2500
2 ^c	I	H	76		
3	Br	Me	70	1700	2100
4	Br	Bu	90	3200	4100
5	I	Pr	65	10100	13200

^a Pd(dba)₃/BINAP was used as catalyst. ^b The polymer is slightly soluble in THF and molecular weights are determined from the soluble portion. ^c The polymer is insoluble in THF.

examined. The α -alkyl substituents can dramatically enhance the solubility and yield of the polymers. For example, when the α -substituent is H (entries 1 and 2) the polymers are insoluble and are obtained in low yields. When monomers with longer alkyl substituents were used, polymers with higher molecular weights ($M_n = 11000$) were obtained after fractional precipitation.

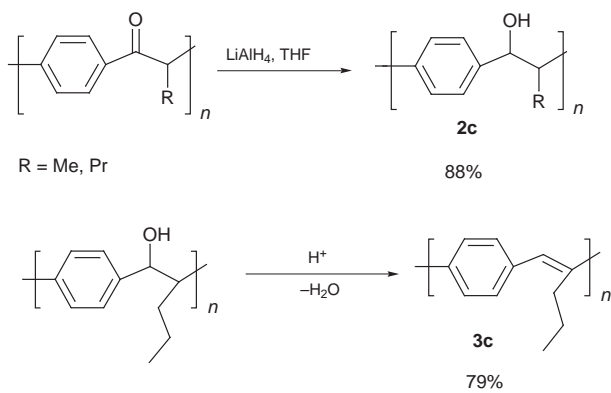
The polymerization was also studied in the presence of phosphines with different steric and electronic properties. As shown in Table 2, polymers were obtained in high yield and with high molecular weights in the presence of both bulky and electron-donating phosphines, such as P*t*Bu₃, which indicates that steric bulk and electron-donating phosphines favor the polymerizations. The results further imply that steric and electronic factors need to balance in order to achieve the optimized polymerization conditions. This observation can be understood from the fact that bulky and electron-donating ligands facilitate both oxidative addition and reductive elimination processes, which are believed to be involved in the rate-limiting steps of the catalytic cycle. We also observed that 4-iodophenyl propyl ketone, as compared to bromovalerophenone, polymerized faster and yielded higher molecular weight polymers. This observation suggests that oxidative addition of Pd⁰ species to the aryl halide is also a crucial step involved in determining the rate of the polymerization.

The polymerization was also investigated in the presence of different solvents. Polar solvents seem to enhance the polymerization. For example, polymers prepared using a catalytic amount of Pd(OAc)₂-ligand exhibited higher molecular weights in THF than in other solvents. Better yields of polymers were also obtained in solvents such as *o*-C₆H₄Cl₂ and Ph₂O. No

Table 2 The effect of phosphine ligands on the polymerization^a

Entry	Ligand	Yield (%)	Cone angle/ ^o	M_n	M_w
1	P <i>t</i> Bu ₃	63	182	11500	15200
2	PCy ₃	20	170	5700	8800
3	P(<i>o</i> -tolyl) ₃	55	194	900	4600
4	PPh ₃	30	145	700	3500
5	DPPF ^b	44		3000	6100

^a Pd(OAc)₂ was used as catalyst and X = Br, R = Pr. ^b 1,1'-Bis(diphenylphosphino)ferrocene.



polymerization was observed when DMA was used as a solvent, which may be attributed to deactivation of the catalysts.

The polymers were isolated by precipitation and the structures of the polymers were determined by spectroscopic techniques. For example, polymer **1c**[†] shows a peak at δ 4.67 in its ^1H NMR spectrum corresponding to the CH resonance. The carbonyl resonance was observed at δ 199.2 and was further confirmed by IR spectroscopy ($\nu = 1696\text{ cm}^{-1}$). The single resonance at δ 53.2 in the ^{13}C NMR spectrum corresponds to the methine carbon in polymer **1b**, indicating that the polymerization is selective. 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 2000 to 16 000 depending on the catalyst, ligand and solvent used.

The carbonyl groups in the polymers can be quantitatively converted to hydroxy groups using LiAlH_4 (Scheme 1). The ^{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 the PPV derivative, polymer **2c** was further treated with a catalytic amount of H_3PO_4 in toluene. Rapid elimination of H_2O was observed to yield polymer **3c**[§] (Scheme 1). The polymer is soluble in common organic solvents, such as THF and CH_2Cl_2 . The IR and ^1H NMR spectra indicated complete elimination. Both ^1H and ^{13}C NMR analysis indicated that the double bonds formed in the polymer backbone are predominantly *trans*. The polymer has a UV absorption ($\lambda_{\text{max}} = 290\text{ nm}$) and exhibits a strong blue emission at 420 nm (Fig. 1) when excitation at 290 nm is applied, which indicates that the polymer is a photoluminescence material.

We have demonstrated that palladium-catalyzed coupling of aryl halides and ketones can be used for polymer synthesis. This has led us to develop a new polymerization reaction and a novel approach to the synthesis of poly(phenylenevinylene) derivatives. Our studies suggest that the steric and electronic properties of the ligands as well as the nature of the solvent have significant effects on the outcome of the polymerization. The polymers synthesized are soluble and exhibit photoluminescence properties. Synthesis of other electro- and/or photoluminescent polymers using this methodology are currently underway.

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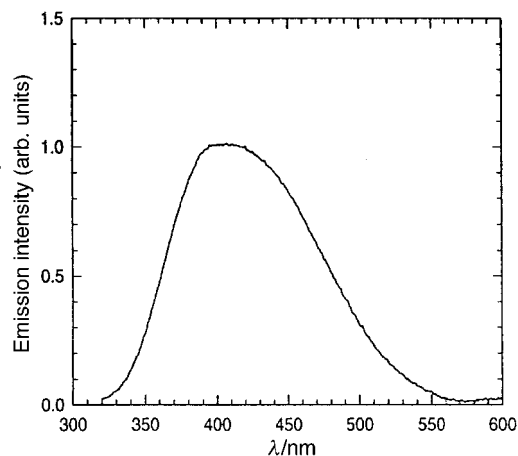


Fig. 1 Photoemission spectrum of **3c**.

Notes and references

Selected data for 1c: $\delta_{\text{H}}(\text{CDCl}_3)$ 7.78 (m, 2H), 7.28 (m, 2H), 4.67 (m, 1H), 2.2–0.81 (br, 7H); $\delta_{\text{C}}(\text{CDCl}_3)$ 199.2, 145.5, 136.2, 129.6, 128.8, 53.2, 36.7, 21.4, 14.3; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3050.5, 3020.3, 2930.7, 1696.2, 1685.7, 1681.2, 1270.9.

Selected data for 2c: $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$ 7.50–6.80 (m, 4H), 4.65 (m, 1H), 3.68 (m, 1H), 2.95–0.85 (br, 8H); $\delta_{\text{C}}(\text{CD}_2\text{Cl}_2)$ 141.7, 128.5, 128.0, 127.6, 79.1, 34.9, 30.3, 21.1, 14.3.

Selected data for 3c: $\delta_{\text{H}}(\text{CDCl}_3)$ 7.35–7.03 (m, 4H), 4.32–4.24 (br, 1H), 2.38–0.87 (br, 7H); $\delta_{\text{C}}(\text{CDCl}_3)$ 129.4, 128.6, 127.6, 126.2, 79.0, 64.5, 28.3, 21.3, 14.3.

- L. Cassar, *J. Organomet. Chem.*, 1975, **93**, 253; N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, 2457; A. Dieck and R. F. Heck, *J. Organomet. Chem.*, 1975, **93**, 259; R. F. Heck, *Acc. Chem. Res.*, 1979, **12**, 146; M. Shibusaki, C. O. J. Boden and A. Kojima, *Tetrahedron*, 1997, **53**, 7371; J. K. Stille, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 508; T. N. Mitchell, *Synthesis*, 1992, 803.
- F. Babudri, S. R. Cicco, G. M. Farinola and F. Naso, *Macromol. Rapid Commun.*, 1996, **17**, 905.
- M. Remmers, M. Schulze and G. Wegner, *Macromol. Chem. Rapid Commun.*, 1996, **17**, 239.
- D. K. Fu, B. Xu and T. M. Swager, *Tetrahedron*, 1997, **53**, 15487.
- N. Miyaki, I. Tomita and T. Endo, *Polym. Bull.*, 1997, **39**, 677; N. Miyaki, I. Tomita and T. Endo, *Macromolecules*, 1996, **29**, 6685.
- G. E. Wneck, J. C. W. Chien, F. E. Karasz and C. P. Lillya, *Polymer*, 1979, **20**, 1441; I. Murase, T. Ohnishi, T. Noguchi and M. Hirooka, *Synth. Met.*, 1987, **17**, 639; J. I. Jin, Y. H. Lee and H. K. Shim, *Macromolecules*, 1993, **26**, 1805.
- D. J. William, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 690; D. H. Hwang, J. I. Lee, H. K. Shim, W. Y. Hwang, J. J. Kim and J. I. Jin, *Macromolecules*, 1994, **27**, 6000.
- J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns and A. B. Holmes, *Nature*, 1990, **347**, 539; G. Gustafsson, Y. Gao, G. M. Treacy, F. Klavetter, N. Colaneri and A. J. Heeger, *Nature*, 1992, **357**, 477; P. L. Burn, A. B. Holmes, A. Krat, D. D. C. Bradley, A. R. Brown, R. H. Friend and R. W. Gymer, *Nature*, 1992, **356**, 47.
- R. A. Wessling and R. G. Zimmerman, *Chem. Abstr.*, 1969, **69**, 87735q; R. A. Wessling, *J. Polym. Sci., Polym. Symp.*, 1985, **72**, 55.
- A. Greiner and W. Heitz, *Macromol. Chem., Rapid Commun.*, 1988, **9**, 581; V. P. Conticello, D. L. Gin and R. H. Grubbs, *J. Am. Chem. Soc.*, 1992, **114**, 9708.
- M. Palucki and S. L. Buchwald, *J. Am. Chem. Soc.*, 1997, **119**, 11108.

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