

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

## Metal-Catalyzed Coupling Reactions In The Synthesis Of New Conducting Polymers

T. M. Swager; M. J. Marsella; Q. Zhou; M. B. Goldfinger

**To cite this Article** Swager, T. M. , Marsella, M. J. , Zhou, Q. and Goldfinger, M. B.(1994) 'Metal-Catalyzed Coupling Reactions In The Synthesis Of New Conducting Polymers', Journal of Macromolecular Science, Part A, 31: 11, 1893 — 1902

**To link to this Article:** DOI: 10.1080/10601329408545889

**URL:** <http://dx.doi.org/10.1080/10601329408545889>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## METAL-CATALYZED COUPLING REACTIONS IN THE SYNTHESIS OF NEW CONDUCTING POLYMERS

T. M. SWAGER,\* M. J. MARSELLA, Q. ZHOU, and M. B. GOLDFINGER

Department of Chemistry and Laboratory for Research on the Structure of Matter  
University of Pennsylvania  
Philadelphia, Pennsylvania 19104-6323

### ABSTRACT

The use of transition metal-catalyzed coupling reactions in the synthesis of conducting polymers is discussed. These reactions are of growing importance in polymer synthesis and are particularly important in the synthesis of highly functionalized conjugated (conducting) polymers. In this report we discuss applications of this methodology for the synthesis of conducting polymer sensory materials and polymers with reactive functional groups. In the sensory polymers we have incorporated crown ether groups which induce perturbations to the polymer's electronic structure when exposed to an alkali metal ion. Our interest in polymers with reactive functional groups is for the development of polymers which can be transformed into novel all-carbon ladder polymers.

### INTRODUCTION

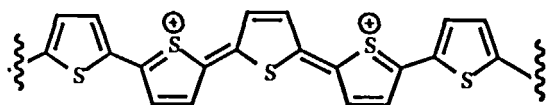
Metal-catalyzed coupling reactions are emerging as powerful tools for step-growth polymerizations and are particularly effective for the formation of highly unsaturated polymers with complex functionality. Cross-coupling methodology was first demonstrated in polymer synthesis in the laboratory of Yamamoto [1] in the preparation of polyphenylenes. Yamamoto further demonstrated cross-coupling methodology for the synthesis of poly(arylene ethynylene)s [2]. Wudl was the first to use coupling reactions to prepare polythiophenes by transition metal coupling

reactions [3]. The polythiophenes synthesized by Wudl gave materials of more certain structure than previously investigated and hence these materials were used for careful studies of the conduction and magnetic properties of these important materials. The advent of soluble conducting polymers and the development of a number of coupling protocols by Stille [4], Heck [5], Kumada [6], and Suzuki [7] has resulted in numerous syntheses of conducting polymers by transition metal coupling reactions. The important aspects of these reactions are their high yields, tolerance of functional groups, and availability of starting materials. In this report, we summarize some of our efforts in the design and synthesis of novel conducting polymers which make use of transition metal-catalyzed coupling reactions.

### DESIGN AND SYNTHESIS OF SENSORY MATERIALS

We have been investigating the application of transition metal-catalyzed cross-coupling reactions for the synthesis of conducting polymers which exhibit sensory properties. Conducting polymers are ideal materials with which to produce sensory devices since their conductivity is very sensitive to chemical composition and electronic perturbations and may vary by more than a factor of  $10^{13}$ . Our initial efforts in this area have focused on producing polymers which are responsive to alkali ions and electron-deficient organic molecules. In principle, however, our design can be applied to any chemical entity since the molecular nature of the sensory materials allows for tailoring of the polymer's response to a given chemical species by the implementation of known molecular recognition principles and/or chemical selectivity [8]. In our approach, conductivity changes are brought about by novel mechanisms which involve the formation of barriers to carrier transport or by introduction of carriers via host-guest-induced doping. There have been previous investigations of conducting polymer-based gas sensors [9]; however, most of these systems are chemically irreversible and have a time-dependent (i.e., integrated) response. The switching processes in our systems are *chemically reversible*, allowing for the formation of sensors which give a steady-state response that does not depend on the exposure time and permits the sensor to return to its original state once the chemical signal is absent.

We have focused our attention on polythiophenes as a result of their environmental stability and the versatile chemistry of thiophene which allows for facile synthesis of functionalized monomers [10]. Typical of conducting polymers, polythiophenes are only highly conductive when carriers have been injected via a redox process. In the case of thiophenes, the dominant carriers are positively charged bipolarons (dications) which delocalize over approximately three rings. The bipolaron structure shown below produces a bond alternation which requires that the center ring have "quinoid" character and produces a double bond between the thiophene rings [11].



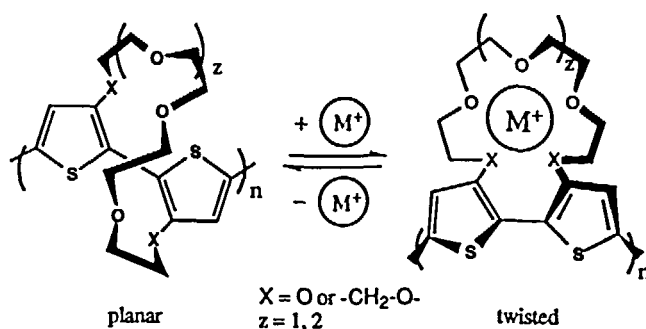
**Bipolaron**

Since propagation of a bipolaron through a polythiophene requires partial double bond character between the rings, we reasoned that a chemically induced twisting of the polythiophene backbone would impede intrachain carrier transport. Given the established nature of crown ether chemistry, we considered that an ion selective twisting would be easily designed. Additionally there is a need for ion sensors since the concentrations of Group 1 and 2 ions are extensively measured in the biological sciences and in health care. To effect this ion selective twisting, we have designed and synthesized the crown ether-containing polymers shown in Scheme 1, in which the crown ether linkages span the bithiophene groups. In the uncomplexed state the polymer's backbone is allowed to adopt a preferred "planar" conformation which maximizes conjugation. Complexation of an ion of the correct size can then induce the desired twist in the polymer's backbone.

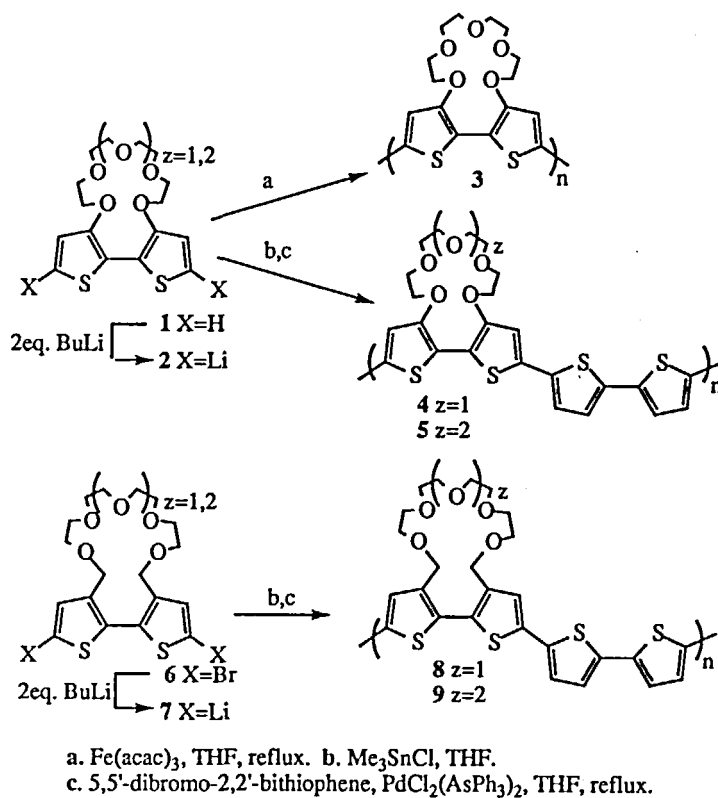
The synthesis of monomers **1** and **6** is reported elsewhere [12]. In our initial studies we were not concerned with production of high molecular weight polymers since it is well known that the electronic structure of conducting polymers is determined at low degrees of polymerization. In the case of polymer **3** we introduced a new polymerization method whereby the dilithiated monomer **2** is formed and then reacted with  $\text{Fe}(\text{acac})_3$  to produce the homopolymer **3** (Scheme 2). In this polymerization, insoluble  $\text{Fe}(\text{acac})_2$  is separated by filtration to produce materials free of the iron salts which typically plague  $\text{FeCl}_3$  oxidative polymerizations. After precipitating **3** in methanol, the degree of polymerization of the soluble (low molecular weight) portion was determined to be 10 thiophene units long by  $^1\text{H-NMR}$  integration of the two doublets resulting from the disubstituted thiophene end groups.

We have also made use of Stille coupling methodology [4] in the synthesis of copolymers. In this case, the dilithio species of **2** and **7** are reacted in situ with trimethyltin chloride and then subjected to palladium catalyzed cross-coupling with 5,5'-dibromo-2,2'-bithiophene. The molecular weights produced in this procedure are solubility limited since these copolymers precipitate during the course of the reaction. The molecular weights as determined by GPC relative to polystyrene standards were determined to be 2800, 3700, 2000, and 1900 for polymers **4**, **5**, **8**, and **9**, respectively. However, the absolute molecular weights may be higher since the absolute molecular weight determined by NMR end-group analysis for **3** shows the true molecular weight to be almost double that determined by GPC (1800 vs 960).

The ion-induced twisting was confirmed by the observation of ionochromic effects, and the results are shown in Table 1. Polymers **3**, **4**, and **5** show large shifts



SCHEME 1.



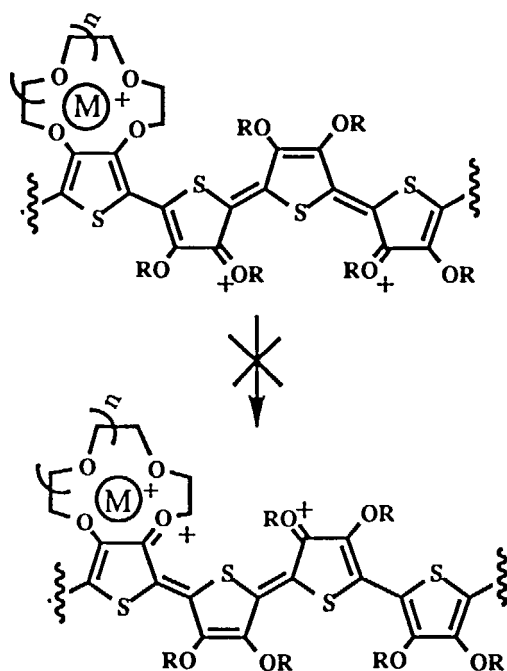
SCHEME 2.

TABLE 1. Ionochromic Response of Polymers in 0.1 M Salt Solutions (acetonitrile)

Polymer	$\lambda_{\max}$ , nm	$\Delta\lambda_{\max}$ , nm		
		K <sup>+</sup>	Na <sup>+</sup>	Li <sup>+</sup>
3	497	22	91	46
4	510	10	63	15
5	524	45	30	13
8	434	-4	3	3
9	432	1	3	4

in  $\lambda_{\max}$  with the appropriate ion, and because the shift occurs in the visible region, a dramatic color change is observed. As anticipated from the binding preferences of their crown ether analogs, polymers **3** and **4** show the largest shift for sodium, and **5** is most responsive to potassium. The large magnitude of the shift despite the low binding constants is ascribed to the additive effect of destroying conjugation at several points along a highly conjugated system. This is supported by the fact that copolymer **4**, in which the number of twisting sites has been reduced, shows a smaller shift than its corresponding homopolymer, **3**. The observed ion-specific effects result from the varying degree of rotation imposed on the bithiophene unit by the ligand's distinct conformational requirements for each metal. We do not disregard the fact that electrostatic variations between the complexed and uncomplexed systems may play a role; however, at this time, we do not attempt to quantify the individual conformational and electrostatic perturbations. The poor ionochromic activity of polymers **8** and **9** is not surprising considering their poor binding affinity (which results in failure of the twist-inducing mechanism) and the loss of electrostatic interaction between the terminal oxygens of the polyether tether and polymer backbone.

We are also using transition metal-catalyzed coupling reactions to synthesize other ion-sensitive polymers which rely on other mechanisms to change the polymer's conductivity. For example, as shown in Scheme 3, we have synthesized polythiophenes which have a crown ether macrocycle tethered between the 3 and 4 positions of the thiophenes. The alkoxides donate electron density into the polymer backbone, and resonance structures which position positive charges on the alkoxide



SCHEME 3.

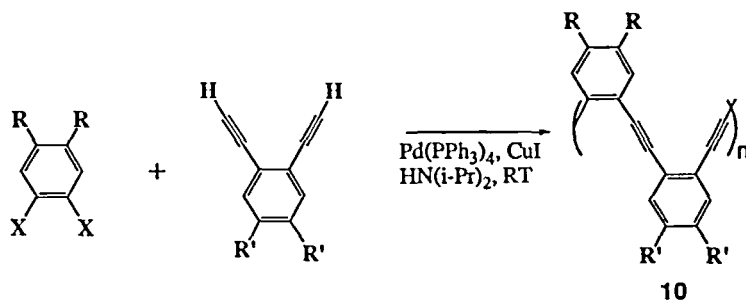
oxygen clearly must play a role in stabilizing the carriers. Ion complexation will serve to reduce the donating ability of the oxygens into the polythiophene backbone and in effect raise the oxidation potential of a particular ring. The effect of ion complexation on intramolecular carrier transport is conceptualized in Scheme 3. The transport of bipolarons is impeded due to the increased oxidation potential of the complexed "crowned" thiophene.

### SYNTHESIS OF GRAPHITE RIBBON PRECURSORS

All carbon ladder polymers (also called graphite ribbons) promise to exhibit particularly good electronic properties, and these materials were recently reviewed by Schluter [13]. All-carbon conjugated polymers generally exhibit greater delocalization and polarizability than polymers containing heteroatoms in their backbone. High delocalization and polarizability are critical features necessary for materials to exhibit high electrical conductivity and nonlinear optical susceptibility [14]. Hence the all-carbon polymers polyacetylene and poly(1,4-phenylene-vinylene) display the highest reported conductivities for organic polymers [15].

Ladder polymers have been studied extensively as a result of their high thermal and environmental stability [16]. These materials typically are heterocyclic fused ring structures which may be synthesized by condensation reactions. While very elegant syntheses of all-carbon ladder polymers (and oligomers) have been reported [13], it can be said that present synthetic procedures are insufficient to realize the true potential of this important class of materials. The limited state of synthetic procedures stems in part from the inherent insolubility of ladder polymers which precludes standard synthetic methods.

We are investigating a new synthetic route to all-carbon ladder polymers with novel architectures by cyclization reactions of poly(1,2-phenylene ethynylene)s [17]. Poly(1,2-phenylene ethynylene)s, **10**, are prepared from 1,2-dihalo-benzenes and 1,2-diethynyl-benzenes by conducting a palladium-catalyzed cross-coupling reaction in concentrated (0.15–0.25 M)  $i\text{-Pr}_2\text{NH}$  solutions (Scheme 4). Under these conditions only small amounts of cyclization products were formed and GPC analysis reveals number-average molecular weights ranging from 53,000 to 170,000, indicating that the reaction proceeds with extremely high conversion. Our synthetic methodology allows for the incorporation of a number of combinations of R and R'



SCHEME 4.

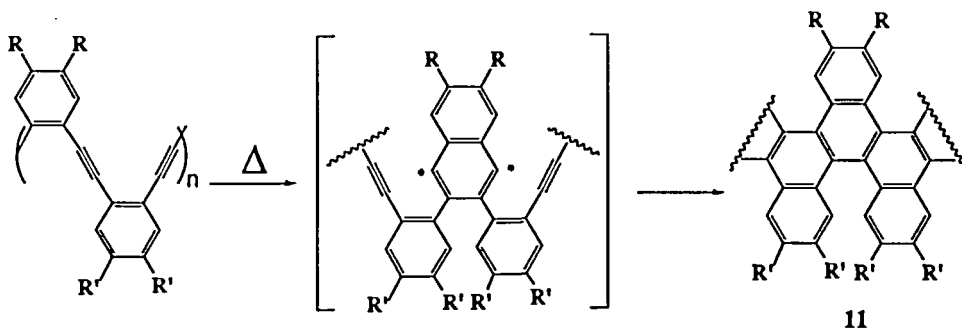
groups, and by variation of these groups we are attempting to induce a thermotropic liquid crystalline state.

We considered that **10** has the potential to undergo ene-diyne cyclizations (Bergman reactions) [18] in a zipper fashion to form an all-carbon ladder polymer **11** as shown in Scheme 5. Sequential ene-diyne cyclizations have been recently shown to produce naphthalene derivatives [18b], and other investigations on well-defined oligomers also have suggested that such a reaction occurs [18c]. DSC analysis of all of the derivatives we have synthesized shows strong exothermic transitions above 170°C. We have found the donor acceptor combination  $R = OC_{10}H_{21}$ ,  $R' = CO_2C_{10}H_{21}$  to exhibit a particularly strong exothermic transition at 190°C ( $\Delta H = 82$  kJ/mol repeat) which is not accompanied by weight loss as determined by TGA analysis. This terminal transformation also results in the disappearance of the acetylene infrared bands, which is consistent with the proposed cyclization.

We have also been investigating routes to graphite ribbons based upon the cyclization of groups pendant to a poly(*p*-phenylene) backbone (Scheme 6). The cyclization of pendant double bonds shown may be performed by the photochemical methods developed by Mallory [19]. The alternative cyclization shown involving the pendant acetylene has not been previously reported and was developed in our laboratory specifically for the synthesis of graphite ribbon polymers. Other syntheses of all-carbon ladder polymers involving poly(*p*-phenylene) precursors have also been reported [20].

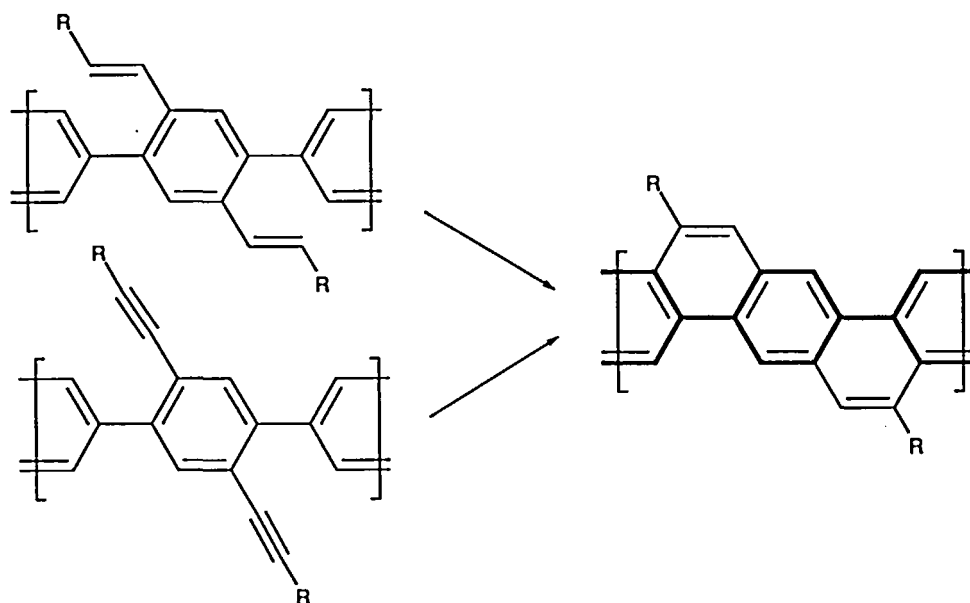
To investigate the transformations of Scheme 7, functionalized monomers **12**, **13**, and **14** were synthesized. This chemistry is made possible by using a palladium catalyst to chemoselectively couple the iodine positions of 1,4-dibromo-2,5-diiodobenzene. The resulting compounds are poised for further cross-coupling at the 1,4 dibromo positions.

We have investigated a number of polymerization protocols for the formation of the precursor polyparaphenylene polymers [21]. In general our best results have been obtained by cross-coupling 1,4-boronic acid phenylene monomers under Suzuki conditions [7]. Photochemical cyclizations of pendant olefins have not been successful; however, we have had considerable success with the cyclization of pendant acetylenes [22].

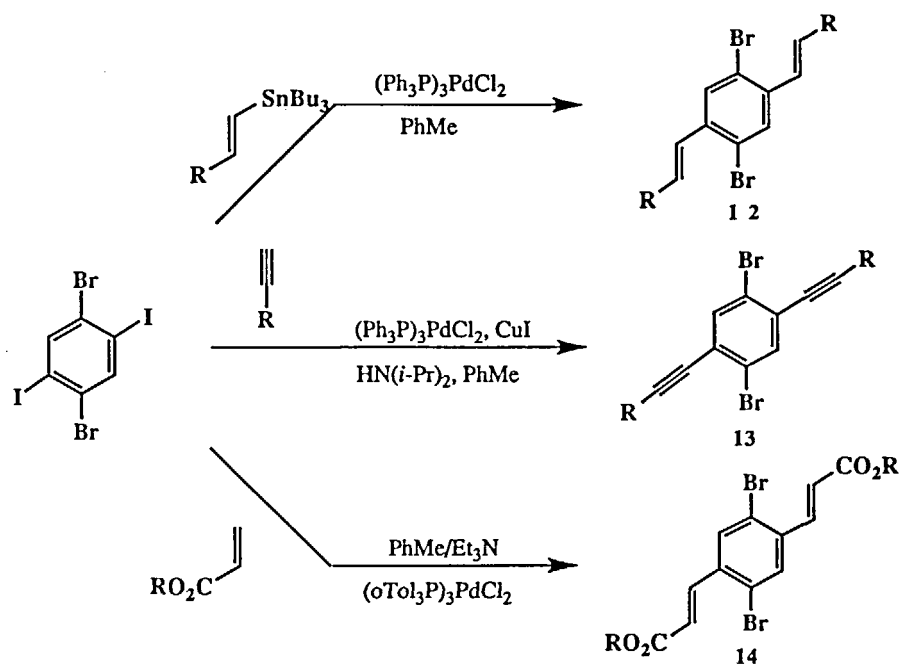


SCHEME 5.





SCHEME 6.



SCHEME 7.

## SUMMARY

We have shown how transition metal cross-coupling reactions can be used to synthesize novel conducting polymers. This synthetic method allows for the synthesis of materials with well-defined structures and also allows for the incorporation of reactive functional groups. In addition, transition metal coupling reactions allow for the incorporation of complex structures in conducting polymers which are capable of molecular recognition. These new types of materials offer exciting new possibilities for the formation of conducting polymer-based sensory materials.

## ACKNOWLEDGMENTS

Funding from the National Science Foundation MRL program (DMR-9120668), a NYI award to T.M.S. (DMR-9258298), and a DuPont Young Professor Grant is greatly appreciated.

## REFERENCES

- [1] T. Yamamoto, Y. Hayashi, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **51**, 2091 (1978).
- [2] K. Sanechika, T. Yamamoto, and A. Yamamoto, *Ibid.*, **57**, 752 (1984).
- [3] M. Kobayashi, J. Chen, T. C. Chung, F. Moraes, A. J. Heeger, and F. Wudl, *Synth. Met.*, **9**, 77 (1984).
- [4] J. K. Stille, *Angew. Chem., Int. Ed. Engl.*, **25**, 508 (1986).
- [5] R. F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, New York, 1985.
- [6] M. Kumada, *Pure Appl. Chem.*, **52**, 669 (1980).
- [7] (a) T. Watanabe, N. Miyaoura, and A. Suzuki, *Synlett.*, p. 207 (1992). (b) A. Suzuki, *Acc. Chem. Res.*, **15**, 178 (1982).
- [8] J-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, **29**, 1304 (1990).
- [9] (a) J. W. Thackeray and M. S. Wrighton, *J. Phys. Chem.*, **90**, 6674 (1986). (b) For a recent review, see G. Zotti, *Synth. Met.*, **51**, 373 (1992).
- [10] For a recent review of polythiophenes, see J. Roncali, *Chem. Rev.*, **92**, 711 (1992).
- [11] J. L. Bredas and G. B. Street, *Acc. Chem. Res.*, **18**, 309 (1985).
- [12] M. J. Marsella and T. M. Swager, *J. Am. Chem. Soc.*, **115**, 12214 (1993).
- [13] A. D. Schluter, *Adv. Mater.*, **3**, 282 (1991), and references therein.
- [14] (a) S. R. Marder, J. E. Sohn, and G. D. Stucky (Eds.), *Materials for Nonlinear Optics: Chemical Perspectives* (ACS Symp. Ser. 445), American Chemical Society, Washington, D.C., 1991. (b) D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, **23**, 690 (1984). (c) P. N. Prasad and B. A. Reinhardt, *Chem. Mater.*, **2**, 660, (1990), and references therein.
- [15] (a) H. Naarmann and N. Theophilou, *Synth. Met.*, **22**, 1 (1987). (b) M. A. Masse, R. J. Composto, R. A. L. Jones, and F. E. Karasz, *Macromolecules*, **23**, 3675 (1990).
- [16] L. Yu, M. Chen, and L. R. Dalton, *Chem Mater.*, **2**, 649 (1990).

- [17] Q. Zhou and T. M. Swager, *Polym. Prepr.*, **34**(1), 193 (1993).
- [18] (a) R. G. Bergman, *Acc. Chem. Res.*, **6**, 25 (1973). (b) K. N. Bharucha, R. M. Marsh, R. E. Minto, and R. G. Bergman, *J. Am. Chem. Soc.*, **114**, 3120 (1992). (c) R. H. Grubbs and D. Kratz, *Chem. Ber.*, **126**, 149 (1993).
- [19] (a) F. B. Mallory and C. W. Mallory, *Org. React.*, **30**, 1 (1984). (b) L. Liu, B. Yang, T. J. Katz, and M. K. Poindexter, *J. Org. Chem.*, **56**, 3769 (1991).
- [20] (a) T. Horn, U. Scherf, S. Wegener, and K. Mullen, *Polym. Prepr.*, **33**(1), 190 (1992). K. Mullen and U. Scherf, *Makromol. Chem., Rapid Commun.*, **12**, 489 (1991). (b) K. Chmil and U. Scherf, *Ibid.*, **14**, 217 (1993).
- [21] M. B. Goldfinger and T. M. Swager, *Polym. Prepr.*, **34**(2), 755 (1993).
- [22] M. B. Goldfinger and T. M. Swager, *J. Am. Chem. Soc.*, In Press.