Poly(aryleneethynylene)s: Syntheses, Properties, Structures, and Applications

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Contents

Uwe Bunz was born in 1963 in Neheim Hüsten, Germany. He received his Dipl. Chem. (1987) and doctoral degrees (Dr. rer. nat., 1990) from the Ludwig-Maximilians-Universität München, where he worked with Prof. G. Szeimies. After a postdoctoral study with Prof. K. P. C. Vollhardt at Berkeley (1991–1992), he joined the Max-Planck-Institut für Polymerforschung in Mainz in 1992. In 1997 he finished his habilitation in the group of Prof. K. Müllen and stayed for another half year at the MPI as a Heisenberg-Scholar. Since Fall 1997 he has been Associate Professor at the University of South Carolina. His research interests are in the area of alkyne-containing polymers and carbon-rich organometallic compounds.

I. Introduction

Conjugated polymers[1] are organic semiconductors and as such important materials for applications in electronic and photonic devices. Prime examples are polymeric light-emitting diodes "the plastic sandwich that glows...",[2] plastic lasers,[3] and polymer-based photovoltaic cells,[4] but at least in principle, conjugated polymers[5] should be able to pertain to all of the functions an inorganic semiconductor displays. That may include their use in semiconductor diodes and FETs,[6] and may lead in the future to "molecular electronics".[7] The primary advantages of organic polymers over their inorganic counterparts is their ease of processing by dip coating, spin casting, printing,[8] or use of doctor blade techniques. However, conjugated polymers are likewise important as sensory materials for water, organic vapors, and explosives either by fluorescence quenching or in artificial nose devices, which change their conductivity upon exposure to a suitable analyte.[9]

From a preparative–synthetic point of view, conjugated polymers are available in a never-ending variety of different chemical structures and topologies (for some examples see Table 1, entries 1, 2, 4, and 11). Like natural macromolecules such as proteins, conjugated polymers have a distinct propensity to develop tertiary structures. These tertiary structures are aggregates involving one or several macromolecules, and depending upon their morphology, there can be dramatic differences in the physical (i.e., optical) properties of different preparations of the same polymer. Most of the conjugated polymers are relatively "stiff" on a molecular basis, and many are actually linear, qualifying as rigid rods.

Chart 1

1

2

3

number   4   5   6   7   8   9   10   11

12   13   14   15   16

Table 1. Important Review Articles Covering the Same, Related, or Adjacent Areas

entry	author	citation	title
1	Giesa, R.	*J. M. S.-Rev. Macromol. Chem. Phys.* **1996**, *36*, 631	Synthesis and Properties of Conjugated Poly(aryleneethynylene)s
2	Martin, R. E.; Diederich, F.	*Angew. Chem.* **1999**, *38*, 1350	Linear Monodisperse π-Conjugated Oligomers: Model Compounds for Polymers and More
3	Schwab, P. F. H.; Levin, M. D.; Michl, J.	*Chem. Rev.* **1999**, *99*, 1863	Molecular Rods. 1. Simple Axial Rods
4	Yamamoto, T.	*Bull. Chem. Soc. Jpn.* **1999**, *72*, 621	π-Conjugated Polymers Bearing Electronic and Optical Functionalities. Preparation by Organometallic Polycondensations, Properties and Their Application
5	Moore, J. S.	*Acc. Chem. Res.* **1997**, *30*, 402	Shape-Persistent Molecular Architectures of Nanoscale Dimension
6	Young, J. K.; Moore, J. S.	In *Modern Acetylene Chemistry*; VCH: Weinheim, 1995	Phenylacetylene Nanostructures
7	Tour, J. M.	*Chem. Rev.* **1996**, *96*, 537	Conjugated Macromolecules of Precise Length and Constitution. Organic Synthesis for the Construction of Nanoarchitectures
8	Swager, T. M.	*Acc. Chem. Res.* **1998**, *31*, 201	The Molecular Wire Approach to Sensory Signal Amplification
9	Müllen, K., Wegner, G., Eds.	VCH: Weinheim, 1998 (book)	Electronic Materials: The Oligomer Approach
10	Neher, D.	*Adv. Mater.* **1995**, *7*, 691	Substituted Rigid Rod-Like Polymers-Building Blocks for Photonic Devices
11	Scherf, U.	*Top. Curr. Chem.* **1999**, *201*, 163	Oligo- and Polyarylenes, Oligo- and Polyarylenevinylenes
12	Conwell, E.	*Trends Polym. Sci.* **1997**, *5*, 218	Excimer Formation and Luminescence in Conducting Polymers
13	Kraft, A.; Grimsdale, A. C.; Holmes, A. B.	*Angew. Chem.* **1998**, *37*, 402	Electroluminescent Conjugated Polymers— Seeing Polymers in a New Light
14	Bunz, U. H. F.; Kloppenburg, L.	*Angew. Chem.* **1999**, *38*, 478	Alkyne Metathesis as a New Synthetic Tool: Ring-Closing, Ring-Opening, and Acyclic
15	Pu, L.	*Chem. Rev.* **1998**, *98*, 2405	1,1′-Binaphthyl Dimers, Oligomers, and Polymers: Molecular Recognition, Asymmetric Catalysis, and New Materials
16	Bunz, U. H. F.	*Angew. Chem.* **1994**, *33*, 1073	Polyynes-Fascinating Monomers for the Construction of Carbon Networks

The class of conjugated polymers which has found the most attention in the past are undoubtedly the poly(*p*-phenylenevinylene)s (PPVs) which "made it big" since Friend's 1990 report of organic polymeric LEDs.[2,10] Other well-established classes of conjugated polymers are the polydiacetylenes,[11] polyphenylenes,[12,13] and polyacetylenes.[14] However, the structurally closest relative to PPV, the poly(phenylene-

Table 2. Selected Original References for the Synthesis of Oligo(phenyleneethynylene)s

authors	citation	title
Huang, S. L.; Tour, J. M.	*J. Am. Chem. Soc.* **1999**, *121*, 4908	Rapid Solid-Phase Synthesis of Oligo(1,4-phenylene ethynylene)s by a Divergent Convergent Tripling Strategy
Schumm, J. S.; Pearson, D. L.; Tour, J. M.	*Angew. Chem.* **1994**, *33*, 1360	Iterative Divergent/Convergent Approach To Linear Conjugated Oligomers by Successive Doubling of the Molcular Length—A Rapid Route to a 128 Å Potential Long Molecular Wire
Adams, R. D.; Barnard, T.; Rawlett, A.; Tour, J. M.	*Eur. J. Inorg. Chem.* **1998**, *429*, 9	The Coordination and Structure of a Thiolate-Terminated "Molecular-Scale Wire" Linked to a Triosmium Cluster
Crisp, G. T.; Bubner, T. P.	*Tetrahedron* **1997**, *53*, 11899	Preparation of sterically constrained arylalkyne oligomers
Ley, K. D.; Li, Y.; Johnson, J. V.; Powell, D. H.; Schanze, K. S.	*J. Chem. Soc., Chem. Commun.* **1999**, 1749	Synthesis and characterization of π-conjugated oligomers that contain metal-to-ligand charge-transfer chromophores
Kukula, H.; Veit, S.; Godt, A.	*Eur. J. Org. Chem.* **1997**, 2777	Synthesis of Monodisperse Oligo(*para*-phenylene-ethynylene)s Using Orthogonal Protecting Groups with Different Polarity for Terminal Acetylene Units
Lavastre, O.; Cabioch, S.; Dixneuf, P. H.; Vohlidal, J.	*Tetrahedron* **1997**, *53*, 7505	Selective and Efficient Access to *ortho, meta,* and *para* Ring-Substituted Phenylacetylene Derivatives $R-[C{\equiv}C-C_6H_4]_x-Y$ (Y=H, NO_2, CN, I, NH_2)
Lavastre, O.; Ollivier, L.; Dixneuf, P. H.; Sibandhit, S.	*Tetrahedron* **1996**, *52*, 5495	Sequential Catalytic Synthesis of Rod-Like Conjugated Poly-ynes
Dhirani, A. A.; Zehner, R. W.; Hsung, R. P.; Guyot-Sionnest, P.; Sita, L. R.	*J. Am. Chem. Soc.* **1996**, *118*, 3319	Self-Assembly of Conjugated Molecular Rods: A High-Resolution STM Study
Höger,S.; Enkelmann, V.	*Angew. Chem.* **1996**, *34*, 2713	Synthesis and X-ray Structure of a Shape-Persistent Macrocyclic Amphiphile
Prest, P. J.; Prince, R. B.; Moore, J. S.	*J. Am. Chem. Soc.* **1999**, *121*, 5933	Supramolecular Organization of Oligo(*m*-phenylene-ethynylene)s in the Solid State
Young, J. K.; Nelson, J. C.; Moore, J. S.	*J. Am. Chem. Soc.* **1994**, *116*, 10841	Synthesis of Sequence-Specific Phenylacetylene Oligomers on an Insoluble Solid Support
Grubbs, R. H.; Kratz, D.	*Chem. Ber.* **1993**, *126*, 149	Highly Unsaturated Oligomeric Hydrocarbons—α-(Phenylethynyl)-ω-Phenylpoly[1,2-phenylene-(2,1-ethynediyl)]
Neenan, T. X.; Whitesides, G. M.	*J. Org. Chem.* **1988**, *53*, 2489	Synthsis of High Carbon Materials from Acetylenic Precursors—Preparation of Aromatic Monomers Bearing Multiple Ethynyl Groups
Neenan, T. X.; Callstrom, M. R.; Scarmoutzos, L. M.; Stewart, K. R.; Whitesides, G. M.; Howes, V. R.	*Macromolecules* **1988**, *21*, 3525	Hyper-Cross-linked Organic Solids—Preparation from Poly(aromatic)diacetylenes and Preliminary Measurements of Their Young Modulus, Hardness and Thermal Stability
Rutherford, D. R.; Stille, J. K.	*Macromolecules* **1988**, *21*, 3530	Poly(ethynylene-2,5-thiophenediylethynylnes)—Processable, Reactive Polymers That Thermally Cross-Link

ethynylene)s (PPEs; see Chart 1), have attracted much less attention in the polymer community, despite their fascinating properties. Only recently the groups of Swager,[15] Müllen,[16] and Weder[17,18] demonstrated that PPEs with their unique property profile are fantastic materials in such different areas as explosive detection,[15] molecular wires in bridging nanogaps,[19,20] and polarizers for LC displays. Chart 1 shows the types of poly(aryleneethynylene)s (PAEs) covered in this review and lists representative examples.

While the syntheses of polymeric−polydisperse phenyleneethynylenes (PEs) have just come into focus the past few years, the situation is different for defined oligomeric PEs, a multitude of architectures and topologies of which have been synthesized and scrutinized by the groups of Moore,[21] Tour,[22] and Youngs[23] and more recently by Höger[24] and Godt.[25]

A. Scope, Limitation, Organization, and Outline of the Review

This review will cover the area of polymeric PEs and their syntheses, properties, structures, morphologies, and applications. The application part will discuss polymeric PEs as molecularly wired sensors, as polarizers for liquid crystalline (LC) displays, and

as light-emitting devices. The review will concentrate upon the developments from 1995 to mid-1999, but include significant earlier references where necessary for discussion. In 1996 Giesa[26] published a review on PAEs, which covers the literature including 1995. The synthesis of PAEs will be restricted to Pd-catalyzed cross couplings and Mo/W-catalyzed alkyne metathesis processes in this review. Other, less effective approaches, such as self-polymerization of cuprous acetylides, dehydrobromination of halogenated PPVs, or generation of PPE by electrochemical reduction of hexahalo-*p*-xylene, are not treated, since they normally furnish difficult-to-characterize, insoluble materials with a high percentage of defect structures.[26]

The synthesis of defined monodisperse linear, cyclic, or dendritic PEs, which have been made in the groups of Moore,[21] Tour,[22] Höger,[24] and Godt,[25] is not covered in this review, but examples will be mentioned where appropriate. The area of defined oligomeric PEs has been covered nicely, and Table 1 lists these and other important/pertinent review articles related to the topic discussed here. The selection is not comprehensive but intended to provide the interested reader a broader introduction, while Table 2 gives an overview of seminal articles which are

related to the discussed field but do not pertain to this review.

The synthesis of PAEs will be reviewed in section II. A critical discussion with respect to reaction conditions for both the Pd-catalyzed couplings (section II.A.) and the alkyne metathesis approach (section II.B) to PPEs will be presented. The discussion of molecular weight determination will be included. In the Pd-catalyzed couplings the influence of substrate structure and reaction conditions including formation of defect structures will be examined for the PPEs. In the case of alkyne metathesis, the influence of substrate, catalyst, and cocatalyst will be discussed. Section III deals with the structure of PPEs and PAEs in solution and in the solid state. Uv/vis and fluorescence spectra and the influence of aggregation on the optical properties of PAEs are covered. A model for the supramolecular solid-state structure and morphologies of PAEs and more specifically of PPEs is discussed. In Section IV applications of PAEs are reviewed. They can act as molecular wires, energy-transfer agents, sensors, and active layers in light-emitting diodes.

II. Syntheses of PAEs

A. Palladium Methodologies

The Pd-catalyzed coupling of terminal alkynes to aromatic bromides or iodides in amine solvents has been known since 1975. It is called the Heck–Cassar–Sonogashira–Hagihara reaction and is probably one of the most frequently used C–C bond forming processes in organic chemistry.[27–29] This coupling is powerful to form C–C single bonds between an sp- and an sp^2-hybridized carbon center. The generally accepted mechanism of this reaction is depicted in Scheme 1 and will be discussed here with respect to its implications in polymer synthesis. In most cases (both for the synthesis of low-molecular-weight organic targets and for the preparation of PAEs) the commercially available $(Ph_3P)_2PdCl_2$ is the catalytic source of Pd. In its oxidized form this catalyst is inactive. In the first step (Scheme 1) two molecules of a cuprated alkyne, **A**, transmetalate the Pd catalyst precursor and form **B**. **B** is not stable under the reaction conditions but reductively eliminates a symmetrical butadiyne and creates the active catalyst **C**. In an oxidative addition the aromatic bromide or iodide forms the intermediate **D**, which after transmetalation with **A** leads to the diorgano-Pd species **E**. This species undergoes reductive elimination to the product and re-forms the active catalyst **C**.
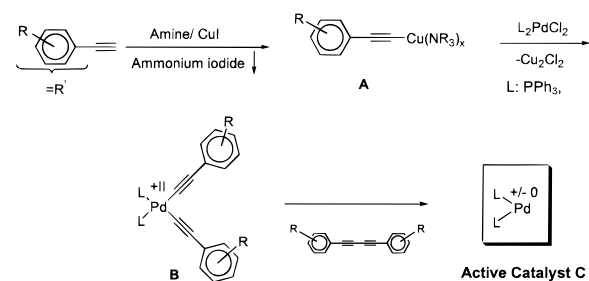
Choice of Halide. Both bromo- and iodoaromatic compounds work in this reaction. All of the reported couplings, involving aryl bromides, have to be conducted at elevated temperatures, at approximately 80 °C. However, the corresponding iodides do react considerably faster, in quantitative yield, at room temperature. As a consequence polymer formation can be conducted under mild conditions when iodides are used, so that problems including cross-linking and formation of defects are minimized. With iodides the oxidative addition (formation of **D**) is much more
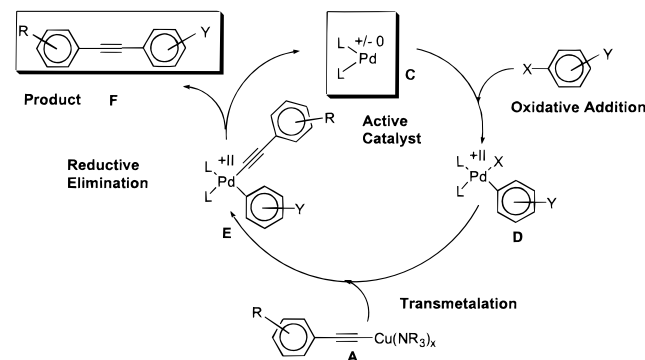
Scheme 1

I. **Overall Reaction:**

R = Alkyl, Aryl, OH, Ether, Ester

X = Br, I
Y = Acc (ester, nitril) or Don (OR, NR₂, alkyl)
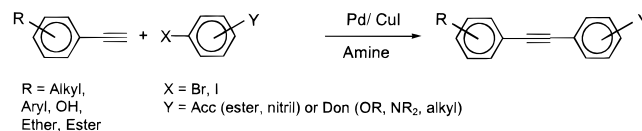
II. **Catalyst Activation:**

III. **Catalytic Cycle**

facile than with the corresponding bromides. The reason for that is probably both thermodynamic as well as kinetic in nature. If available, iodoarenes are the preferred substrates for Pd-catalyzed couplings.

Choice of Substituents on the Haloarene. The active catalyst of type **C** is an electron-rich species, and as a consequence, oxidative addition, i.e., the formation of **D** (from **C** and an aromatic halide), is dramatically influenced by the nature of the substituents Y on the aromatic nucleus. The more electron-withdrawing Y is, the faster its oxidative addition to the electron-rich Pd^0 proceeds. Consequently, an electron-withdrawing substituent Y on the halide improves both the rate and yield of these coupling reactions. *Ortho-* and *para-*positioned acceptor substituents are more efficient than ones placed in the *meta-*position.

Choice and Amount of Catalyst and Role of the Cu Cocatalyst. Most frequently 0.1–5 mol % $(Ph_3P)_2$-$PdCl_2$ and varying amounts of CuI are used in both "organic" and polymer-forming reactions. In cases where the haloarene is sufficiently active (typically iodoarenes), much smaller amounts (0.1–0.3%) should be sufficient. The successful start of the reaction can be monitored by the increase of turbidity of the reaction mixture, indicating the formation of insoluble ammonium halides. If very small amounts of catalyst are used, it may be necessary to add another batch to the reaction mixture until the reaction

starts. Heating the reaction mixture to 40−50 °C sometimes helps to initiate the coupling. On a large scale and conducted at high concentration, the mixture warms during the course of the reaction. In the experience of the author, the "organic" couplings for iodoarenes take approximately 1−2 h until they are complete. This is not true for polymerizations. To complete the reaction, it is necessary to stir the reaction mixture for extended periods of time (24−48 h) to ensure the consumption of the monomers and obtain polymers of high molecular weight. The activation step (if using Pd^{2+}) uses up some of the alkyne present in the reaction mixture. It thus leads to an imbalanced stoichiometry and to the formation of 1−10% of the corresponding diyne during the activation step (depending upon the amount of catalyst used). That is no problem when making low-molecular-weight compounds. It necessarily decreases the molecular weight and the degree of polymerization (DP) if not a small excess of diyne is used in the reaction mixture. This will offset the amount of alkyne consumed by the Pd^{2+} precatalyst. However, the disadvantage of the approach is the presence of several percent of butadiyne defects in the formed PAEs. Heitz,[30] Moore,[31] Wrighton,[32] and Swager[33] independently developed methods to circumvent this problem. Heitz[30] reduced $(Ph_3P)_2PdCl_2$ in the presence of 1 equiv of triphenylphosphine to obtain a solution of "$Pd(PPh_3)_3$", which he used in situ, while Moore favors the commercially available Pd_2dba_3 in combination with a suitable phosphine for the synthesis of large PE dendrimers.[31] All together, Pd^0 as catalyst precursor should circumvent the formation of butadiyne defect structures; however, to achieve this, even trace amounts of oxygen have to be rigorously excluded. If $Pd(PPh_3)_4$ is employed with aromatic iodides at temperatures around 70 °C in diisopropylamine, this protocol can lead[32−34] to the formation of high-molecular-weight PPEs. However, even with a Pd^0 catalyst source, Swager[33] reports that a small excess of bisalkyne has to be used to obtain high-molecular-weight materials.

CuI as cocatalyst seems to be necessary for the conversion of dibromoarenes into the corresponding alkynylated products, but Linstrumelle[35] demonstrated that if iodoarenes are coupled in the presence of a suitable amine, CuI can be omitted. The presence of CuI however does not seem to harm the progress of the reaction, and insofar it can always be added. Its proposed role is the formation of a copper(I) σ- or π-acetylide to activate the alkyne toward transmetalation. The matter has been discussed thoroughly by Osakada and Yamamoto.[36]

Choice of Amine and Solvent. While Giesa[26] points out in his review that the role of the amine is considered to be uncritical, that is unfortunately not true. A good choice of amine to couple aromatic iodides seems to be diisopropylamine, which has been put to use with great success for the formation of PPEs. It seems to work particularly efficiently in combination with a Pd^0 source such as $(PPh_3)_4Pd$ at elevated temperatures. Generally, the yield and purity of the coupling products in the Heck−Cassar−Sonogashira−Hagihara reactions are very dependent

Scheme 2
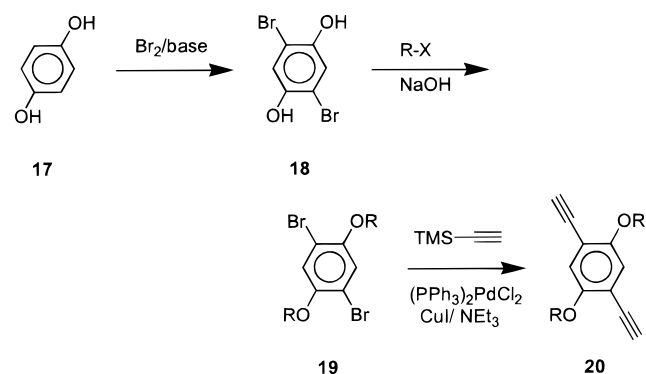
upon the careful choice of amine and cosolvent. For small organic targets the role of the amine in these couplings was examined.[35] It was found that piperidine, pyrrolidine, and morpholine often work very well. Particularly piperidine is very powerful for these couplings and seems to outperform triethylamine in the case of the iodides. However, for unclear reasons, piperidine is not ideal for the coupling of aryl bromides to terminal alkynes. The classic amine base used for bromides is triethylamine at 80 °C, but according to Tour,[38] Hünig's base di-(isopropyl)ethylamine is a much better choice. The author of this review has had similar experiences.[39] It is generally a good idea to conduct these reactions in concentrated or highly concentrated solutions to ensure fast coupling. However, in concentrated solutions the heat development of the reaction can be quite substantial, and mild cooling may be necessary. Sometimes it is desirable to add a cosolvent to ensure solubility of the formed polymer. Piperidine and triethylamine are not prime solvents for PPEs. THF, ethyl ether, and toluene have been used, but chloroform and dichloromethane should likewise work as additives.

1. Dialkoxy-PPEs: A Case Study

Early attempts to prepare the parent PPE led to the formation of infusible, insoluble, low-molecular-weight oligomers.[26] The first success of preparing soluble PPE derivatives was achieved by Giesa.[40] The attachment of long alkoxy groups to the linear, rigid PPE backbone was expected to furnish polymers with increased solubility. The choice of alkoxy groups was based on the simplicity of the synthetic access to the corresponding monomers, and dialkoxy-substituted PPEs are the most easily synthesized representatives of the PPE class. Giesa's synthesis started with the alkylation of dibromohydroquinone, **18**, to obtain the monomer **19**[40] (Scheme 2). Alkynylation of **19** and standard deprotection lead to the second monomer **20**. Palladium/CuI-catalyzed coupling of **19** to **20** in a mixture of triethylamine/pyridine furnished polymers with a degree of polymerization (DP) of 10−15 as deeply colored solids, the dissolvable fractions of which formed highly fluorescent solutions in aromatic hydrocarbons. Despite the long alkoxy groups (R, R′ = hexyl, decyl, heptadecyl) attached, the solubility of the polymers **1** was not high, and in some cases even low. The minute solubility in combination with the deep coloring of their products suggests that

Table 3. Examples of Dialkoxy-PPEs 1: Substituent Pattern, End Groups, Catalyst System, Solvent, and Molecular Weight

Entry/Cpd	R¹	R²	R³	R⁴	Halide	End group	Catalyst	Solvent	DP	Mw/Mn	Comment
1[a] 1a	$C_{18}H_{37}$		$C_{18}H_{37}$		Br	Br	$(PPh_3)_2PdCl_2$ CuI	NEt_3/pyridine	10-20	Multi-modal	
2[b] 1b	$C_{10}H_{21}$		$C_{10}H_{21}$			Br	$PdCl_2$/PPh_3 $Cu(OAc)_2$	NEt_3/THF	15-25		Authors claim DP of approx 150
3[b] 1c	$C_{12}H_{25}$		$C_{12}H_{25}$		Br	Br	$PdCl_2$/PPh_3 $Cu(OAc)_2$	NEt_3/THF	15-25	1.5, gpc	
4[c] 1d	$C_{16}H_{33}$		C_8H_{17} / CH_3	C_8H_{17} / CH_3		I	$(PPh_3)_4Pd$/CuI	$HN(iC_3H_7)_2$	100 gpc	1.5	Copolymer
5[c] 1e	$C_{16}H_{33}$		$C_{16}H_{33}$		I	[aryl structure: OMe, MeO, –(CH₂)₆Br]		$HN(iC_3H_7)_2$	40 NMR	1.5	
6[c] 1e	$C_{16}H_{33}$		$C_{16}H_{33}$			[anthracenyl–≡–Ph structure]		$HN(iC_3H_7)_2$	22 NMR	2.2	
7[d] 1f	$C_{18}H_{37}$		$C_{18}H_{37}$		Br	Br	$(PPh_3)_4Pd$/CuI	NEt_3/toluene	10-100	N.D.	only UV
8[e] 1g	C_8H_{17}		$C_{16}H_{33}$		I	Phenyl	$(PPh_3)_4Pd$ CuI	$HN(iC_3H_7)_2$	24 NMR		
9[e] 1h	C_8H_{17}		2-methylpropyl						22 NMR	N.D.	
10[e] 1i	C_8H_{17}		3-(dimethylamino)propyl						28 NMR		
11[e] 1j	C_8H_{17}		—(CH₂)₇—CO₂H						Insol.		
12[f] 1k	CH_3	$C_{10}H_{21}$	CH_3	$C_{10}H_{21}$	I	I	$(PPh_3)_4Pd$ CuI	$HN(iC_3H_7)_2$ toluene	49	3.2	10% excess of diiode used
13[g] 1l	C_8H_{17}		2-Ethylhexyl		I	I	$(PPh_3)_4Pd$/CuI	$HN(iC_3H_7)_2$ toluene	116	2.9, gpc	
14[h] 1m	2-(S)-Methylbutyl		2-(S)-Methylbutyl		Br	Br	$(PPh_3)_4Pd$/CuI	NEt_3/THF	36	2.1	
15[i] 1g	C_8H_{17}		$C_{16}H_{33}$		I	I	$(PPh_3)_4Pd$ CuI	$HN(iC_3H_7)_2$ toluene	70 gpc	?	

[a] Giesa, R.; Schulz, R. C. *Macromol. Chem. Phys.* **1993**, *191*, 857. [b] Moroni, M.; LeMoigne, J.; Luzzati, S. *Macromolecules* **1994**, *27*, 562. [c] Swager, T. M.; Gil, C. J.; Wrighton, M. S. *J. Phys. Chem.* **1995**, *99*, 4886. [d] Davey, A. P.; Elliott, S.; O'Connor, O.; Blau, W. *J. Chem. Soc., Chem. Commun.* **1995**, 1433. [e] Weder, C.; Wrighton, M. S. *Macromolecules* **1996**, *29*, 5157. [f] Kim, J. S.; McHugh, S. K.; Swager, T. M. *Macromolecules* **1999**, *32*, 1500. [g] Steiger, D.; Smith, P.; Weder, C. *Macromol. Rapid Commun.* **1997**, *18*, 643. [h] Fiesel, R.; Scherf, U. *Macromol. Rapid Commun.* **1998**, *19*, 427. [i] Yang, J. S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864.

Schulz' PPEs were substantially cross-linked.[40] Structurally defined and defect-free derivatives of **1** are brilliantly yellow-orange powders, which show a green tinge in daylight due to efficient fluorescence, but are never brown or rusty-red materials.[41]

An improved synthesis of **1** was developed by Moroni et al.[42] (Table 3, entries 2 and 3), who coupled **19** and **20** (R = dodecyl) in the presence of $PdCl_2$, $Cu(OAc)_2$, and triphenylphosphine in a triethylamine/THF (Scheme 3) mixture. The authors claimed to have formed PPEs with a DP of approximately 150 and attributed the high molecular weight to the presence of THF as solubilizing cosolvent. Their claim with respect to molecular weights is unsubstanti-

Scheme 3
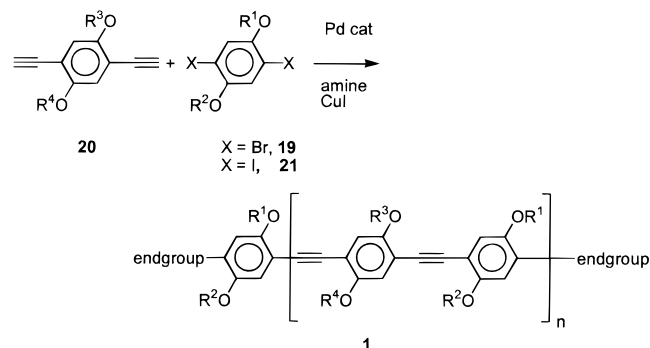
ated: (a) In the (displayed) ^{13}C NMR spectrum of their "high-molecular-weight polymer", end group signals are clearly visible. The sensitivity of ^{13}C NMR spectroscopy is such that approximately 5–10% of an impurity can be detected. As a consequence, the DP of Le Moigne's material cannot exceed 20–25 PE units. (b) In the experimental part of their paper the authors state that 1.8 mmol of **19** and 1.8 mmol of **20** are treated with 0.2 mmol of $PdCl_2$ and 0.03 mmol of $Cu(OA)_2$.[42] To form the active catalyst, 0.23 mmol of diyne **20** will have to be used to reduce both the Cu^{2+} and the Pd^{2+} species into their active zerovalent form. The presence of diyne defects is thus necessary, and an imbalanced stoichiometry must result. As a consequence, these PPEs **1** are expected to show a DP not exceeding 20, even after fractionation, and that is exactly what is seen in the ^{13}C NMR spectrum. The authors describe their dialkoxy-PPEs as red-orange materials, suggesting at least some cross-linking to have occurred under these relatively harsh reaction conditions. The cross-linking may be responsible for the GPC and light-scattering data and the massive overestimation of their molecular weights.

By a similar method, utilizing 2,5-bis(2-(S)-methylbutoxy)-1,4-diethynylbenzene (**20**) and 2,5-bis(2-(S)-methylbutoxy)-1,4-dibromobenzene (**19**) (Table 3, entry 14), Scherf[43] prepared a chiral dialkoxy-PPE, **1m**, utilizing $Pd(PPh_3)_4$ and CuI in boiling triethyl-

amine/THF. The chiral **1m** had a DP of approximately 40 according to GPC, reinforcing the notion that it is difficult to make high-molecular-weight PPEs by the use of brominated monomers.

Cross-linking seems to be a general problem when working at elevated temperatures. The problem is circumvented if the coupling can be conducted at room temperature or up to 70 °C. Wrighton (Table 3, entries 4−6 and 8−10) reported the coupling of the reactive 2,5-diiodo-1,4-dialkoxybenzenes to 2,5-diethynyl-1,4-dialkoxybenzenes in a diisopropylamine/toluene mixture under Pd(PPh$_3$)$_4$/CuI catalysis. This protocol furnishes PPEs which according to GPC measurements have DPs of up to 100.[32,44] The authors of that study prepared end-capped PPEs in which either anthracene or bromoalkyl-substituted dialkoxybenzenes are the chain terminators (Table 3, entries 5 and 6). The DP of these polymers is dependent on the amount of end-capper used, and end-functionalized PPEs with a DP of 20−40 were reported. Weder and Wrighton prepared a series of dialkoxy-substituted copolymers **1** (Table 3, entries 8−11) with interesting side chains including ones with 3-(dimethylamino)propyl (**1i**) and 7-carboxyheptyl (**1j**) groups.[45,46] To control molecular weight, the authors added iodobenzene as end capper and isolated PPEs **1** with DPs of 20−30 (Table 3, entries 8−11). These PPEs seem well defined and only have phenyl end groups according to ^{1}H NMR spectroscopy and elemental analysis. Weder[34] accessed a polymer, **1l**, by the same method with ethylhexyloxy and octyloxy solubilizing groups (Table 3, entry 13). He produced a high-molecular-weight polymer, which according to gel permeation chromatography (GPC) shows a DP of 230 phenyleneethynylene units. His rationalization for the high molecular weight is the supposed solubility-enhancing power of the branched ethylhexyl side chain. While that is certainly true, a DP of >200 is quite surprising for these Pd-catalyzed polycondensations, because it suggests that the efficiency of the coupling reaction must exceed 99.5% per coupling step. However, the reported yield is not quantitative but only 87%, suggesting fractionation. Similar PPEs have been made by Swager[47] (Table 3, entry 12), who reported a DP of approximately 50 for a dialkoxy-PPE, **1k**, after fractionation. To limit the molecular weight, Swager had used 1.1 equiv of the diiodide to ensure the complete consumption of the diyne and the presence of defined iodine end groups.

2. Alkoxy Copolymers and Acceptor-Substituted PPEs

The Pd-catalyzed couplings are not only useful for the preparation of fully alkoxy-substituted PPEs **1**. Combination of dialkoxy-substituted diiodides with different aromatic diynes leads to other classes of PPEs (Scheme 4). West[48] has utilized this strategy to make a PPE, **2d**, in which unsubstituted benzene rings alternate with alkoxy-substituted ones (Table 4, entries 5 and 6). If not 1,4-diethynylbenzene but diethynylpentiptycene was used, Swager and Yang[49] obtained a highly porous PPE with the exotic structure **30a** (Table 4, entries 13−15). The synthesis of the extremely bulky diethynylpentiptycene is a four-step process and discussed here (Scheme 5).

Scheme 4
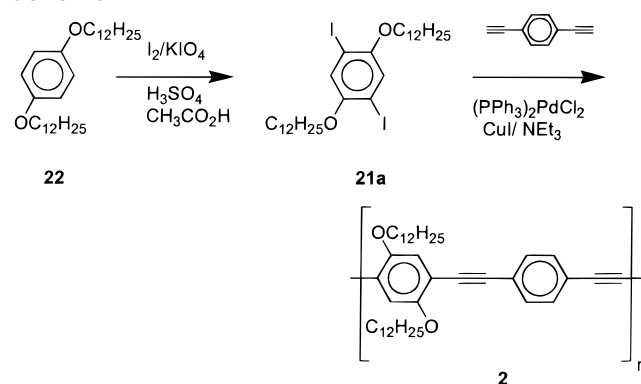
Scheme 5
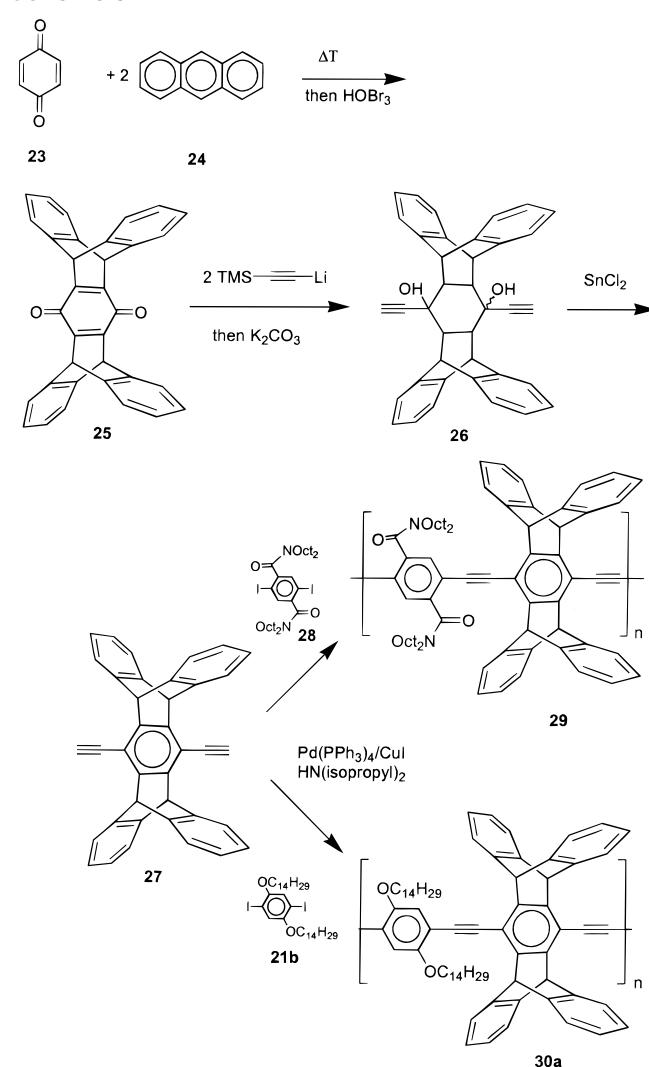
Diels−Alder reaction of benzoquinone with an excess of anthracene furnishes the extended quinone **25** after oxidation with HOBr$_3$. Nucleophilic addition of Li−C≡C−SiMe$_3$ and aqueous workup lead to a diastereomeric mixture of two diols. Tin(II) chloride conveniently deoxygenates the diols **26** to the diethynylated pentypticene derivative **27** after cleavage of the trimethylsilyl groups with NaOH. It should be possible to scale-up the reaction to multigram quantities and develop diethynylpentypticene **27** into a cornerstone monomer for further PPE syntheses.

Table 4. PPE–PPE Copolymers Cotaining Dialkoxy-Substituted or Acceptor-Substituted Arene Rings

Entry/Cpd	R^1	R^2	R^3	R^4	Halide	End group	Catalyst	Solvent	DP	M_w/M_n	Comment
1[a] 2a	(structure: Br–C≡C–phenyl–C≡C–Br)		(structure: $(HO)_2B$–arene–$B(OH)_2$)			-C≡C-Br	$(CH_3CN)_2PdCl_2$ $AsPh_3$, Ag_2O	THF/H_2O	15 based on PE-units.	3.5	The authors used a boronic acid coupling of bromoalkynes with aryl boronic acids. Unusual approach
2[a] 2b	(structure: Br–C≡C–phenyl–C≡C–Br)		(structure: H_3C ... $(HO)_2B$–arene–$B(OH)_2$ ... $O{-}CH_3$)			-C≡C-Br			13 based on PE units	3.6	
3[a] 2c	(structure: Br–C≡C–phenyl–C≡C–Br)		(structure: Ph ... $(HO)_2B$–arene–$B(OH)_2$)			-C≡C-Br			30 based on PE units	1.3	
4[b] -	(structure)		(structure)		Br	Br	$Pd(PPh_3)_4$	THF/H_2O	67	8.5	Some other more complicated PPE-PPP-PPV copolymers are described in this interesting paper
5[c] 2d	H	H	OC_6H_{13}	OC_6H_{13}	I	I	$(PPh_3)_2PdCl_2/$CuI	Toluene/NEt_3	27	2.4	
6[d] 2d	H	H	OC_6H_{13}	OC_6H_{13}	I	I	$(PPh_3)_2PdCl_2/$CuI	NEt_3	37 NMR	Not determined	
7[e] 2e	$C_{10}H_{21}$	$C_{10}H_{21}$	(structure: amide $N(Oct_2)$)	(structure: amide $N(Oct_2)$)	I	I	$(PPh_3)_4Pd/$CuI	$HN(iC_3H_7)_2$	510 (GPC)	2.9	3 % excess of alkyne component leads to high molecular weight polymers
8[e] 2f	(structure: ether chain)				I	I			210 (GPC)	1.8	
9[j] 2g	OCH_3	OCH_3	Ph	H	Br	Br	$(PPh_3)_2PdCl_2/$CuI	NaOH/toluene mix $BzMe_3N^+$ X^- PTC	67, DP_w	Not determined	See Giesa's Review
10[g] 2h	(structure: ester)	H	(structure: ester)	H	Br	-C≡C-Ph	"$Pd(0)(PPh_3)_3$"	Toluene/NaOH $Bu_4N^+Br^-$ H_2O	58	8.2	
11[g] 2i	(structure: acetyl arene)	H	(structure: acetyl arene)	H	Br	?	"$Pd(0)(PPh_3)_3$"	Toluene/NaOH $Bu_4N^+Br^-$	Insoluble	Not determined	
12[g] 2j	CO_2H	H	CO_2H	H	-	C≡C-Ph	Hydrolysis of the ester		58	8.2	
13[h] 30a	(structure)		$O{-}C_{14}H_{29}$	$O{-}C_{14}H_{29}$	I	I	$(PPh_3)_4Pd/$CuI	$HN(iC_3H_7)_2$	117(234)	Not determined	Parenthesis # of PE-units in chain
14[h] 30a									147(294)	2.6	
15[h] 29	(structure: amide $N(Oct_2)$)		(structure: amide $N(Oct_2)$)		I	I	$(PPh_3)_4Pd/$CuI	$HN(iC_3H_7)_2$	31 (62)	3.1	
16[i] 2k	(structure: $OC_{12}H_{25}$, $C_{12}H_{25}HN$)				I	I	$PdCl_2/PPh_3$ $Cu(OAc)_2$	NEt_3/THF			
17[i] 2l	$NH{-}C_{12}H_{25}$		$NH{-}C_{12}H_{25}$		Br	Br			Authors claim DP of 2100 by GPC	4.7	EA and catalyst composition suggest a DP of 8-15.
18[j] -	Structure of repeating unit (structure, $OC_{18}H_{37}$, $C_{18}H_{37}O$)				?	?	?	?	80 GPC	3.2	
19[k] -	C≡C-C_6H_{13}		O-$C_{16}H_{33}$		I	I	$(PPh_3)_4Pd/$CuI	$HN(iC_3H_7)_2$ toluene	Partially Soluble	Not determined	

[a] Koch, F.; Heitz, W. *Macromol. Chem. Phys.* **1997**, *198*, 1531. [b] Remmers, M.; Schulze, M.; Wegner, G. *Macromol. Rapid Commun.* **1996**, *17*, 239. [c] Pang, Y.; Li, J.; Hu, B.; Karasz, F. E. *Macromolecules* **1998**, *31*, 6730. [d] Li, H.; Powell, D. R.; Hayashi, R. K.; West, R. *Macromolecules* **1998**, *31*, 52. [e] Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12593. [f] Solomin, V. A.; Heitz, W. *Macromol. Chem. Phys.* **1994**, *195*, 303. [g] Häger, H.; Heitz, W. *Macromol. Chem. Phys.* **1998**, *199*, 1821. [h] Yang, J. S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864. [i] Moroni, M.; LeMoigne, J.; Pham, T. A.; Bigot, J. Y. *Macromolecules* **1997**, *30*, 1964. [j] Walters, K. A.; Ley, K. D.; Schanze, K. S. *J. Chem. Soc., Chem. Commun.* **1998**, 1115. [k] Goldfinger, M. B.; Swager, T. M. *Abstr. Pap. Am. Chem. Soc. 210* **1995**, (135-PMSE, Part 2).

The synthesis of high-molecular-weight PPEs is of interest, because mechanical and film-forming properties are dependent upon molecular weights. High molecular weights are expected if the utilized diha- lide (diiodide, dibromide) is strongly acceptor substi- tuted. This case is realized in Swager's bisamide polymer **2e** (Table 4, entry 7).[33] Its molecular weight is substantial. A polymer with up to 500 repeating

units (according to GPC and light scattering, discussion vide infra)[50] has been obtained, making it the PPE with the highest molecular weight obtained by the Pd-catalyzed reaction (for high- and ultrahigh-molecular-weight PPEs via alkyne metathesis, see section I.A). According to the authors, it was mandatory to utilize a small excess (approximately 3%) of the bisalkyne monomer. This excess was necessary despite the use of Pd(PPh$_3$)$_4$ as catalyst precursor, already containing Pd^0, which obviously does not need to be reduced. It is suspected that small amounts of oxidants or an unknown side reaction lead to the untimely consumption of the alkyne functionality. Heitz (Table 4, entry 10) achieved the introduction of one carboxylic group per repeating unit into PPEs.[30] He polymerized (Scheme 7) a trimethylsilyl-protected bisdiyne with the corresponding dibromide in a water/NaOH/toluene mixture in the presence of a phase transfer agent, Bu$_4$N$^+$Br$^-$, and the Pd catalyst. This catalyst was formed by reduction of (PPh$_3$)$_2$PdCl$_2$ with SnCl$_2$ in the presence of 1 equiv of PPh$_3$. No amine is necessary in this reaction protocol, which according to the authors furnishes the soluble ester-substituted PPE **2h** in high yields and with a DP of approximately 50. The experimental trick is to cleave the trimethylsilyl groups of the monomer in situ under the influence of the NaOH. This protocol (a) leads according to the authors to PPEs without diyne defects and (b) makes the deprotection step unnecessary. The PPE **2h** is well soluble due to the presence of the ethylhexyl ester groups. Saponification leads to the corresponding PPE−polycarboxylate **2j**, soluble in aqueous NaOH (Scheme 7).[30]

While acceptor-substituted PPEs can be obtained as high-molecular-weight polymers, the synthesis of the monomers is not trivial. Contrary to the case of the alkoxy-PPEs **1** in which the iodide substituent can be introduced directly, that is not possible for strongly acceptor-substituted benzenes, and insofar indirect routes have to be employed. The groups of Swager,[33] Heitz,[30] and Le Moigne[42] have developed excellent synthetic accesses to these interesting monomers, two examples of which are discussed. The first is Le Moigne's amino ester synthesis (Scheme 6).[51]
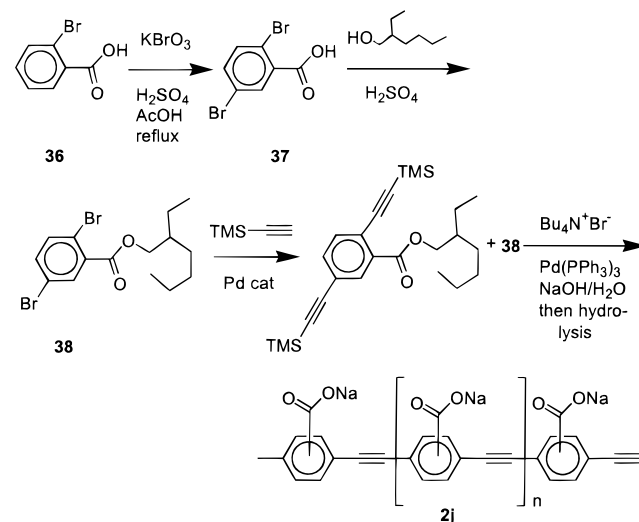
Scheme 6
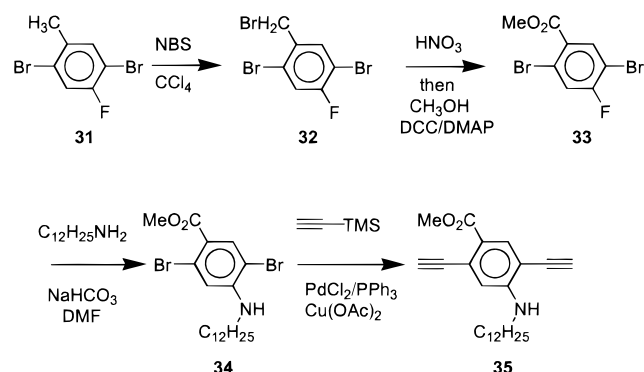
The key step is the nucleophilic substitution of the activated fluorine substituent in **33** by dodecylamine under mild conditions, leading to **34**. This step is

followed by standard synthetic manipulations, leading to the diyne **35**. The second example is Heitz' synthesis of dibromobenzoic acid[30] (Scheme 7). The

Scheme 7

authors start from commercially available 2-bromo-benzoic acid (**36**), which is brominated in the 4-position by potassium bromate in a mixture of H$_2$SO$_4$ and acetic acid at 120 °C. The bromination procedure furnishes the acid **37** in high yields, and Fischer esterification with ethylhexanol finishes the synthesis to **38**. Clever combination of aromatic substitution and side group manipulation thus allow for a wide variety of donor- and acceptor-substituted PPE precursors to be made in multigram quantities and without prohibitive synthetic effort.

3. Alkyl- and Aryl-Substituted PPEs

Alkyl- and aryl-substituted PPEs **3** are hydrocarbons and as such the least electronically perturbed PPEs, resembling most the completely insoluble parent PPE. Attempts to make the parent PPE have been reviewed and will not be discussed here.[26] Bochmann[52] and Heitz[53] independently reported the synthesis of alkyl-substituted polyaryleneethynylenes, in which the aryl groups are 2,2'-dimethylbiphenyl, anthryl, or biphenyl units. None of the polymers are of particularly high molecular weight due to their insolubility. Novak[54] recently presented a more sophisticated approach toward the synthesis of unsubstituted polyaryleneethynylenes. His concept is similar to that of Scherf[55] utilizing a soluble precursor (Scheme 8), which eliminates a volatile fragment upon heating. Starting from a quaterphenylene−norbornadiene copolymer (**41**) with a DP of 63 (M_w/M_n = 1.8), pyrolysis extrudes bis(carbethoxy)cyclopentadiene under formation of the completely insoluble quaterphenyleneethynylene **42**.

The first "real" dialkyl-substituted PPEs were reported by Bunz and Müllen in 1995.[58] The group at the Max-Planck Institut prepared the corresponding iodinated (**45a**) and alkynylated (**46**, **47a**) precursors starting from 1,4-dichlorobenzene (Scheme 9).[56]

Kumada coupling furnishes 1,4-dihexylbenzene (**44a**) (the route is universally applicable, for the

Scheme 8
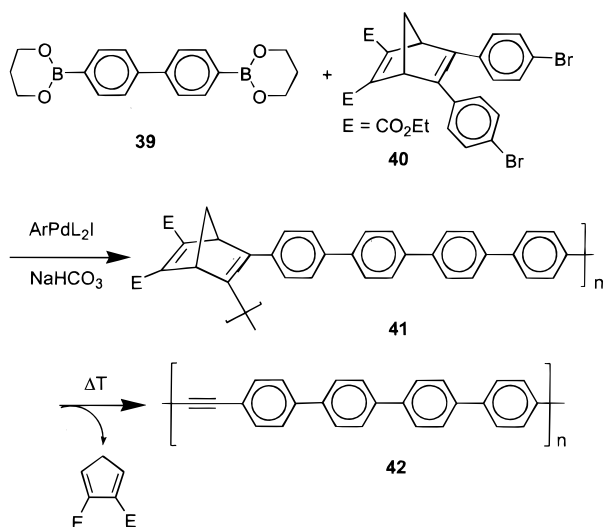
synthesis of *any p*-dialkylated benzene), which is iodinated by a mixture of KIO_4/I_2 in H_2SO_4, acetic acid, and chloroform. The iodination of alkyl-substituted benzenes is not as facile as that of bisalkoxy-substituted arenes. It is advised to work in concentrated solution and check the progress of the iodination by NMR spectroscopy. All of the diiodinated dialkyl-benzenes show a singlet at δ 7.8 for the aromatic protons, while the arene protons of the starting materials give rise to a singlet at δ 7.1. In some cases the reaction can take several days, and it may be necessary to add more oxidant.

Coupling of **45a** with an excess of trimethylsilyl-acetylene under Pd catalysis furnishes **47a** in high yield after deprotection by potassium carbonate. If an excess of diiodide is used, the corresponding monoalkynylated iodobenzene **46** can be isolated after repeated chromatography. The synthesis of the PPEs **3a** is straightforwardly performed by Heck−Cassar−Sonogashira−Hagihara[27−30] coupling in tri-ethylamine at room temperature with $(PPh_3)_2PdCl_2$/ CuI as catalyst. The molecular weights of dihexyl-

PPE **3a** are independent of the utilized monomer (i.e., if an AB (**46**) or an AA (**45a**) + BB (**47a**) polycondensation is performed), and materials with a DP of 30−60 are isolated according to elemental analysis and GPC. The molecular weight distribution M_w/M_n = 2.4 is typical for a step-growth polycondensation. Discrepancies in the molecular weights when comparing the values obtained from elemental analysis with those from GPC are not surprising. GPC overestimates molecular weights of rigid-rod-type polymers by a factor of approximately 2.[22]

The end groups in **3a** made by Bunz and Müllen are assumed to be mostly iodine substituents, even though some dehalogenation under reduction or phosphonium salt formation cannot be excluded.[57] To circumvent the problems associated with ambiguous polymer termini, Müllen devised an elegant strategy to control the end groups of PPEs. The strategy allows their convenient manipulation, so that PPEs with different and defined head and tail groups are available.[58] Treatment of 4-iodonitrobenzene (**48**) (Scheme 9) with an equimolar amount of $Pd(PPh_3)_4$ forms an organometallic intermediate, **49**, which is reacted with *n* equiv of **46**. An intermediate Pd-functionalized oligomer or polymer, **50** (depending upon the amount of AB monomer added), forms, which is end-capped by the addition of an excess of **51**. PPE **52** displays defined end groups and is void of diyne defects, due to the use of a Pd^0 source. The isolated PPE is donor−acceptor-substituted. The presence of both end groups is clearly visible in the UV/vis spectrum. For long oligomers (*n* > 6) the end groups are merely observed as a shoulder but are clearly identified. The group at the Max-Planck Institut performed MALDI-TOF spectrometry upon their oligomeric mixtures **52** and demonstrated unequivocally the absence of defects.

The synthesis of end-capped PPEs is not restricted to organic terminators. It could be extended to organometallic ones, and Hopkins[59] recently reported a tungsten−carbyne-capped tolane (**57**; Scheme 10). If introduced into a Müllen-type scheme,[58] it would

Scheme 9

Scheme 10

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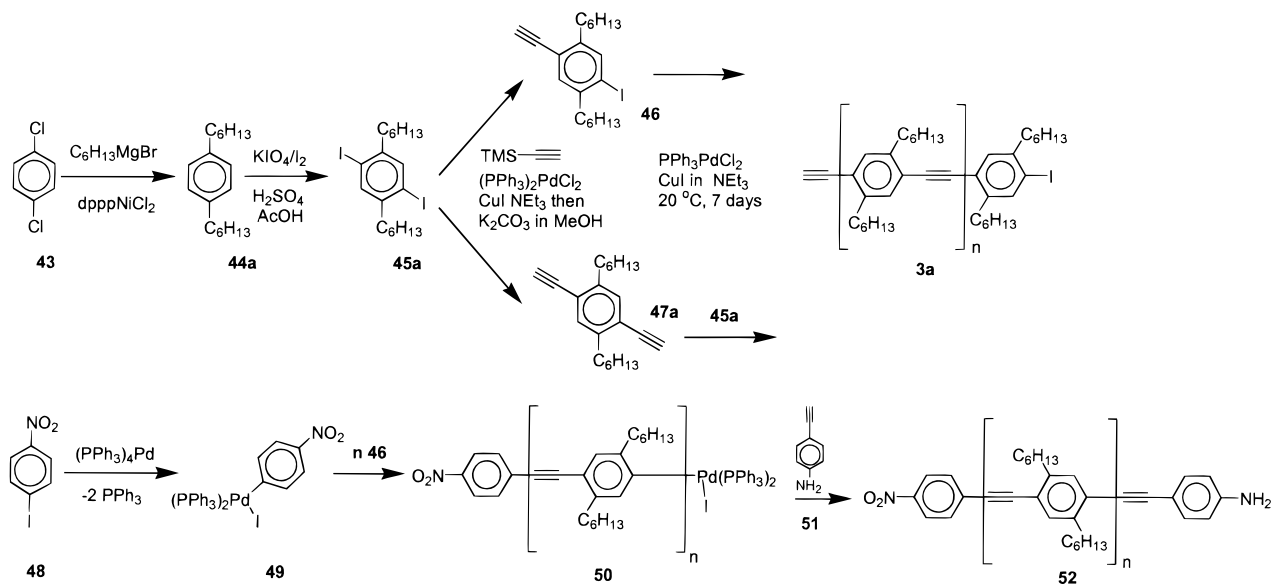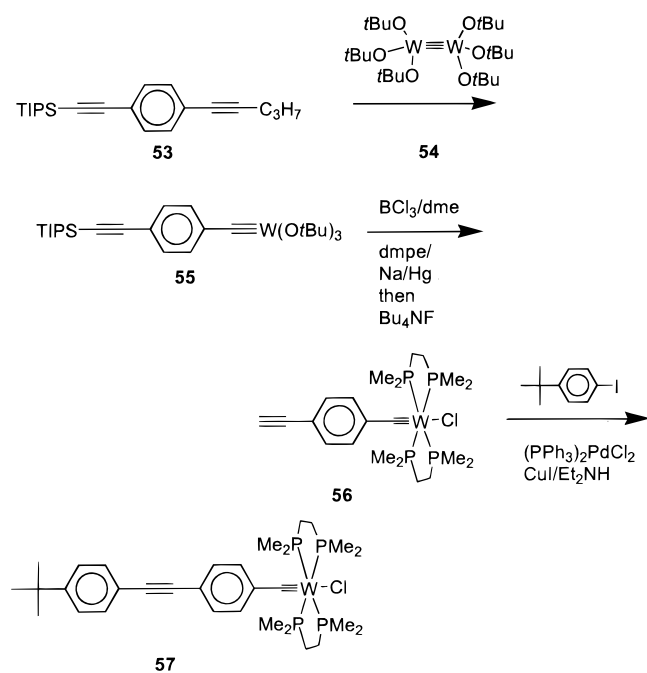
lead in a facile way to organometallic end-capped PPEs. The headgroups then could be utilized either for further functionalization or as electroactive reporter groups, making long PPEs redox active. Charged headgroups may allow as well for the formed PPEs to assume novel supramolecular structures.

In extension of his earlier developed method, Müllen[58] was able to make a PPE, which carries thio-(dimethylcarbamoyl) substituents at both ends. The DP was adjusted to 20–30 by varying the amount of the added end cappers. Molecular weight determination was performed by NMR, GPC vs polystyrene, and GPC vs a poly(p-phenylene) (PPP) standard. NMR values and GPC vs polystyrene values are off by a factor of 2, with the GPC (as expected) giving the higher value. GPC with a PPP standard was attempted but overestimates the molecular weights by a factor of 1.2–1.5. The polydispersities were inconspicuous and ranged from 2 to 3.5. These thio-terminated PPEs are of interest to bridge nanogaps in microelectrodes, 20–30 nm apart.[20]

The performance of metal-catalyzed reactions in aqueous media is an attractive concept, for the ecological and economic benefits, which could arise. This concept was tested for PPEs by Li et al.[60] They treated p-diiodobenzene, 4,4′-diiodobiphenyl, or 1,4-diiododurene (1,4-diiodotetramethylbenzene) with acetylene gas in a mixture of acetonitrile, triethylamine, and water. As coupling catalyst the authors utilized a mixture of palladium acetate, triphenylphosphine, and CuI. The resulting polymers however were insoluble and of low molecular weight.

4. Meta-Linked PPEs (Table 5)

The same authors were more successful when they applied their *in aqua* concept to the synthesis of water-soluble, carboxyl-substituted *m*-PPE[61] (Table 5, entry 1). Reaction of 3,5-diiodobenzoic acid with acetylene gas under Pd–Cu catalysis furnishes a

dark brown material, soluble only in dilute aqueous NaOH. The authors have determined the molecular weight of the material by agarose electrophoresis and measure an M_w of 66 000. However, neither M_n nor the polydispersity of **12a** (Chart 1, R = CO_2H) is determined, so the real molecular weight is not known. The dark color of their material must result from the presence of butadiyne and hexatriyne linkages in their polymer, prone to cross-linking. Alternatively, the intermediary formation of some free H–C≡C–[C≡C–]$_n$C≡C–H in the course of the reaction will lead to small amounts of highly conjugated, dark side products, obviously impossible to separate from **12a**. The polyynes will react under cycloaddition-type reactions with any conjugated material present.

The synthesis of alkyl-substituted *meta*-linked PPEs was reported by Müllen and Bunz[16] (Table 5, entries 7–9). The preparation of the monomers follows a route different from that of the hitherto mentioned ones (Scheme 11). Starting from **58**,

Scheme 11

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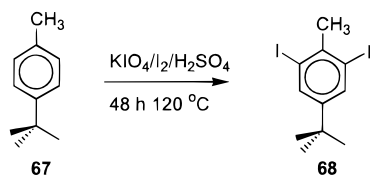
12

63

64

65

66
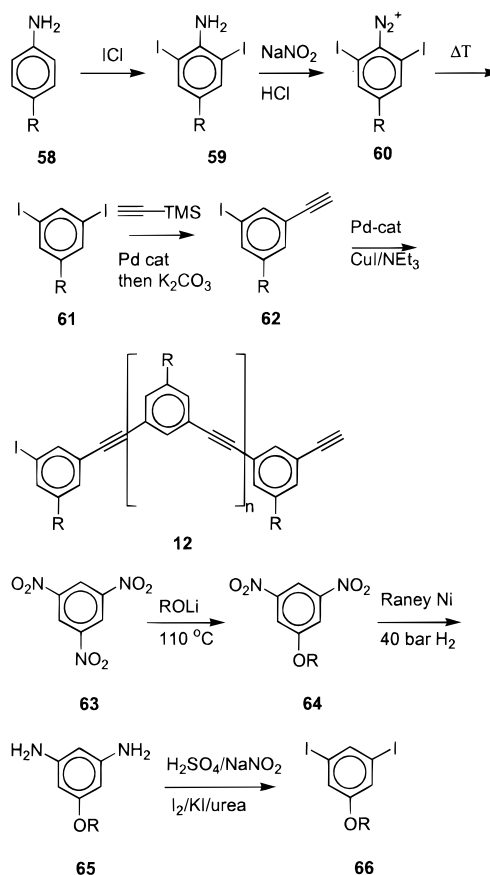
iodination with ICl furnishes regioselectively the corresponding 3,5-diiodides **59**. Removal of the amino group is achieved by thermal decomposition of **60**. Two alternative routes have to be mentioned. One route starts from trinitrobenzene **63** (Scheme 11), in which one of the nitro groups is replaced by an alkoxy substituent in a nucleophilic substitution. The remaining nitro groups are reduced and transformed into iodo functionalities by a double-Sandmeyer-type reaction (50% yield, sequence **64**–**66**). The easiest access to *m*-diiodobenzenes (Scheme 12) starts from

Table 5. Synthesis of *meta*- and *meta-co-para* Connected PPEs

Entry/Cpd	Diyne	Dihalide	End group	Catalyst	Solvent	DP	M_w/M_n	Comment
1[a] 12a	H-C≡C-H	(CO2H structure)	I or CC-H	CuI/Pd(OAc)₂/(m-SO₃NaPh)₃P	NaOH/H₂O NEt₃	Only M_w reported. DP based on M_w 400		Dark brown material, no ¹³CNMR characterization
2[b] 12b	(nitroxide structure)	(tert-butyl structure)				12 (24)	1.8	Number in parentheses refers to phenylene-ethynylene units.
3[b] 12c	(C6H13 structure)	(C8H17 structure)		5 mol% Pd(PPh₃)PdCl₂/ CuI	NEt₃ Pyridine	11(23)	1.8	
4[b] 12d	(nitroxide structure)	(nitroxide structure)	I			7	Not determined	Free spins survive coupling conditions. Pyridine as solvent seems to be better with respect to radical stability
5[c] 12e	(nitroxide structure)	(tert-butyl structure)				9 (18) GPC 6 (12) EA	Not determined	
6[d] 15a	(diyne structure)	Br...Br OC₂₁H₄₃	Br	Pd(PPh₃)PdCl₂/ CuI	NEt₃	78	Not listed	Not clear if DP is based on M_w or M_n.
7[e] 12f	(tert-butyl structure)		I			23(16)	1.4	Values for DP are determined by GPC vs. polystyrene standard. The values in parentheses are determined by elemental analysis
8[e] 12g	(Hexyl structure)		I	5 mol% (PPh₃)PdCl₂/ CuI	NEt₃	22(15)	1.7	
9[e] 14a	(OC6H13 structure)		I			25 (13)	1.7	
10[f] 13	(OC12H25, CH3 structure)		I	dppfPdCl₂/ CuI	N(iC₃H₇)₂	28	3.8	
11[g,f] 15b	(diyne structure)	OC₈H₁₇, C₈H₁₇O structure	I	1 mol% (PPh₃)PdCl₂/ CuI	Toluene/ NEt₃	81	2.4	Very soluble
12[h,f] 15c	(OCH₃, CO₂Me structure)	(crown ether structure)	I	(PPh₃)₄Pd/CuI	HN(iC₃H₇)₂	22	2.8	
13[h,f] 15d		OC₁₀H₂₁, C₁₀H₂₁O structure				417	1.7	Partially insoluble

[a] Li, C. J.; Slaven, W. T.; Chen, Y. P.; John, V. T.; Rachakonda, S. H. *J. Chem. Soc., Chem. Commun.* **1998**, 1351. [b] Miura, Y.; Ushitani, Y. *Macromolecules* **1993**, *26*, 7079. Miura, Y.; Ushitani, Y.; Inui, K.; Teki, Y.; Takui, T.; Itoh, K. *Macromolecules* **1993**, *26*, 3698. [c] Miura, Y.; Issiki, T.; Ushitani, Y.; Teki, Y.; Itoh, K. *J. Mater. Chem.* **1996**, *6*, 1745. [d] Kondo, K.; Okuda, M.; Fujitani, T. *Macromolecules* **1993**, *26*, 7832. [e] Mangel, T.; Eberhardt, A.; Scherf, U.; Bunz, U. H. F.; Müllen, K. *Macromol. Rapid Commun.* **1995**, *16*, 571. [f] Kang, B. S.; Kim, D. H.; Lim, S. M.; Kim, J.; Seo, M. L.; Bark, K. M.; Shin, S. C.; Nahm, K. *Macromolecules* **1997**, *30*, 7196. [g] Pang,Y.; Li, J.; Hu, B.; Karasz, F. E. *Macromolecules* **1998**, *31*, 6730. [h] Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12593.

Scheme 12

(Reaction scheme: 4-tert-butyltoluene **67** → with KIO₄/I₂/H₂SO₄, 48 h 120 °C → diiodo product **68**)

4-*tert*-butyltoluene (**67**), which upon reaction with KIO₄/I₂/H₂SO₄ at elevated temperature furnishes 1-*tert*-butyl-3,5-diiodo-4-methylbenzene (**68**) in high yields.[62] The bulky *tert*-butyl group protects its *ortho* positions in **67** efficiently, so only the positions adjacent to the methyl group are iodinated.

Partial reaction of **61** with trimethylsilylacetylene under Pd conditions (Scheme 11) furnishes the mononethynylated iodobenzenes **62** after deprotection.[16] The AB monomers **62** were reacted under standard Pd-coupling conditions and transformed into the polymers (R = hexyl or *tert*-butyl) in good to excellent yields with a DP of 20 (Table 5, entries 7–9). The synthesis of the hexoxy-substituted polymer **14a** (Chart 1, R = hexyl) follows the same procedure. The relatively low degree of polymerization is an inherent problem utilizing a palladium(II) catalyst precursor, matters are aggravated by the formation of cyclic oligomers.

The stable *meta*-polymers (**12**, **14**; Chart 1; Table 5, entries 7–9) are obtained as off-white powders,

soluble in dichloromethane, chloroform, benzene, and THF. In a similar study Shin[63] (Table 5, entry 10) prepared alkoxy-substituted *m*-PPEs by Pd-catalyzed polymerization of the corresponding AB monomer with a DP of 28. While these polymers are the unfunctionalized parent ethers, Miura[64,65] (Table 5, entries 2−5) made a series of *m*-PPEs, which carry free radical species in their 5-position. The coupling of the persistent radicals with suitable diiodoben- zenes in pyridine/triethylamine mixtures furnishes polymers **12b**−**e**, but of low molecular weight. An interesting observation was that the radical-carrying monomers were not stable to triethylamine. However, they survived the coupling if it was conducted in a mostly pyridine-containing solvent. It is noticeable that none of the involved palladium species react with the free organic nitroxide radicals, again stress- ing the high selectivity and mildness of this reaction. The polymer **12d** (Table 5, entry 4), which carries a free radical on every repeating unit, is slightly blue and forms a blue solution in toluene. It is not ferromagnetic, but paramagnetic, and thus does not represent a molecular magnet.

While the *m*-PPEs are effectively nonconjugated, *p*-PPEs are so rigid that solubility, processability, and film-forming properties are adversely affected if not very long alkyl chains are used in their solubilization. As a consequence, Pang[66] (Table 5, entry 11) com- bined both types of monomers to form a copolymer in which *m*-phenylene rings and 1,4-dialkoxyphe- nylenes are separated by alkyne units. The DP of the processable and sufficiently soluble polymer **15b** was examined by GPC and exceeds 80. The optical properties of this polymer are determined by the extended trimeric repeating unit *m*-phenylene− C≡C−*p*-dialkoxyphenylene−C≡C−*m*-phenylene. The concept of inserting *m*-phenylene units into PPEs to increase processability had already been realized earlier by Swager, who synthesized similar polymers (**15c**,**d**) of high molecular weight (Table 5, entries 12 and 13). If the diiodide is of the cyclophane type (Table 5, entry 12), these PPEs can be used in sensory applications.[33]

5. Thiophenyleneethynylenes and Related PAEs

One of the founding fathers of the PAE field is Yamamoto,[67−76] who early on concentrated upon PAEs in which ethynylene groups link pyridines and thiophene units (Table 6). He established the use of a mixture of triethylamine/Pd(PPh₃)₄/CuI as an ef- fective catalyst system for these polymerizations. The use of the Pd⁰ catalyst reduces the amount of diyne defect structures in the formed PAEs because none of the alkyne component needs to be consumed for formation of the active species. Clearly, the disad- vantage of Pd(PPh₃)₄ is that it is relatively sensitive and commercial batches will vary greatly in quality and activity. Only bright-yellow Pd(PPh₃)₄ guaran- tees good activity, yet even pure Pd(PPh₃)₄ is less active when compared to (PPh₃)₂PdCl₂ as a conse- quence of the presence of the two additional PPh₃ ligands.

Yamamoto pioneered solubilizing side chains in PAEs, and in 1993[68,69] he reported independently of

Giesa and Schulz[40] processable PAEs (see Tables 6 and 7). The 2,5-diiodo-3-hexylthiophene building block was coupled to a variety of diynes to furnish PAEs. The used diynes include 1,4-diethynylbenzene, 2,5- and 2,6-diethynylpyridine, and 2,5-diethynyl-3- hexylthiophene (Table 6, entries 1−6).[68,69] Unfortu- nately, most of the polymers were not characterized by GPC, and the molecular weights obtained by light scattering suggest DPs in the range of hundreds to thousands, which must be greatly overestimated. In the case of the poly(3-hexylthienyleneethynylene) (**16a**) Yamamoto (Table 7, entry 5) reports an M_w by light scattering, which would correspond to ap- proximately 1000 repeating units. A proton NMR of **16a** is displayed in the same paper (Table 7, entry 5), and clearly shows small end group signals, which can be accorded to thienyl protons adjacent to iodo substituents. A rough estimate of DP (which is based on M_n but not on M_w) suggests an upper value of 25 repeating units. The general problem associated with light scattering of conjugated rigid rods is that (a) association and aggregation processes can artificially increase the obtained value and (b) no information about polydispersity is available; i.e., no realistic molecular weight can be extracted from light scat- tering alone. Later Yamamoto performed an interest- ing optimization study for the synthesis of **6a** (Table 6, entry 3) utilizing *p*-diethynylbenzene and HIT (3- hexyl-2,5-diiodothiophene). In this carefully con- ducted study, the authors conclude that with their catalyst system Pd(PPh₃)₄/CuI (5 mol % each) a DP of ∼100 with an M_w/M_n of 2.6 can be reached. These values look very realistic for a carefully optimized step-growth condensation, where traces of oxidants are excluded (for a discussion of molecular weight and structure see III.A).

If HIT and HET (3-hexyl-2,5-diethynylthiophene) are coupled under Pd catalysis to form PTE (poly- (thienyleneethynylene)), **16a** (Table 7, entries 5 and 9) forms as a regiorandom polymer, in which head- to-head (HH) and head-to-tail (HT) sequences are almost statistically distributed (Chart 2). By a careful

Chart 2

HH orientation   **16a**, R =C₆H₁₃   HT orientation
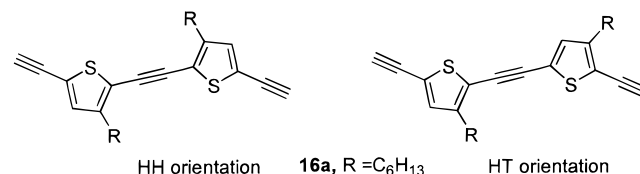
synthesis of the starting materials, Pang (Table 7, entries 7−9) was able to produce PTEs **16a** in which specifically only *one* regioisomeric form is present. The regioregular polymers have optical and electronic properties different from each other and from the regiorandom PTE **16a**. Pang's coupling method is a variant of Yamamoto's original receipt using 1 mol % (PPh₃)₂PdCl₂ in the presence of CuI in triethyl- amine. The reported DPs range from 60 to 80, which is a respectable result and gets close to the theoretical limit (∼100) imposed by the presence of the Pd⁺² catalyst.

Table 6. Synthesis of PAEs in Which One Unit Is a Phenylene Ring

Entry/Cpd	Alkyne	Halide	End group	Catalyst	Solvent	DP	M_w/M_n	Comments
1[a] 6a	(diethynylbenzene)	(thiophene, C₆H₁₃)	I	(PPh₃)₄Pd/CuI	NEt₃	DPw 135 (360)	Not determined	DP determined by light scattering in parentheses. No polydispersity data
2[b] 6b	(diethynylbenzene)	(thiophene; O₂N, NO₂, Br, Br)	Br	(PPh₃)₄Pd/CuI	NEt₃/toluene	Insol.	Not determined	
3[c] 6a	(diethynylbenzene)	(thiophene, C₆H₁₃)	I	(PPh₃)₄Pd/CuI 5 mo% each, 12h, 60 °C	NEt₃/toluene	108	2.6	Optimization study; gpc vs polystyrene
4[d] 8a	(diethynylbenzene)	(benzimidazole, OH)	Br	(PPh₃)₄Pd/CuI	NEt₃/toluene	33		gpc vs polystyrene standard, polydispersities were not determined
5[d] 8b	(OC₁₂H₂₅, C₁₂H₂₅O)	(benzimidazole, OH)				5		
6[d] 15e	(structure)	(benzimidazole, OH)				72		
7[e] 6a	(thiophene–phenylene, C₆H₁₃)		I	(PPh₃)₂PdCl₂ CuI	NEt₃	99	1.4	Different regioisomeric polymers with different properties are obtained
8[e] 6a	(diethynylbenzene)	(thiophene–phenylene–thiophene, C₆H₁₃, C₆H₁₃)	I	(PPh₃)₂PdCl₂ CuI	NEt₃	89	2.0	
9[e] 6a	(diethynylbenzene)	(thiophene, C₆H₁₃)	I	(PPh₃)₂PdCl₂ CuI	NEt₃	56	2.1	
10[f] 6a	(diethynylbenzene)	(thiophene, C₆H₁₃)	I	(PPh₃)₂PdCl₂ CuI	NEt₃	128	2.3	
11[f] 6c	(OC₈H₁₇, C₈H₁₇O)	(thiophene, C₆H₁₃)	I	(PPh₃)₂PdCl₂ CuI	NEt₃	52	2.2	
12[f] 6d[f]	(OC₈H₁₇, C₈H₁₇O)	(thiophene)	I	(PPh₃)₂PdCl₂ CuI	NEt₃	45	2.1	
13[g] 9	(OC₈H₁₇, C₈H₁₇O)	(bipyridine, Br)	Br	(PPh₃)₄Pd CuI	HN^{i}Pr₂	21 VPO 25 gpc	1.9	
14[h] 15f	(C₁₂H₂₅O, CH₃)	(thiophene)	I	dppfPdCl₂·CH₂Cl₂ CuI	NEt₃	9	2.4	
15[h] 15g	(C₁₂H₂₅O, CH₃)	(bithiophene)	I	dppfPdCl₂·CH₂Cl₂ CuI	NEt₃	18	3.3	
16[h] 15h	(C₁₂H₂₅O, CH₃)	(terthiophene)	I	dppfPdCl₂·CH₂Cl₂ CuI	NEt₃	8	6.0	

[a] Takagi, M.; Kizu, K.; Miyazaki, Y.; Maruyama, T.; Kubota, K.; Yamamoto, T. *Chem. Lett.* **1993**, 913. Yamamoto, T.; Takagi, M.; Kizu, K.; Maruyama, T.; Kubota, K.; Kanbara, H.; Kurihara, T.; Kaino, T. *J. Chem. Soc., Chem. Commun.* **1993**, 797. [b] Yamamoto, T.; Muramatsu, Y.; Shimizu, T.; Yamada, W. *Macromol. Rapid Commun.* **1998**, *19*, 263. [c] Yamamoto, T.; Honda, K.; Ooba, N.; Tomaru, S. *Macromolecules* **1998**, *31*, 7. [d] Hayashi, H.; Yamamoto, T. *Macromolecules* **1998**, *31*, 6063. [e] Li, J.; Pang, Y. *Macromolecules* **1998**, *31*, 5740. [f] Pang, Y.; Li, J.; Barton, T. J. *J. Mater. Chem.* **1998**, *8*, 1687. [g] Egbe, D. A. M.; Klemm, E. *Macromol. Chem. Phys.* **1998**, *199*, 2683. [h] Kang, B. S.; Kim, D. H.; Lim, S. M.; Kim, J.; Seo, M. L.; Bark, K. M.; Shin, S. C.; Nahm, K. *Macromolecules* **1997**, *30*, 7196.

The quest for regioregularity is not restricted to PTE **16a** but occurs as well in the alternating copolymerization of HIT with *p*-diethynylbenzene and poly(phenyleneethynylenethienyleneethynylene) (PPETE, **6**; Charts 1 and 2). Yamamoto reported the regiorandom **6a** in 1993 (Table 6, entries 1 and 3), and Pang later prepared the regiorandom **6a** with his catalyst system with a DP varying from 60 to 120 (Table 6, entries 7–9). The introduction of solubilizing groups into the diyne, utilizing long-chain dialkoxy substituents (Table 6, entries 11 and 12), furnished new derivatives (**6c,d**) of these alternating copolymers, but did not increase the molecular weight substantially. The authors report a DP of ~50 by

Table 7. Synthesis of PAEs in Which No Unit Is a Phenylene Ring

Entry/ Cpd	Alkyne	Halide	End group	Catalyst	Solvent	DP	M_w/M_n	Comments
1[a]	(structure)	(structure)	I	(PPh₃)₄Pd/CuI	NEt₃ toluene	71 (1800)		M_W-values obtained by gpc . Values from light scattering in parenthesis. Neither DP_M nor polydispersity are determined.
2[a]	(structure)	(structure)	Br			Insoluble		
3[a]	(structure)		Br			(2100) in CO₂H₂		
4[b]	(structure)	(structure)	I			212 gpc vs PS		M_w/M_n not determined
5[c] 16a	(structure)	(structure)	I			(1000)		¹H NMR is displayed in paper and shows end groups. P_n is approx. 10-20
6[e]	(structure)	(structure)	Br			(2530)		
7[d] 16a	(structure)		I	(PPh₃)₂PdCl₂ 1 mol%	NEt₃ toluene	56	1.9	Regioregular polythiophenylene-ethynylenes
8[d] 16a	(structure)	(structure)	I	CuI		78	7.8	
9[e] 16a	(structure)	(structure)	I					Regioirregular PTE
10[f] 16b	(structure)		Br	(PPh₃)₄Pd/CuI	NEt₃ toluene	25 gpc vs. PS	ND	Polymer was oxidized to polyradical
11[g]	(structure)	(structure)	I	(PPh₃)₄Pd/CuI	NEt₃ toluene	6	2	Partially soluble gpc vs polystyrene
12[g]	(structure)	(structure)	I	(PPh₃)₄Pd/CuI	NEt₃ toluene	(1100)	ND	M_w obtained by light scattering. No gpc data
13[h]	(structure)	(structure)	Br	(PPh₃)₄Pd/CuI	NEt₃ toluene	11		gpc vs PS standard, polydispersities were not determined
14[i]	(structure)	(structure)	I	PdCl₂, PPh₃, Cu(OAc)₂	HN(iPr)₂	23	2	

[a] Takagi, M.; Kizu, K.; Miyazaki, Y.; Maruyama, T.; Kubota, K.; Yamamoto, T. *Chem. Lett.* **1993**, 913. Yamamoto, T.; Takagi, M.; Kizu, K.; Maruyama, T.; Kubota, K.; Kanbara, H.; Kurihara, T.; Kaino, T. *J. Chem. Soc., Chem. Commun.* **1993**, 797. [b] Yamamoto, T.; Honda, K.; Ooba, N.; Tomaru, S. *Macromolecules* **1998**, *31*, 7. [c] Yamamoto,T.; Yamada, W.; Takagi, M.; Kizu, K.; Maruyama, T.; Ooba, N.; Tomaru, S.; Kurihara, T.; Kaino, T.; Kubota, K. *Macromolecules* **1994**, *27*, 6620. [d] Li, J.; Pang, Y. *Macromolecules* **1997**, *30*, 7487. [e] Pang, Y.; Wang, Z. C.; Barton, T. J. *Polym Prepr.* **1996**, *212*, 123. [f] Hayashi, H.; Yamamoto, T. *Macromolecules* **1997**, *30*, 330. [g] Yamamoto, T.; Shimizu, T. *J. Mater. Chem.* **1997**, *7*, 1967. [h] Hayashi, H.; Yamamoto, T. *Macromolecules* **1998**, *31*, 6063. [i] Beginn, C.; Grazulevicus J. V.; Strohriegl, P.; Simmereer J, Haarer, D. *Macromol. Chem. Phys.* **1994**, *195*, 2353.

GPC. Even though a diethynylbenzene module separates the stereogenic centers in **6**, the two regioregular (Table 6, entries 5 and 6) polymers **6a** can be made by judicious choice of the monomers in good yields and with DPs around 100. The stereoisomers can be distinguished by NMR and by their optical properties. In a similar study Kang probed the synthesis of *m*-phenyleneethynylene(oligothienylene)s **15** (Chart 1; Table 6, entries 14−16) by coupling 4-alkoxy-3,5-diethynyltoluene to 2,5-diiodothiophene,

5,5′-diiodobithiophene, and 5,5″-diiodoterthiophene. Their reported DPs however are low, probably due to ring closure of the formed oligomers.

Very recently, PAEs with more complicated structures have been synthesized. These PAEs include, for example, **16b** (Table 7, entry 10), a phenol-substituted thiophene, a TTF, a carbazole, or a benzimidazole moiety in the main chain (Table 7, entries 10−14). While the DPs are not very high, these polymers demonstrate the scope of this reaction. Yamamoto's

phenoxy-substituted PAT **16b** (Table 7, entry 10) is a promising material because it can form persistent, stable, oxygen-centered radicals upon oxidation.

6. Organometallic PAEs (Table 8)

The introduction of organometallic π-complexes into the main chain of PAEs should access polymers with novel properties and structural features unattainable by their purely organic counterparts. Particularly NLO[77] behavior, liquid crystallinity, and redox chemistry are attractive in combination with a never-ending variation of organometallic topologies.[77,78] The field of metal-bridged alkynes and aryleneethynylenes is not covered, because these structures do not represent PAEs.[77] The first reported organometallic PAE was Wright's[79] chromotrene polymer (Table 8, entry 8), which however was synthesized by a Stille rather than a Heck—Cassar—Sonogashira—Hagihara coupling. The reason for the use of the tin methodology is the obvious sensitivity of the $Cr(CO)_3$ grouping against base and/or enhanced temperatures. The obtained DP of Wright's polymer was low.

If however the more robust CpCo(cyclobutadiene) nucleus or suitably functionalized ferrocenes are used, the classic Pd-catalyzed couplings work well. The group of Bunz (Table 8, entries 1—6) described the synthesis of a new class of polymers, in which CpCo-stabilized, diethynylated cyclobutadienes **71** are coupled to diiododialkylbenzenes **45**[37] and 2,5-diiodoalkylthiophenes.[80] The authors use piperidine as amine solvent in combination with $(PPh_3)_2PdCl_2$, and found that it works much better than triethylamine. Particularly, polydispersities, but as well the molecular weights, were unacceptable with NEt_3 as base/solvent. The DPs were determined by GPC and are on the order of 20—50, which would be expected for an experimental setup which utilizes a Pd^{+2} catalyst. The organometallic monomer **71** was first made by Vollhardt in 1979 in an elegant 2+2-cycloaddition of bistrimethylsilylbutadiyne (**69**) over $CpCo(CO)_2$ (**70**) and subsequent cleavage of the trimethylsilyl groups on the alkynes[81] (Scheme 13).

Scheme 13
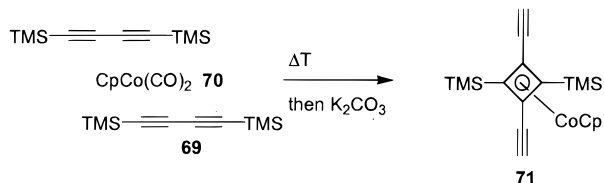
Gratifyingly, the trimethylsilyl groups placed on the ring are more stable and stay, unless **71** is treated in $Me_4N^+F^-$ in warm DMSO. The trimethylsilyl groups on the ring are valuable solubilizing substituents, which do not change the properties of the monomer. In most cases it is not warranted or desirable to remove them.

Yamamoto reported 1997 similar polymers in which 1,1'-diiodoferrocene was the organometallic monomer (Table 8, entries 13—17). Several aromatic diynes were coupled to it. The DPs of the polymers **11** were not very high, due to the known sluggishness of diiodoferrocene in Pd-catalyzed coupling reactions. Diiodoferrocene is handicapped for these reactions in two ways: (a) as an electron-rich organometallic system, its reactivity is a priori reduced (see Scheme 1 and discussion) and (b) the steric hindrance imparted by the relatively bulky CpFe fragment further slows the oxidative addition to the Pd catalyst. The Yamamoto polymers **11** are not rigid rods anymore due to the free rotation of the Cp rings around the iron center. Insofar solubility should be less of a problem here. A related approach to ferrocene-containing PAEs has been used by Plenio[82] to make some attractive rigid rods in which the organometallic groups are linked in a 1,3-fashion by alkynes (Table 8, entries 18 and 19; Scheme 14). These

Scheme 14
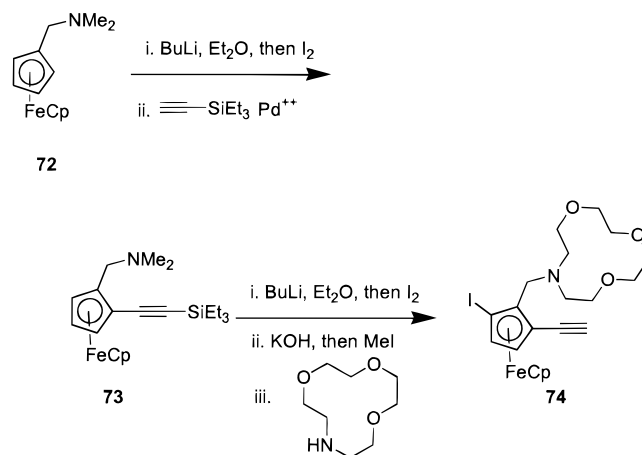
polymers are the hitherto *only* known purely organometallic PAEs. The synthesis of the monomer **74** (Scheme 14) cleverly exploits the sequential double *ortho*-metalation of (dimethylaminomethyl)ferrocene **72** to obtain 2-ethynyl-5-iodo-1-(dimethylaminomethyl)ferrocene by a repeated metalation/iodination/coupling strategy.[82] In the second metalation Plenio observed that the presence of triethylsilyl groups on the alkyne is preferable to trimethylsilyl substituents, due to the instability of the latter ones versus the conditions of the metalation. The recorded molecular weight of Plenio's polymer is surprisingly high (DP up to 150; Table 8, entry 19); however, the authors attribute this to an aggregation phenomenon involving the polar amino groups.

Tamao (Table 8, entries 9—12) has synthesized an interesting series of polymers containing silole units utilizing Stille chemistry.

7. AB and ABA Block Copolymers with PPE Segments

Block copolymers with nonmiscible segments[83,84] are fascinating objects, forming a variety of different phases and supramolecular structures. The rigid PPE backbone should be an ideal candidate for an almost perfect rod-type building block in AB or ABA block copolymers, but only very recently, Müllen[85] and Godt[86] independently reported the synthesis of AB and ABA block copolymers containing small-to-moderately-sized PPE oligomers.

## Table 8. Synthesis of Organometallic PAEs

Entry/ Cpd	Alkyne	Halide	End group	Catalyst	Solvent	DP	M_w/M_n	Comments
1[a] 10a	(structure)	(structure)	I	$(PPh_3)_2PdCl_2$ CuI	Piperidine	18	2.6	Other examples are described. First thermotropic liquid crystalline organometallic polymer.
2[a] 10a	(structure)	(structure)	I			12	4.1	
3[a] 10a	(structure)	(structure)	I			18	1.7	
4[b] 10a	(structure)	(structure)	I			18	1.4	
5[b] 10a	(structure)	(structure)	I			27	2.1	
6[b] 10a	(structure)	(structure)	I			15	3	
7[b] 10a	(structure)	(structure)	I			42	2.6	
8[c] -	(structure)	(structure)	SnMe3		Stille conditions	18	Not determined	Determined by elemental analysis
9[d] -	(structure)	(structure)	Br	Pd_2dba_3 furfuryl$_3$P	Stille conditions THF	insoluble		
10[d] -	(structure)	(structure)				18	7	
11[d] -	(structure)	(structure)				insoluble		
12[d] -	(structure)	(structure)				19	4.4	
13[e] -	(structure)	(structure)	I	$Pd(PPh_3)_4$ CuI	$HN(iPr)_2$	DP_W 5	Not determined	Only light scattering or Mw-values from gpc are given. No polydispersity information.
14[e] 11a	(structure)	(structure)	I			DP_W 68	Not determined	
15[e] 11b	(structure)	(structure)	I			DP_W 85	Not determined	
16[e] -	(structure)	(structure)	I			DP_W 11	Not determined	
17[e] -	(structure)	(structure)	I	Via Kumada-type coupling of Grignard		ND	Not determined	
18[f] -	(structure)		I	$Pd(PPh_3)_4$ CuI	$HN(iPr)_2$	bimodal		No M_n or DP provided
19[f] -	(structure)					145	1.05	Authors suspect association in gpc determination of molecular weight

[a] Altmann, M.; Bunz, U. H. F. *Angew. Chem.* **1995**, *34*, 569. [b] Altmann, M.; Enkelmann, V.; Lieser, G.; Bunz, U. H. F. *Adv. Mater.* **1995**, *7*, 726. [c] Wright, M. E. *Macromolecules* **1989**, *22*, 3257. [d] Yamaguchi, S.; Iimura, K.; Tamao, K. Chem. Lett. **1998**, 89. [e] Yamamoto, T.; Morikita, T.; Maruyama, T.; Kubota, K.; Katada, M. *Macromolecules* **1997**, *30*, 5390. [f] Plenio, H.; Hermann, J.; Leukel, J. Eur. J. *Inorg. Chem.* **1998**, 2063.

Starting from a PPE ester, Müllen[85] demonstrated (Scheme 15) that saponification of **75** and subsequent coupling of **76** to a methyl-end-capped poly(ethylene oxide) (DP of 17; addition of toluenesulfonic acid/ Steglich's base) led to the desired block copolymer **77**. The copolymer was carefully analyzed by NMR and

Scheme 15

75

76

77
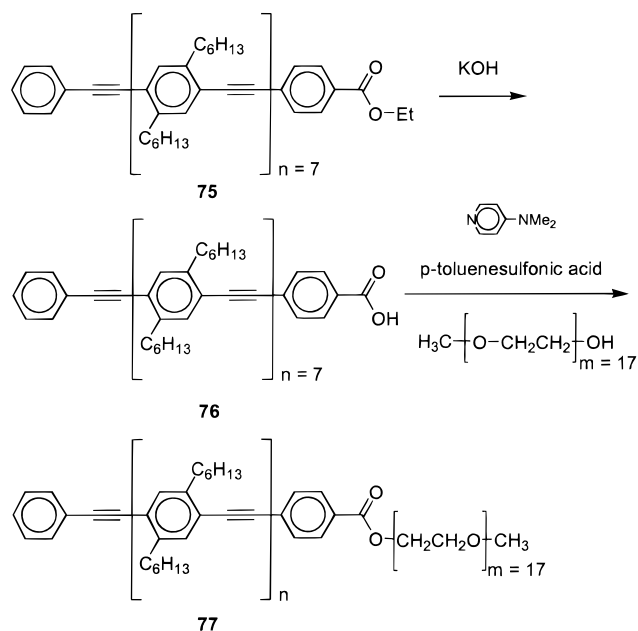
mass spectrometry. MALDI-TOF spectrometry fully supported the suggested structure.

Godt's approach is similar (Scheme 16), utilizing a PE dimer carrying a carboxylic acid functionality. Coupling **78** to polyisobutyleneethanol (PIOH) in the presence of the activating agent diazodiethylcarboxylate (DEAD) and triphenylphosphine furnishes an AB miniblock copolymer **79** after deprotection of the triisopropylsilyl groups. Eglinton-type coupling leads to the dimer **80**, an ABA block copolymer. Structure elucidation was performed by NMR and GPC, both supporting the suggested composition. It remains to be seen how phase behavior, morphology, and supramolecular ordering in block copolymers **77** and **80** differ from the properties of the respective single blocks, and whether typical lamellar structures will be observed in the TEM.

8. Structural Defects and Problems Associated with the Pd Methodologies[57]

There are several shortcomings of the Pd methodology. The molecular weights are sensitive to reaction conditions and solvents (vide supra). As a consequence, some of the low-molecular-weight materials obtained in the couplings (Tables 3−8) do not neces-

sarily reflect limits of the method per se but are rather a result of suboptimal choice of reaction conditions. From the authors experience, protocols developed by Swager,[33] Wrighton,[32] Pang,[66] or Altmann[37] seem to give the most reliable results, but even in the optimum cases there are problems to be considered in this widely used (and very valuable!) method.

Formation of Diyne Defects. Even under strict exclusion of air and with the use of Pd^0 catalysts, diyne defects occur. Swager[33] remarks that 1.03 equiv of bisalkyne must be used with 1.0 equiv of the aromatic diiodide to obtain high-molecular-weight PPEs. This is the case even if acceptor-substituted diiodides in combination with a Pd^0 source are used. Heitz[30] looked specifically into this question and finds in model studies that diyne formation is more prevalent if donor-substituted diiodides are coupled. The source of oxidant for the bisalkynes however is not clear in these Pd$^{(0)}$-catalyzed couplings, and may involve either adventitious oxidizing agents, including air in the reaction mixture, or a disproportionation of the product of the oxidative addition to Pd^0. That however would suggest that (hard-to-detect) biaryl linkages form. This point is open to further examination.[57]

Only Low-to-Moderate-Molecular-Weight Polymers Form if Not Highly Activated Diiodides Are Used. Dialkoxy- and dialkyldiiodobenzenes give, even under optimum conditions, mostly PPEs with DPs less than 100 according to GPC, which itself overestimates DPs.

Dehalogenation and Phosphonium Salt Formation (Substitution of the Iodide End Group By Triarylphosphine, Leading to Phosphonium-Substituted Chains). According to Novak,[57] who has investigated this topic, *all* of the Pd-catalyzed coupling reactions suffer to some degree from dehalogenation reactions and substitution of the iodides by triarylphosphines in a Pd-catalyzed side reaction. These side reactions will (a) decrease the degree of polymerization and (b) lead to less defined end groups. Müllen (vide infra)[58] has demonstrated that the use of a preformed catalyst accesses materials of relatively low molecular weight but with well-defined end groups.

Removal of Palladium- and Phosphorus-Containing Catalyst Residues. The polymer formation occurs in a mixture of amine and an arene or THF as cosolvent. It is accompanied by the precipitation of

Scheme 16

78

79

80
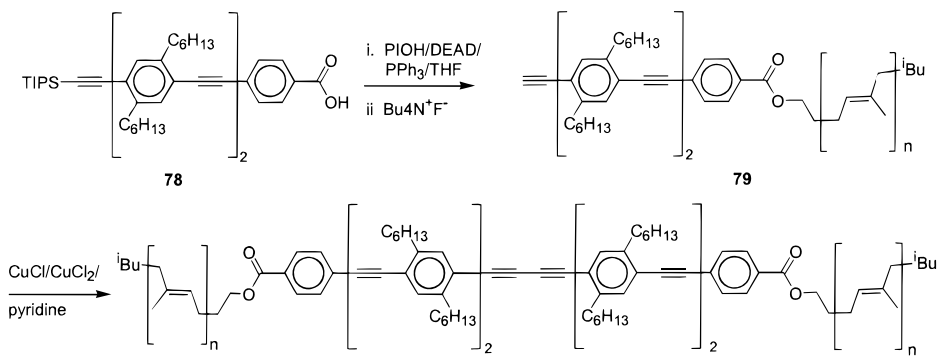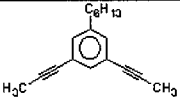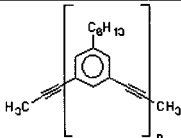
Table 9. PPEs by Alkyne Metathesis

Entry/**Cpd**	Monomer	Polymer	Catalyst	Conditions	DP	M_W/M_n	Comments
1^a **3a**	Hexyl	Hexyl	$(t\text{BuO})_3\text{W}{\equiv}\text{C}t$	80 °C, vac	94	2.1	
2^a **3b**	Phenyl	Phenyl	Bu in	85 °C vac	4–5	2.0	
3^a **12g**			trichloro-benzene	85 °C vac	15	2.1	
4^b **3a**	Hexyl	Hexyl	Mo(CO)6/4-chlorophenol	180 °C N_2 purge	182	5.4	
5^b **3c**	Dodecyl	Dodecyl	1,2-dichloro-benzene	150 °C	639	6.9	
6^b **3d**	Nonyl	Nonyl		150 °C	189	3.1	
7^b **3e**	Hexyl/dodecyl	Copolymer		150 °C	87	3.7	
8^b **3f**	2-Ethylhexyl	2-Ethylhexyl		175 °C	1260	3.5	
9^b **3g**	3,7-Dimethyloctyl	3,7-Dimethyloctyl	4-CF_3-phenol as cocatalyst	130 °C	286	5.3	chiral
10^b **1n**	Isopentoxy	Isopentoxy	4-CF_3-phenol as cocatalyst	130	65	2.5	

[a] Weiss, K.; Michel, A.; Auth, E. M.; Bunz, U. H. F.; Mangel, T.; Müllen, K. *Angew. Chem.* **1997**, *36*, 506. [b] Kloppenburg, L.; Song, D.; Bunz, U. H. F. *J. Am. Chem. Soc.* **1998**, *120*, 7973. Kloppenburg, L.; Jones, D.; Bunz, U. H. F. *Macromolecules* **1999**, *32*, 4194.

large amounts of ammonium salts and in some cases by the formation of Pd black. Workup procedures have to make sure that the catalyst residues are removed efficiently. However, these have a solubility behavior similar as PPEs, so removal by precipitation into methanol may not be too efficient. This point deserves more attention and could be clarified by ^{31}P spectroscopy of the isolated polymers.

As a consequence, it would be important to have an alternative synthesis of PPEs, non-Pd-based, which would overcome some or all of the above-mentioned deficiencies.

B. Alkyne Metathesis: An Efficient Way to High-Molecular-Weight PPEs

The classic Pd-catalyzed Heck–Cassar–Sonogashira–Hagihara reaction forms the single bond between the arene ring and the alkyne triple bond. It should be equally possible to form the C–C triple bond during the polymerization reaction. In the case of double bonds this has been achieved by McMurry[87] coupling, condensation reactions,[12] and alkene metathesis.[88] However, there is no analogue of the McMurry reaction in alkyne chemistry, and likewise, high-yielding condensation methods are not well-developed for the synthesis of triple bonds. Alkyne metathesis in homogeneous solution on the other hand has been known since 1974. It was discovered by Mortreux and Blanchard, who treated tolanes with a mixture of molybdenum hexacarbonyl and 4-chlorophenol. At elevated temperatures they found clean substituent exchange.[89] Later Schrock demonstrated that defined molybdenum–or tungsten–carbyne complexes are active in alkyne metathesis, suggesting that the Mortreux catalysts likewise form these species in situ.[90] In 1995 Mori[91] showed that the Mortreux systems[89] are valuable for preparative work. She metathesized a series of substituted alkynes to their corresponding homo- and heterodimers, but the yield of this reaction was not always high. The

subject of alkyne metathesis has been reviewed recently.[89]

1. Syntheses

In 1997, Bunz, Weiss, and Müllen[92] reported the first use of Schrock's tungsten–carbyne[93] for the preparation of some PPEs including 2,5-dihexyl-PPE **3a** (Table 9, entries 1–3). The dipropynylated monomer **81a** (Scheme 17, Table 9) was treated with the

Scheme 17
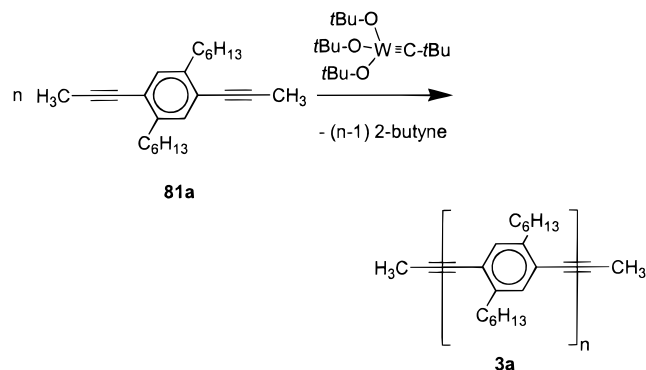
tungsten carbyne in carefully dried solvents under strict exclusion of air and water at elevated temperatures for 12–16 h. Under these conditions PPEs **3a** formed via alkyne metathesis with a DP of 94, which makes the method competitive with the Pd-catalyzed couplings. In the case of the *m*-dipropynyl compound and a dipropynylated terphenyl, **81b**, the recorded molecular weights are much lower, due to either formation of cycles or the insolubility of the formed all-unsaturated diphenyl-PPE **3b**.

While the Schrock catalyst $(t\text{BuO})_3\text{W}{\equiv}\text{C}$-$t$Bu is superbly active, it has to be synthesized, and it is very sensitive toward air and particularly water. As a consequence the preparation of PPEs utilizing Schrock carbynes is not particularly practical. On the other

hand, the Mortreux systems do work in non-dried, non-purified, off-the-shelf solvents and form from commercially available precursors in situ. However, the yield of the metathesis products is only moderate, making these catalysts unattractive for the formation of PPEs.[91] If the efficiency of alkyne metathesis with these instant catalysts could be improved, they should be superb candidates for the formation of high-molecular-weight PPEs. Alkyne metathesis then would suffer neither from the restrictions of the Pd-catalyzed reactions nor from the sensitivity of the commercially *un*available Schrock carbyne complexes.

Kloppenburg, Pschirer, and Bunz[41,94] optimized the reaction conditions of alkyne metathesis utilizing Mo-$(CO)_6$ and 4-chlorophenol by increasing the reaction temperature from 105 to 130−150 °C. This was coupled with a purge of nitrogen to remove the formed 2-butyne. Model studies showed that dimerization of propynylated benzenes and naphthalenes is facile under these optimized conditions. The dimers **83**, **85**, and **87** are obtained in yields above 90% after chromatography and crystallization (Scheme 18). The results suggested that alkyne metathesis with this "instant" catalyst system should be a powerful tool for the preparation of alkyl-substituted PPEs **3**.

Scheme 18
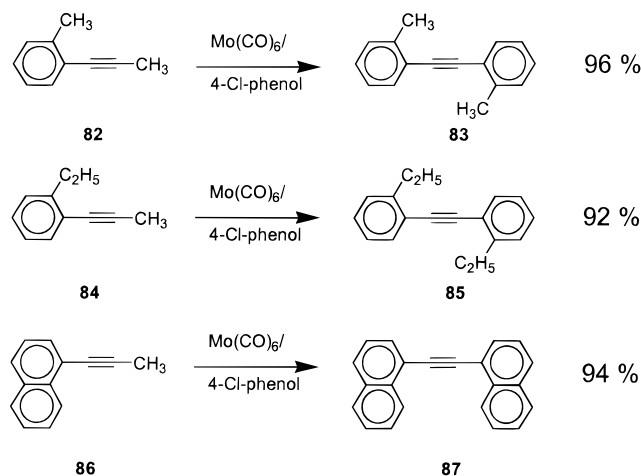
The Bunz group revealed that a series of differently substituted dipropynylated benzenes, **81a,c−g** furnished dialkyl-PPEs **3** of high and very high molecular weight upon metathesis with the instant catalysts[96] (Scheme 19). The experimental setup of this reaction is simple and involves the mixing of the monomer with 5−10 mol % $Mo(CO)_6$, and 4-chlorophenol in off-the-shelf 1,2-dichlorobenzene. The
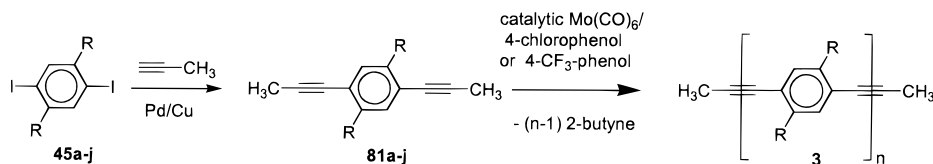
mixture is heated for 16−30 h to 130−150 °C under introduction of nitrogen. The successful formation of polymer is accompanied by a color change leading to a highly fluorescent purple-blue reaction mixture. Visible fluorescence is an excellent indicator for the formation of a conjugated polymer and usually starts after the reaction mixture is heated for 0.5−1 h. Dilution of the "polymerized" reaction mixture with chloroform and successive acid and base washes to remove catalyst residues is the preferred workup. This treatment is followed by multiple precipitations of **3** into methanol. The yields of PPEs made by alkyne metathesis are often quantitative, and the polymers are brilliantly yellow solids.[98]

In the case of dihexyl-PPE **3a** Bunz et al. obtained a polymer with a DP of 1.8×10^2 (GPC) which was not very soluble anymore.[96] Changing the side chains to the more solubilizing ethylhexyl, dodecyl, or dihydrocitronellyl (chiral) substituents furnished PPEs **3** with a DP of up to 1.2×10^3 (ethylhexyl), which is remarkable[96] and even surpasses the molecular weights of acceptor-substituted PPEs made by Swager.[33]

Alkyne metathesis is not limited to the preparation of dialkyl-substituted PPEs **3**. Dialkoxy-substituted PPEs **1** can likewise be obtained, but with a lower DP. To this end it is necessary to use 4-CF_3-phenol as cocatalyst, because 4-chlorophenol only leads to low-molecular-weight oligomers.

An important question is the dependence of the molecular weight and the polydispersity of the formed PPEs with respect to the reaction time.[97] In a time experiment, aliquots of the reaction mixture were removed after defined time intervals and examined. The molecular weight/time graph shows a roughly sigmoid shape. At the beginning the molecular weight increases slowly, followed by a region of fast increase. After approximately 30 h the molecular weight levels off. This behavior is in good agreement with a polycondensation mechanism for the formation of PPEs by alkyne metathesis. At the beginning a slow increase in DP occurs until almost all of the propyne groups of monomers **81** and dimers have been consumed. After that, every successful metathesis event will increase the molecular weight substantially. Later the concentration of the end groups is low, and catalyst decomposition may be prevalent.

A similar trend is observed for the polydispersities of the formed PPEs. At the beginning the polydispersity increases fast, to level off after about 24 h at a value of approximately 3−5. These values are higher than for a classic Flory−Schulz distribution,[97] but it may be an effect of increased reactivity of the larger oligomers toward further metathesis. How-

Scheme 19

Substituent Key **a** Hexyl; **b** nonyl; **c** dodecyl; **d** isopentyl; **e** ethylbutyl; **f** ethylhexyl; **g** 2,5,5-trimethylhexyl; **h** 3,7-dimethyloctyl; **i** isopentyloxy; **j** cyclohexyl

ever, the molecular weight distribution is monomodal. The PPEs were examined by ^{1}H NMR and ^{13}C NMR spectroscopy. End groups could not be detected anymore. ^{13}C NMR spectroscopy indicates the presence of only one alkyne signal at approximately 83 ppm and three resonances for the aromatic carbons in the range of 110−140 ppm. No additional bands indicating cross-linking or other structural defects were observed. The end groups of metathesis PPEs **3** are probably propyne groups, but the very high molecular weights make it difficult to ascertain their nature.

2. Comparison of the Schrock versus the Mortreux–Bunz Alkyne Metathesis Systems

Schrock's (tBuO)$_3$W≡C−tBu. This very active catalyst is able to perform productive alkyne metathesis already at 80 °C.[90,92,93] In addition it shows good heteroatom tolerance. A significant disadvantage is the multistep preparation requiring careful exclusion of air and water during the synthesis. The sensitivity of the catalyst to air and water greatly hampers its handling after it has been made. In addition, monomers and solvents have to be rigorously dried and purified to do successful metathesis, and the metathesis itself has to be carried out under carefully controlled, anhydrous conditions. These difficulties together place the Schrock catalyst at a disadvantage for an organic or polymer chemist who wants to explore alkyne metathesis.

Mortreux−Bunz Catalyst System (Mo(CO)$_6$/4-Chlorophenol in 1,2-Dichlorobenzene). This catalyst system forms in situ from its constituents at temperatures ranging from 130 to 150 °C in the presence of the monomer **81** *in nondried, off-the-shelf solvents from commercially available and inexpensive precursors.*[94−96,98] While this catalyst is not particularly tolerant of heteroatoms with exception of oxygen functionalities, it metathesizes aromatic hydrocarbons in high yield and with unsurpassed ease. Untrained undergraduate students and high school research participants have used it in the Bunz group with great success.[98] It seems to be an ideal system to make every conceivable hydrocarbon topology. The work done in South Carolina has just opened the door, and the Mortreux−Bunz systems will evolve into massive competition for the Pd-catalyzed couplings of the Heck−Cassar−Sonogashira−Hagihara type. Simplicity of preparation and robustness give these catalyst systems a superior appeal.

III. Properties and Structures of PAEs

A. Molecular Weights of PAEs: Tricks and Traps

1. PPEs

PPEs are rigid rods. As such they are highly anisotropic. Molecular weight determination of rigid rods is not trivial. GPC uses polystyrene, a flexible coiled polymer as standard, overestimating molecular weights. GPC vs polystyrene however is by far the most commonly used method for both the determination of molecular weight and molecular weight distribution. It would be highly desirable to have a scaling factor or an equation which would convert GPC vs polystyrene values into "real" molecular weights.[97] The groups of Tour and of Müllen have investigated this point. Tour prepared a series of defined oligomers and compared their real molecular weight with the molecular weights obtained by GPC.[22] He found out that the molecular weights are overestimated by GPC by a factor of 2−3. Müllen investigated some polymeric PEs and performed end group analysis by ^{1}H NMR spectroscopy, which gives DPs based on M_n. Comparison to GPC shows that up to a DP of ∼50 (determined by ^{1}H NMR) GPC with polystyrene standards overestimates molecular weights by a factor of 2.[58] The Bunz group has made similar observations with respect to **3** and found that molecular weights determined by end group analysis (^{1}H NMR, where possible) vs GPC differ by a factor of approximately 1.5−2.[95,96]

While low-molecular-weight PPEs are certainly rigid rods, the question arises where this picture breaks down, i.e., above which DP PPEs would have to be considered to be flexible. Above this threshold PPEs could then either be true coils, or, more likely, fit the Kratky−Porod model of wormlike chains.[99] Cotts and Swager[50] investigated the equilibrium flexibility of PPEs by light scattering and found that the persistence length of PPEs was approximately 15 nm, which equals 20 PE repeating units. Above that value PPEs behave as wormlike chains and should not be considered as rigid rods anymore. This is in good agreement with calculated results obtained for PPPs.[100] In another study[42] the exponent α of the Mark−Houwink equation was determined for an alkoxy-substituted PPE. The authors claimed that α reached a value of 1.92, close to the theoretical maximum of α = 2, which would indicate a rigid, straight rod. The molecular weight determination of this PPE however was incorrect, and the measured coefficient is probably an artifact.

Despite the work already published, it would be attractive to prepare a large oligo-PE macromonomer, make PPEs, and perform GPC with the option to observe well-resolved signals. These could be used for calibration and absolute molecular weight determination of PPEs.

2. Other PAEs

In most cases PAEs have been characterized by either light scattering or GPC with polystyrene as standard. The values obtained by GPC experience the same systematic error, i.e., overestimation of the molecular weight as discussed for the PPEs. However, PAEs, which deviate from linearity, display a more coiled conformation in solution, and a better match of the real molecular weights with the ones obtained by GPC is expected.

Pang has performed a quite rigorous examination of differently substituted PAEs containing thienylene and/or *m*-phenylene units by light scattering and viscosimetry.[66,101,105] He obtained Mark−Houwink coefficients α ranging from 0.68 to 1.06 for his polymers, suggesting (Chart 3) that the PAEs are semiflexible and not rigid rods. This supports Cott's

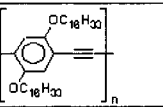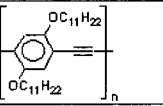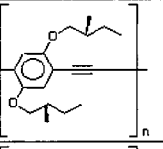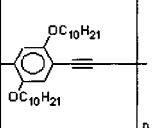## Table 10. Spectroscopic Properties of Dialkoxy-PPEs 1
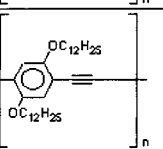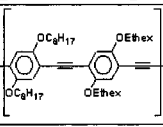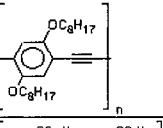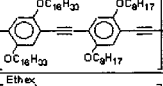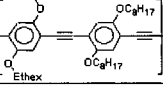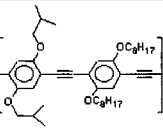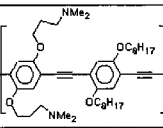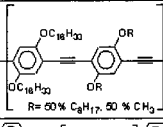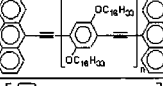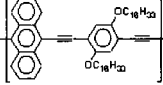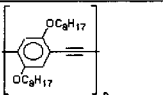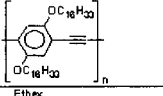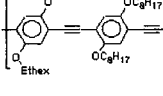
Entry Cpd	Polymer	Absorption [nm]		Emission [nm]		Comment
		Solution	Film	Solution	Film	
1[a] 1e	$OC_{18}H_{38}$ / $OC_{18}H_{38}$	410	Not determined	Not determined	Not determined	
2[a] 1n	$OC_{11}H_{22}$ / $OC_{11}H_{22}$	425	Not determined	Not determined	Not determined	
3[b] 1m		CHCl₃ 420 Dodecanol 430	424 nm	501,477	529,499	
4[c] 1b	$OC_{10}H_{21}$ / $OC_{10}H_{21}$	THF 429	455	Not determined	Not determined	
5[c] 1c	$OC_{12}H_{25}$ / $OC_{12}H_{25}$	THF 425	453	473	558	
6[d] 1l	OC_8H_{17} OEthex / OC_8H_{17} OEthex	CHCl₃ 453	Not determined	508, 478	Not determined	
7[e] 1o	OC_8H_{17} / OC_8H_{17}	449	475 (483 annealed)	474, 505 [0.83]	503 (535a) [0.36]	In solid-state fluorescence the transitions sharpen up after annealing, so that in some cases the lowest wavelength transition is the peak of maximum intensity. In other cases this transition is only a shoulder. Only the shortest wavelength contribution is given. For more detail see original paper. Values for annealed films in parentheses. Fluorescence quantum yield in [] parenthesis
8[e] 1g	$OC_{18}H_{38}$ OC_8H_{17} / $OC_{18}H_{38}$ OC_8H_{17}	448	482 (498 a)	473, 506 [0.86]	534 (526a) [0.33]	
9[e] 1l	Ethex / OC_8H_{17} / Ethex	449	473 (484a)	474, 506 [0.86]	491 (496a) [0.31]	
10[e] 1h	OC_8H_{17} / OC_8H_{17}	449	470 (479a)	473, 505 [0.82]	491 (503a) [0.28]	
11[e] 1i	NMe₂ / OC_8H_{17} / OC_8H_{17} / NMe₂	442	476 (485a)	472,505 [0.62]	500 (535a) [0.07]	
12[f] 1d	$OC_{18}H_{38}$ OR / $OC_{18}H_{38}$ OR R= 60% C₈H₁₇, 50 % CH₃	452	Not determined	482 [0.40]	Not determined	
13[f] 1e	$OC_{18}H_{38}$ / $OC_{18}H_{38}$	500 sh	Not determined	524	Not determined	
14[f] 4a	$OC_{18}H_{38}$ / $OC_{18}H_{38}$	543	Not determined	590 [0.05]	Not determined	

Table 10 (Continued)

Entry Cpd	Polymer	Absorption [nm]		Emission [nm]		Comment
		Solution	Film	Solution	Film	
15[g] 1o		415	Not determined	[0.50]	Not determined	Sparse data. No emission peaks given. λ_{max} of 415 nm suggests very short oligomers
16[g] 1e		425	Not determined	Not determined	Not determined	
17[h] 1l		Not determined	Film, PPE in polyethylene dispersed Not determined	Not determined	Film, PPE in polyethylene dispersed 490 nm, drawn film 540 pristine in pe	

[a] Giesa, R.; Schulz, R. C. *Macromol. Chem.* **1990**, *191*, 857. [b] Fiesel, R.; Scherf, U. *Macromol. Rapid Commun.* **1998**, *19*, 427. [c] Moroni, M.; LeMoigne, J.; Luzzati, S. *Macromolecules* **1994**, *27*, 562. [d] Steiger, D.; Smith, P.; Weder, C. *Macromol. Rapid Commun.* **1997**, *18*, 643. [e] Weder, C.; Wrighton, M. S.; Spreiter, R.; Bosshard, C.; Günter, P. *J. Phys. Chem.* **1996**, *100*, 18931. [f] Swager, T. M.; Gil, C. J.; Wrighton, M. S. *J. Phys. Chem.* **1995**, *99*, 4886. [g] Davey, A. P.; Elliott, S.; O'Connor, O.; Blau, W. *J. Chem. Soc., Chem. Commun.* **1995**, 1433. [h] Weder, C.; Sarwa, C.; Bastiaansen, C.; Smith, P. *Adv. Mater.* **1997**, *9*, 1035.

analysis of equilibrium flexibilities in PPEs.[50] An interesting observation is that Pang's values for α are not only dependent upon the backbone structure (the less straight the backbone structure, the smaller is α), but also dependent upon the substituent pattern. The most rigid polymer, i.e., the one with the highest α value, is the regioregular version of **6a**, suggesting that the conformation of these kinked rods is substantially influenced by their substituents!

Chart 3
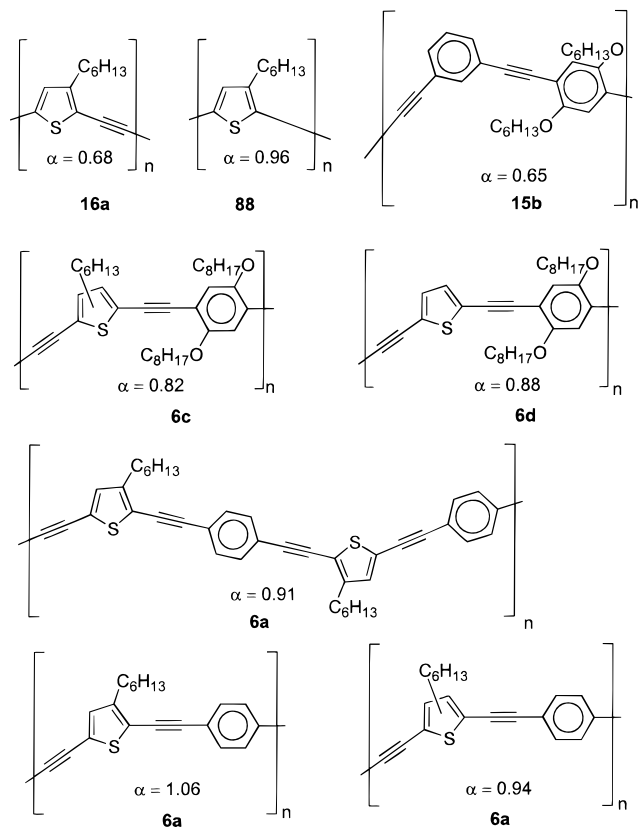
B. Optical Spectroscopy, Fluorescence, and Evidence of Aggregate Formation by UV/Vis Spectroscopy

1. UV/Vis Spectroscopy

The main interest in PPEs and PAEs has historically been their electronic properties as conjugated polymers. Their optical properties (including references) are listed in Tables 10–14. As a general rule for PAE UV/vis spectra in solution, dialkyl-substituted *p*-PPEs **3** (Table 12) show a prominent absorption at 384–388 nm. If every second benzene ring is substituted by alkoxy groups (**2**, Table 11), this absorption shifts to 410–414 nm, while the fully alkoxy-substituted PPEs **1** (two alkoxy groups per benzene ring) display their main transition at 442–452 nm (Table 10). Lower values suggest very short polymers, in which the convergence length is not yet reached. Generally, donor substituents lead to considerable bathochromic shifts, while acceptor substitution does not seem to change the electronic situation of PPEs dramatically, with ester-substituted representatives displaying a λ_{max} of 383–404 nm. Introduction of a 2,5-thiophene unit into the chain of a PPE has an effect similar to that of the introduction of two alkoxy groups, so poly(2,5-thienylene-ethynylene)s **16** show absorptions in the range of 437–441 nm (Table 13, entries 8 and 17–19) (up to 460 nm for **16b**; Table 13, entry 5) in solution.

Introduction of *meta* substituents breaks conjugation efficiently, so that *meta* PPEs can appear colorless with λ_{max} of 288–388 nm (Table 12, entries 2–4; Table 11, entries 14, 16, 26, and 28), depending strongly upon the nature of their substituent. An alternating polymer with *para*-linked 2,5-dialkoxy-benzene and *m*-phenylene units shows a λ_{max} of 375 nm in solution (Table 11, entry 13). Most of the absorption data obtained for PAEs in dilute solution can be extrapolated from the knowledge of the electronic properties of its constituents. Until now no

Table 11. Spectroscopic Properties of Partially Dialkoxy-Substituted PPEs
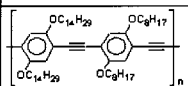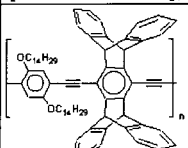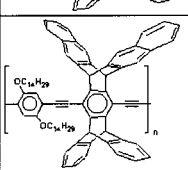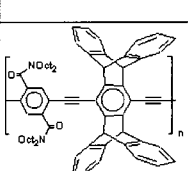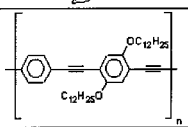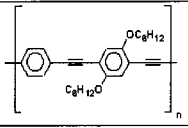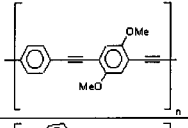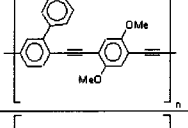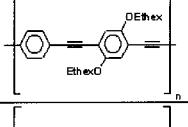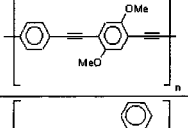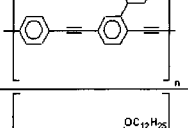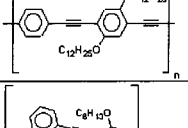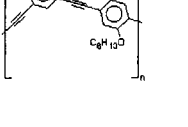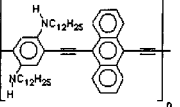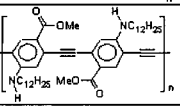
Entry	Polymer	Absorption [nm]		Emission [nm]		Comment
Cpd		Solution	Film	Solution	Film	
				[] quantum yield fluorescence		
1[a] 1p		453	483	478 [0.27]	496 [0.09]	
2[a] 30a		441	448	457 [0.50]	460 [0.33]	
3[a] 30b		441	431	459 [0.33]	463,497 [0.76]	
4[a] 29		372	370	421 [0.61]	423 [0.42]	
5[b] 2d		332, 414	452	449, 474 [1.00]	478, 511	
6[b] 2m		332, 410	454	448, 474 [1.00]	507	
7[c] 2b		396		440		Short oligomers
8[c] 2n		411	Nd	Nd	Nd	
9[d] 2a		404	Nd	446	Nd	
10[d] 2b		392	Nd	438	Nd	
11[d] 2c		376	Not determined	411	Not determined	
12[e] 2d		411	428	452 [0.45]	Not determined	
13[e] 15b		375	387	413 [0.44]	518 PL 525 EL bright fluorescence	

Table 11 (Continued)

Entry Cpd	Polymer	Absorption [nm]		Emission [nm]		Comment
		Solution	Film	Solution	Film	
14^f 13		337	Not determined	378 [0.28]	Not determined	
15^g 15a		Not determined	335	Not determined	Not determined	
16^h 12a		288	Not determined	Not determined	Not determined	
17^i 2h		404	376	426, 468	516 PL 557 EL	
18^j -		THF 425	469	Not determined	Not determined	
19^j 4		THF 508	521	Not determined	Not determined	
20^j -		THF 404	412	Not determined	Not determined	
21^j 2o		THF 383	405	Not determined	Not determined	
22^j 2p		THF 408	412	Not determined	Not determined	
23^k -		378	Not determined	424 [> 80%]	Not determined	
24^l -		410	Not determined	433 [0.60]		
25^m 2f		427	Not determined	459 [0.70]	Not determined	
26^m 15c		388	Not determined	418 [0.33]	Not determined	
27^m -		428	Not determined	459 [066]	Not determined	
28^m 15d		388	Not determined	418 [0.50]	Not determined	
29^n -		432	450	Not determined	Not determined	

Table 11 (Continued)

Entry	Polymer	Absorption [nm]		Emission [nm]		Comment
Cpd		Solution	Film	Solution	Film	
30[n] -		485	491	Not determined	Not determined	
31[n] -		469 THF 446 DMF	470	Not determined	Not determined	

[a] Yang, J. S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 5321, 11864. [b] Li, H.; Powell, D. R.; Hayashi, R. K.; West, R. *Macromolecules* **1998**, *31*, 52. [c] Solomin, V. A.; Heitz, W. *Macromol. Chem. Phys.* **1994**, *195*, 303. [d] Koch, F.; Heitz, W. *Macromol. Chem. Phys.* **1997**, *198*, 1531. [e] Pang, Y.; Li, J. *Macromolecules* **1998**, *31*, 6730. [f] Kang, B. S.; Kim, D. H.; Lim, S. M.; Kim, J.; Seo, M. L.; Bark, K. M.; Shin, S. C.; Nahm, K. *Macromolecules* **1997**, *30*, 7196. [g] Kondo, K.; Okuda, M.; Fujitani, T. *Macromolecules* **1993**, *26*, 7382. [h] Li, C. J.; Slaven, W. T.; Chen, Y. P. John, V. T.; Rachakonda, S. H. *J. Chem. Soc., Chem. Commun.* **1998**, 1351. [i] Häger, H.; Heitz, W. *Macromol. Chem. Phys.* **1998**, *199*,1821. [j] Moroni, M.; LeMoigne, J.; Luzzati, S. *Macromolecules* **1994**, *27*, 562. [k] Remmers, M.; Schulze, M.; Wegner, G. *Macromol. Rapid Commun.* **1996**, *17*, 239. [l] Walters, K. A.; Ley, K. D.; Schanze, K. S. *J. Chem. Soc., Chem. Commun.* **1998**, 1115. [m] Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12593. [n] Moroni, M.; Le Moigne, J.; Pham, T. A.; Bigot J. Y. *Macromolecules* **1997**, *30*, 1964.

examples are known in which the sum of the optical properties of the monomeric constituents would defy the correct estimation of the absorptive properties of the resulting PAE polymer. In the following sections the optical spectra of some classes of PAEs are discussed in more detail.

Dialkoxy-PPEs (Table 10). Values for λ_{max} of dialkoxy-substituted PPEs in solution are reported to range from 410,[40] 420,[43] and 429,[42] to 448−453 nm.[34] Preferred solvents are THF or chloroform. The observed *range* in λ_{max} is somewhat unexpected. Generally the polymers showing an absorption of <440 nm have been made by the coupling of dibromodialkoxy-substituted benzenes **19** to the corresponding diethynylarenes **20**. It is known (vide supra) that bromides are much less efficient in these couplings than the corresponding iodides, suggesting that the formed polymer chains are considerably shorter. Alternatively it could be possible that the iodo substituents at the end of the chains exert a substantial bathochromic shift on the optical behavior of even long dialkoxy-PPEs. However, Wrighton et al.[44] have prepared a dialkoxy-PPE, **1**, with a DP of 22, endcapped by a 4-alkyl-substituted benzene ring. This polymer shows a λ_{max} of 446 nm. Unfortunately, and contrary to the case of the dialkyl-[25,58] or monoalkyl-substituted PPEs,[22] where extensive studies on the synthesis of monodisperse, defined oligomers has been performed, no information is available for dialkoxy-substituted PPEs. The optical data suggest that in the case of the dialkoxy-PPEs **1** the convergence length is not reached if bromine-substituted monomers are used. The molecular weights seem to be too low. This is in marked contrast to a claim[42] that PPEs of high molecular weights can result when dibromides are used as coupling partners. From the absorption data the DP must be low. A similar conclusion holds from Davey's[106] work, who claims to have DPs of "tens to hundreds". A λ_{max} of 415 nm however suggests that only short oligomers have formed in the course of that reaction.

Aggregation and solid-state behavior are fascinating topics in the science of conjugated polymers,[107] in which morphology and supramolecular ordering

have an immediate effect on optical properties. It is insofar important that the absorption spectra of many dialkoxy-substituted PPEs have been investigated in thin films. While Scherf's[43] chiral dialkoxy PPE does not show any bathochromic shift when the solution spectra are compared to the solid-state spectra, Le Moigne's dialkoxy-PPEs show a bathochromic shift of 25−28 nm when measured in the solid state.[42] Wrighton[44−46] carefully examined PPE films and found in annealed films (thermal treatment) bathochromic shifts ranging from 35 to 50 nm. In addition to the bathochromic shift, the corresponding absorption bands tend to get much sharper in the solid state after annealing, suggesting a higher order in these films (for details see Table 10).

Alkoxy/Alkyl-, Alkoxy/H-, or Acceptor-Substituted PPEs (Table 11). If every second of the benzene rings is unsubstituted or substituted by alkyl groups, λ_{max} is blue-shifted. Several groups have made alternating copolymeric PPEs of this type. Swager's[15,44] pentypticene copolymers (**29**, **30**) are different and will be discussed separately at the end of this subsection. Depending upon the substitution pattern and the therefrom resulting molecular weights, λ_{max} in solution varies in these materials **2** from 392 to 411 nm (Table 11, entries 5−10). The polymers with the shortest wavelength absorption carry methoxy substituents, i.e., are very short and not well-soluble, while the polymers showing a λ_{max} of 411 nm are substituted by long or branched alkoxy chains and have a substantial molecular weight. West (Table 11, entries 5 and 6) finds a bathochromic shift of 38−44 nm in thin films of **2d**, while Pang (Table 11, entry 12) observed for the same polymer a bathochromic shift of only 17 nm when going from solution into the solid state. The difference may originate from the sample history. Spin-cast films can be made very fast and may be highly disordered, while solution-cast films form slowly and a highly ordered morphology might arise, which normally shows a more bathochromically shifted absorption.

Swager's polymers (**29**, **30**; Table 11, entries 2−4)[15,49] are unusual, because one benzene ring is embedded into a pentypticene framework, while the other part

of the PPE polymer is a dialkoxy-substituted benzene. This arrangement leads to the formation of a porous polymer morphology in which the polymer chains do not interact efficiently. Absorption is observed at 441 nm in solution, which changes to 448 nm when the sample is examined in the solid state. Interestingly, 448 nm is close to the solid-state absorption of West's polymer (**2d**; Table 11, entries 5 and 6), which is, from its electronic situation, very similar. A possible explanation for this behavior may be that the peculiar substitution pattern in Swager's porous polymer forces the polymer chains into coplanarity (discussion of this effect vide infra) and thus leads to a bathochromic shift of λ_{max} already in solution. In West's polymers **2d** and **2m**, according to this picture, *the phenyl rings would assume coplanarity and maximization of conjugation with concomitant bathochromic shift only upon transition into the solid state*. This explanation is tentative.

Dialkyl-PPEs **3** have been examined by the Bunz group.[108,109] Their optical properties in solution and in the solid state are well-understood (Table 12, entry 6−9). While in solution only a broad band centered at 385 nm is observed, thin films of these materials are distinctly yellow with a sharp absorption at λ_{max} of 435 nm. The absorption behavior is mostly independent of the alkyl substituent. To understand the nature of the transition from solution to the solid state, the solvatochromic behavior of PPEs was examined. Solvatochromic behavior in conjugated polymers has long been known and has been documented by Rughooputh and Wudl[110] for polythiophenes. In the case of the dialkyl-PPEs **3** addition of a nonsolvent (methanol) to a chloroform solution of **3** leads to the development of a new and very sharp band centered at 435 nm, which corresponds to the absorption observed in the solid state. In addition, the transition observed in chloroform at 385 nm is shifted to 400 nm and vibronic structure develops.

To obtain more information about this interesting behavior, Bunz and Scherf[109] examined a chirally substituted dialkyl-PPE, **3i** (Scheme 19), by CD spectroscopy. Upon addition of a nonsolvent a strong bisignate Cotton effect evolved, which was most developed at 437 nm. The *g* value of 0.008 is considerably stronger than that for a similar alkoxy-substituted PPE, **1m**, investigated earlier by Scherf.[43] It approaches the values observed for polythiophenes[111] or PPVs.[112] At 437 nm the aggregate-induced band is at a maximum, which suggests that side-chain ordering must influence the electronic properties of the main chain substantially.[109] In the dialkyl-PPEs, however, not only do we observe solvatochromic behavior but thermochromicity is displayed in thin solid films. At temperatures above 190 °C, the film spectra of a copolydidodecyl/dihexyl-PPE, **3e**, resemble the ones taken in chloroform at ambient temperature and the feature at 435 nm has completely disappeared.[120]

The optical behavior (i.e., thermochromicity and solvatochromicity) of the PPEs can have two causes. It could be that aggregates consisting of many PPE chains form in the solid state, and the electronic communication of the π-systems via tight packing

and a $\pi-\pi$-stacking effect leads to the observed bathochromic shift.[107] Alternatively, the occurrence of the red-shifted feature is a single molecule effect, similarly to that observed by Roughopoot et al.[110] for polythiophenes, in which planarization of the π-system is induced by aggregation. The forced planarization then leads to increased conjugation and thus to a lower band gap. The rotation around the triple bond of an alkyne in solution is relatively facile and has a barrier of less than 1 kcal/mol.[113] Intuitively, the rotationally invariant triple bond should allow the communication of two conjugated moieties attached to it at every 90°. As a consequence, if that picture is right, the HOMO−LUMO gap should likewise be rotationally independent. However, calculations showed[120] that the band gap in a large oligomer is substantially dependent upon the dihedral angle the participating benzene rings assume with respect to each other. In the planarized form the band gap reaches a global minimum. From these calculations and independent structural information (vide infra) Bunz et al.[120] concluded that aggregate-induced planarization is the reason for the occurrence of the bathochromically shifted feature in dialkyl-PPEs. Support for this proposal comes from another direction. Scherf[121] prepared and investigated a series of ladder polymers which contained the PPP backbone. In solution and in the solid state the phenyl rings of regular dialkyl-substituted PPPs are considerably twisted with respect to each other to escape the *van der Waals* repulsion. In the ladder polymer, not solid-state packing but chemical tethering leads to forced planarization of the PPP backbone. And here likewise a dramatic red shift and a considerable sharpening of the absorption bands (in comparison to the PPPs) is observed as a consequence of planarization, both in solution and in the solid state.

It will be interesting to note whether similar optical behavior, i.e., the occurrence of an aggregate-induced band, can be detected in differently substituted PPEs and PAEs. The future will tell whether the bathochromic shift observed for dialkoxy-PPEs is likewise due to planarization or has a different origin, but a paper by Scherf[43] shows that dialkoxy-PPEs **1m** display a moderate Cotton effect in poor solvents with a distinct negative maximum at 475 nm ($g = 0.001$). The similarity of dialkyl- and dialkoxy-substituted PPEs with respect to their CD spectra suggests, but does not prove, that a related mechanism of aggregate formation may be at work.

2. Fluorescence Spectroscopy (Tables 10–14)

Light-emitting polymers are an important class of materials due to the promise which is brought by the aspects of applications (see references in Table 1). Early on, the marked fluorescence of PPEs in dilute solution was noted. Later on, it was shown that the fluorescence quantum yield of PPEs and PAEs in solutions can reach unity; i.e., every absorbed photon is re-emitted (Table 12, entries 6−9). The rigid character of the PPEs seems to make intramolecular dissipation difficult, and insofar fluorescence is efficient. The attractive fluorescence behavior suggested that PAEs may find use in optoelectronic devices (vide infra).

**Table 12. Spectroscopic Properties of Alkyl-Substituted and *meta*-PPEs**

Entry Cpd	Polymer	Absorption [nm] Solution	Absorption [nm] Film	Emission [nm] Solution	Emission [nm] Film	Comment
1[a] 3a	(structure, C_8H_{13} substituted dialkyl-PPE)	388	Not determined	428	Not determined	
2[a] 12g	(structure, C_8H_{13} meta-PPE)	307	Not determined	Not determined	Not determined	
3[a] 12f	(structure, tert-butyl meta-PPE)	307	Not determined	Not determined	Not determined	
4[a] 14a	(structure, OC_8H_{13} meta-PPE)	327	Not determined	Not determined	Not determined	
5[b] 52	O_2N—⟨⟩—≡—⟨C_8H_{13}⟩—≡—⟨⟩—NMe_2 (structure)	n = 0, 415 nm; n = 1, 345 nm; n = 4, 385 nm; n = 6, 387 nm solution-data	Not determined	Not determined	Not determined	
6[c] 3a	H_3C—≡—⟨C_8H_{13}⟩—≡—CH_3 (structure)	384	435	425, 450sh [1.00]	520	Aggregation behavior of PPEs is studied in detail.
7[c] 3c	H_3C—≡—⟨$C_{12}H_{25}$⟩—≡—CH_3 (structure)	384	435	425, 450sh [1.00]	520	
8[c] 3f	H_3C—≡—⟨Ethex⟩—≡—CH_3 (structure)	384	435	425, 440sh [1.00]	480	
9[c] 3h	H_3C—≡—⟨⟩—≡—CH_3 (structure, branched alkyl)	384	435	425, 450sh [1.00]	480	
10[d] 12d	(structure, ammonium-oxide meta-PPE)	370, 585, 622	Not determined	Not determined	Not determined	
11[e] 12c	(structure, C_8H_{13} meta-PPE with N–O group)	371, 620	Not determined	Not determined	Not determined	
12[f] 12e	(structure, meta-PPE with N–O group)	302, 500	Not determined	Not determined	Not determined	

[a] Mangel, T.; Eberhardt, A.; Scherf, U.; Bunz, U. H. F.; Müllen, K. *Macromol. Rapid Commun.* **1995**, *16*, 571. [b] Francke, V.; Mangel, T.; Müllen, K. *Macromolecules* **1998**, *31*, 2447. [c] Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Bunz, U. H. F. *Macromolecules* **1998**, *31*, 8655. [d] Miura, Y.; Issiki, T.; Ushitani, Y.; Teki, Y.; Itoh, K. *J. Mater. Chem.* **1996**, *6*, 1745. [e] Miura, Y.; Ushitani, Y.; Inui, K.; Teki, Y.; Takui, T.; Itoh, K. *Macromolecules* **1993**, *26*, 3698. [f] Miura, Y.; Ushitani, Y. *Macromolecules* **1993**, *26*, 7079.

Alkoxy-PPEs. In solution all dialkoxy-PPEs **1** show a strong emission at 472–482 nm (depending on the substituent) irrespective of their molecular weight (Table 10). A second, weaker shoulder is observed at 500–506 nm. The quantum efficiencies for dialkoxy-PPEs range from 0.27 to 0.86, depending upon the

Chart 4
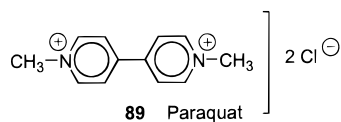
substituent pattern and research group. Dioctyloxy-PPE **1o** shows a quantum yield of 0.86 (Table 10, entry 7) according to Wrighton, while Davey et al. reported a value of 0.50 for a polymer of the same constitution, but made by a different route (Table 10, entry 15). To explain this variance, it must be assumed that the emission efficiency is influenced by small amounts of impurities, which quench the fluorescence of **1o**, suggesting the presence of defect structures. That assumption is not unreasonable, and it has been demonstrated by Swager[50] that the addition of a fluorescence-quenching paraquat derivative (Chart 4) can shut down the emission of certain PPEs completely (vide infra).

Efficient solid-state photoluminescence is one of the necessary but not sufficient preconditions for the successful application of a conjugated polymer in solid-state optoelectronic devices. Several groups independently examined the solid-state fluorescence of PPEs. Depending upon the sample history, morphology, and research group, the emission maximum in **1** can range from 490 to 558 nm. Generally, annealed samples show a more distinct bathochromic shift, for the emission in thin films, while DP does not seem to influence the position of the maximum at all. Introduction of anthracene groups either into the backbone or at the end of the PPE leads to a behavior in which light is emitted mainly by the anthracene chromophores under a decrease in fluorescence yield.

Wrighton (Table 10, entries 7−11) and Swager (Table 11, entry 1) determined the fluorescence quantum yields of some representatives of **1** in the solid state. Their quantum yields fall in a range between 0.09 and 0.33. Due to the problems in obtaining quantum yields in the solid state, it is difficult to assess the validity of these numbers. In addition, sample history and morphology certainly influence the quantum yields, and a direct comparison of these values may not have much meaning.

Mixed Alkoxy/Alkyl-PPEs. West (Table 11, entries 5 and 6) reported fluorescence of polymers **2d,m** to occur at 449 and 448 nm in solution. Heitz (Table 11, entries 7−10) earlier reported emissions for similar polymers ranging from 438 to 446 nm, carrying methoxy or ethylhexyloxy side chains. These values are in good accord with West's results, while Pang observed for **2b** a slightly bathochromically shifted emission at 452 nm with a quantum yield of 0.45 (Table 11, entry 12).

In the solid state a bathochromic shift of the emission to 478 nm in **2a** and to 507 in **2b** occurs. The dramatic difference in luminescence must result from small changes in morphology, which enables the emission from excimers or other aggregates. Swager's pentypticene-containing PPEs (**29**, **30a**) show almost invariant emission in solution and in the solid state (Table 11, entries 2−4). In **29** the emission (solution, 457 nm) is red-shifted by only 3 nm when fluores-

cence is compared in solution vs the solid state. Additionally the quantum yields of the emission of **29** and **30** in the solid state is very high (0.42 and 0.33). The fluorescence of thin films of **30b** depends on film thickness, and in thick films the main emission is shifted from 463 to 497 nm. The reason for this behavior is exciplex formation of naphthalene units in neighboring PPE chains.

Dialkyl-PPEs (Table 12). Fluorescence of dialkyl-substituted PPEs **3** has been examined by Bunz and Studer-Martinez (Table 12, entries 6−9). In dilute chloroform solution these materials display a purple-blue fluorescence at 428−435 nm with a shoulder which can range from 440 to 450 nm. The quantum yields of the fluorescence in solution was determined to unity, suggesting that no competing pathways for dissipation exist for these rigid molecules. Again in the solid state the fluorescence is strongly red-shifted. A shoulder at 480 nm is accompanied by a broad, featureless transition centered at 500 nm. The occurrence of this broad feature suggests that the emission comes from excimer-type arrangements in the solid state.

m-PPEs (Table 11, Entries 13−16, 26, and 28; Table 12, Entries 2−4 and 10−12). Several examples of *meta*-linked PPEs have been reported. They are better soluble and processable than their *para*-connected counterparts, and their fluorescence is blue-shifted due to the break of conjugation. Quantum yields have been determined in dilute solution and range from 0.33 to 0.44. Pang has reported that a *m−p*-PPE (Table 11, entry 13) shows bright fluorescence in the solid state centered at 525 nm. Substantial bathochromic shifts (105 nm) occur upon examination of the polymers in thin films when compared to solution.
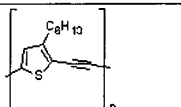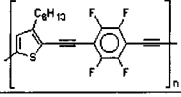
Thiophene-Containing PAEs (Table 13). Independently the groups of Yamamoto and Pang have prepared and examined a series of thiophene-containing PAEs. The most interesting ones with respect to their optical properties are copolymers [−thiophene−≡−benzene−≡]$_n$− (TEPE **6**) and the poly(thienyleneethynylene)s **16**. If one alkyl group is present on the thiophene ring, different tacticities for the polymer under consideration are possible. In Table 13, entries 6, 10, 11, 15, and 16, three tacticities of TEPE **6a** have been realized. One in which the thiophene alkyl groups are randomly oriented, one in which only HT dyads occur, and one in which HH and TT alternate (Chart 2). In solution these polymers **6** show quantum efficiencies of ∼0.50 regardless of their tacticity. In the solid state emission is observed between 525 nm (only HT) and 534 nm (only HHTT), and the tacticity has only a small influence on the emission wavelength. However, when the relative quantum yields of the materials are compared in the solid state, the HHTT material **6a** displayed an emission 6 times as strong as the regiorandom representative. It must be a consequence of solid-state order in **6a**.

A similar effect has been observed in the solid-state fluorescence of the poly(3-hexylthienyleneethynylene)s **16a**. In this case the regioregular HT polymer is qualitatively the strongest emitter in the solid state.

Table 13. Spectroscopic Properties of Thiophene-Containing PPEs

Entry Cpd	Structure	Absorption λ$_{max[nm]}$		Emission [nm]		Comment
		solution	Film	Solution	Film	
				[] quantum yield of fluorescence		
1[a] 15f		365	Not determined	410 [0.18]	Not determined	
2[a] 15g		388	Not determined	451 [0.09]	Not determined	
3[a] 15h		407	Not determined	485 [0.02]	Not determined	
4[b] 6d			Not determined	Not determined	505 PL 520 EL	
5[c] 16b		460	Not determined	535	Not determined	Oxidation to radical reported, but no spectral data recorded. Oxidized polymer is "red"
6[d] 6a		403	410	455,485	582	
7[d] -		426	432	465, 495	592	
8[d] 16a		438	446	510, 538	529, 558	
9[d] -		360	350	430	Not observable	
10[e] 6a		Run1 411 Run2 418 Run3 409 Run4 409	Not determined	459, 488 459, 485 458, 484 454,485 [0.26-0.35]	Not determined	
11[f] 6a		413	421 (MM **1998** *31*, 5740	455, 480 [0.47]	530 rel quatum efficiecy 1	
12[f] 6c		457	Not determined	492, 524 [0.47]	Not determined	
13[f] 6d		444	Not determined	485, 518 [0.37]	Not determined	
15[g] 6a		415	431	453, 478 [0.53]	534 rel quatum efficiecy 6	
16[g] 6a		414	408	453,479 [0.53]	525 rel. quatum efficiecy 2.4	
17[h] 16a		441	486	506,536 [0.20]	575 strong fluorescence	
18[h] 16a		437	488	505,535 [0.18]	575	

Table 13 (Continued)

Entry	Structure	Absorption $\lambda_{max\,[nm]}$		Emission [nm]		Comment
Cpd		solution	Film	Solution	Film	
19[h] **16a**		437	487	505,535	Not determined	
20[i] –		370	Not determined	Not determined	Not determined	

[a] Kang, B. S.; Kim, D. H.; Lim, S. M.; Kim, J.; Seo, M. L.; Bark, K. M.; Shin, S. C.; Nahm, K. *Macromolecules* **1997**, *30*, 7196. [b] See Table 12, entry 2. [c] Hayashi, H.; Yamamoto, T. *Macromolecules* **1997**, *30*, 330. [d] Yamamoto, T.; Takagi, M.; Kizu, K.; Maruyama, T.; Kubota, K.; Kanbara, H.; Kurihara, T.; Kaino, T. *J. Chem. Soc., Chem. Commun.* **1993**, 797. [e] Yamamoto, T.; Honda. K.; Ooba, N.; Tomaru, S. *Macromolecules* **1998**, *31*, 7. [f] Pang, Y.; Li, J.; Barton, T. B. *J. Mater. Chem.* **1998**, *8*, 1687. [g] Li, J.; Pang, Y. *Macromolecules* **1998**, *31*, 5740. [h] Li, J.; Pang, Y. *Macromolecules* **1997**, *30*, 7488. [i] Li, J.; Pang, Y.; Barton, T. J. *Polym Prepr.* **1996**, Aug, 333.

The position of the emission maximum (575 nm) is indistinguishable in HHTT and HT polymers, while Yamamoto's regiorandom polymer of the same constitution (**16a**) shows emission maxima at 529 and 558 nm in the solid state. Again, solid-state ordering must be the explanation for these differences in emissive behavior.

If instead of one thiophene unit a bi-, ter-, or quaterthiophene is connected by a 1-alkoxy-4-methyl-2,5-diethynylbenzene, the emission in solution is red-shifted from 410 to 485 nm, and at the same time the fluorescence quantum yield (solution) drops from 0.18 to 0.02, suggesting that these materials will not be particularly useful as active layers in light-emitting devices.

Miscellaneous PAEs (Table 14). Several other PAEs have been examined with respect to emission. The most interesting ones are PAEs in which pyridine (**7**), benzimidazole (**8**) (Table 14, entries 7−9), or bipyridine (**9**) (Table 14, entry 1) units are separated by alkoxy-substituted diethynylbenzenes or diethynyl-(3-hexylthiophene) **15**. These polymers display high fluorescence, which can be pH dependent. A decrease in pH leads to a bathochromic shift in the emission of the imidazoles **8** and may thus find use in sensory applications. Bipyridine-containing PPE **9** may be useful to detect and connect polymer chains by metal ions in a supramolecular fashion. However, solid-state emission of these materials is mostly not reported.

Miscellaneous Photophysical Properties of PPEs. Wrighton[44] has estimated the lifetime of the main emission band of dialkoxy-substituted PPEs (**1**) centered at 480 nm to be $\tau_{fl} < 1$ ns. If anthracene moieties are present, a second emission at 549 nm is observed, which has a lifetime of approximately 1 ns. This band is probably due to anthracene-localized emission in the solid state. Swager[33] has determined the lifetimes of several dialkoxy-substituted PPEs. He finds lifetimes τ_{fl} for the main emission band ranging from 0.64 to 1.88 ns. The lifetime is increased by *meta* linkages and decreased by the presence of acceptor substituents. The same authors reported the synthesis of porous PPEs **29** and **30a** containing pentypticene moieties.[15] These PPEs show regardless of the substituent pattern lifetimes of τ_{fl} 0.47−0.54 ns in solutions and a lifetime of 0.05−0.09 ns in the

solid state.[15,49] If the pentypticene parts of these polymers are fused to naphthalene (**30b**), the emission band shifts to 500 nm in thin films and displays a lifetime τ_{fl} of 0.54 ns, which was attributed to the formation of naphthalene exciplexes in the solid state. Schanze[122] determined τ_{fl} to be 0.5 ns for a biphenyl-containing PPE in solution, a value in excellent agreement with Swager's measurements. The authors determined the singlet/triplet splitting in this polymer to be 63 kcal and conclude from their observed rates for intersystem crossing that nonradiative decay occurs via defect sites in the polymer. Davey et al.[123] have independently determined τ_{fl} to range from 0.44 to 0.46 ns in solution, if alternating thiophene or pyridine-*co*-alkoxy-PAEs are investigated. It is interesting to note that in solution almost all PAEs show a τ_{fl} of approximately 0.5 ns, regardless of whether thiophene, benzene, or pyridine units are separated by alkyne linkages. The explanation for high fluorescence quantum yields and the observed lifetimes originates from the distinct bond alternation in the PAEs, which leads to a favorable orbital ordering according to the Pariser−Parr−Pople model.[123]

There has been some interest in PPEs as NLO materials, and several groups have determined χ^3 values for PPEs. West[114] has measured and discussed χ^3 values for PPEs **2d**. The authors find that the susceptibilities obtained by their group (4×10^{-11} esu) coincide with the ones reported by Weder and Wrighton (thin film, 10^{-11} esu).[46] The values of these groups are in variance with the susceptibilities (4.6×10^{-10} esu) claimed by LeMoigne.[115] A series of thiophene-containing examples have been examined with respect to their NLO properties, and Yamamoto[75] reported χ^3 values ranging from 3×10^{-11} to 4.2×10^{-11} esu. A thiophene−pyridine-containing PAE was likewise examined by this group and gave a value of 4.7×10^{-11} esu.[70] For a mixed *m*−*p*-alkoxy-PPE, Kondo claimed a χ^3 value of 1.8×10^{-9} esu, which seems to be unrealistically high in the light of the other reported measurements.[116]

IV. Structural Model(s) for PPEs

PPEs and PAEs are ideally conjugated linear macromolecules (in a strict sense) if all bond angles

Table 14. Spectroscopic Properties of PAEs Containing Heteroaromatic and Non-Benzene Rings

Entry Cpd	Structure	Absorption λ_{max} [nm] solution	Film	Emission [nm] Solution	Film	Comment
1[a] -	(structure: OC8H17 / C8H17O)	415, dioxane	Not determined	450 [0.78]	Not determined	
2[b] -	(structure: OR / RO)				480	Nature of the R-groups unclear. SS numbers estimated from supplied graphs.
3[b] 4c	(structure: OR / RO)				590 EL	
4[c] -	(structure)	340		430		
5[c] -	(structure: Se)	462	460	523	520, 550, 575	
6[d] -	(structure: C8H19)	370	Not determined	Not determined	Not determined	
7[e] 8a	(structure: OH)	363 DMF 408 DMF/NaOH 320 TFA		434, TFA [0.065] 463, DMF [0.006]		
8[e] 8b	(structure: OH, C12H25O)	410 CHCl3 342 TFA 670 upon ox to polyradical	410	495, TFA [0.14] 475, DMF [0.19] 511, CHCl3 [0.1]		
9[e] -	(structure: OH)	383 DMF 397 TFA due to planarization?		478, TFA [0.015] 454, DMF [0.004]		
10[e] 8c	(structure: OH)	353 DMF 397 DMF/NaOH 341 TFA 650 upon ox to polyradical	362	421, TFA [0.18] 463, DMF [0.006]		

[a] Egbe, D. A. M.; Klemm, E. *Macromol. Chem. Phys.* **1998**, *199*, 2683. [b] Hirohata, M.; Tada, K.; Kawei, T.; Onoda, M.; Yoshino, K. *Synth. Met.* **1997**, *85*, 1273. [c] Yamamoto, T.; Takagi, M.; Kizu, K.; Maruyama, T.; Kubota, K.; Kanbara, H.; Kurihara, T.; Kaino, T. *J. Chem. Soc., Chem. Commun.* **1993**, 797. [d] Beginn, C.; Grazulevicius, J. V.; Strohriegl, P. *Macromol. Chem. Phys.* **1994**, *195*, 2353. [e] Hayashi, H.; Yamamoto, T. *Macromolecules* **1998**, *31*, 6063.

of the participating arenes are at 180°. If however 2,5-linked thiophene units are introduced into the PAE backbone, the linearity and rigidity of the polymer chain decrease substantially as has been shown by Pang[66,101−105] when he evaluated the exponent α of the Mark−Houwink equation (Chart 3).

Solid-state ordering of rigid-rod polymers generally obeys Neher's rule,[117] which states that hairy rigid rods come in three structural types depending upon the concentration of solubilizing side chains per repeating unit. If the side-chain concentration is very high, such as in dialkyl- or dialkoxy-substituted PPPs, a planar arrangement of the polymeric backbone is not accessible. Instead the polymer chain assumes a cylindrical shape, and no close contacts between the aromatic backbones occur. If the con-
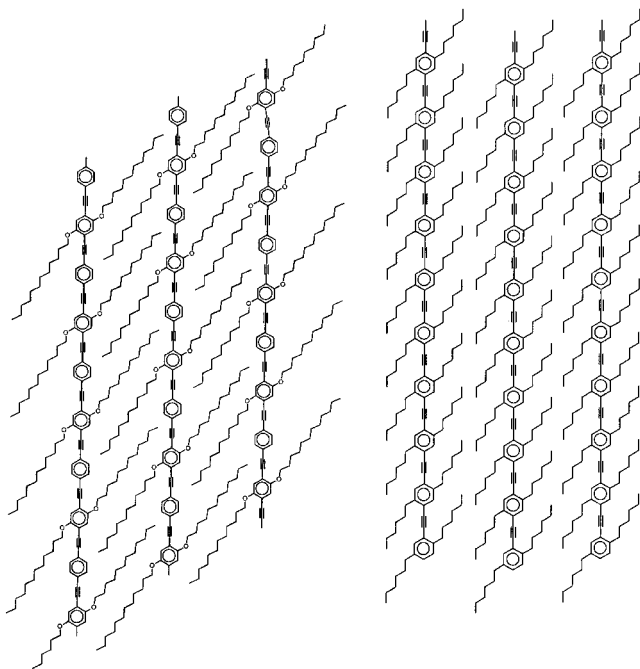
Figure 1. (a, left) Interdigitated structure of PPEs. (b) Lamellar structure of PPEs.

centration of the side chains is decreased, a lamellar or doubly lamellar morphology results in which the structure of the polymer is almost completely dominated by side-chain packing, particularly if long alkyl or alkoxy groups are present on the rigid backbone. This type of structure has first been found by Wegner[118] and later by Ringsdorf.[119] If the side-chain concentration decreases further, efficient interaction between the solubilizing groups of two different polymer chains occurs and an interdigitated phase will result. In the case of the PPEs both lamellar and interdigitated phases have been observed, while cylindrical morphologies have been suggested but not proven.[15,49] Structural work has mostly been done on PPEs, so the solid-state structures and morphologies of other PAEs are less known.

A. Structures at Ambient Temperature

Structure of PPEs in the Bulk. To examine PPEs with respect to their bulk structure, powder diffraction and electron microscopy are the main tools. Due to the rigidity of these polymers, diffraction data in combination with force-field calculations give excellent models of solid-state ordering in PPEs. The first structural characterization of dialkoxy-PPEs **1** has been performed by LeMoigne. The authors concluded (correctly) from X-ray diffraction that dialkoxy-PPEs assume a lamellar structure.[42] Table 15 shows the data for structurally characterized PPEs. Two types of structures are found in PPEs, viz., interdigitated and lamellar structures (Figure 1). Interdigitated structures show small angle *d*-spacings in their powder diffraction pattern, which correspond approximately to the dimension of the extended length of their solubilizing group. Interdigitated structures have been found in the case of West's PPE **2d**,[48] in which dialkoxy-substituted and unsubstituted ben-

zene rings alternate, and in LeMoigne's ester-substituted PPEs,[42] in which every benzene ring carries one solubilizing group. Alternatively, an interdigitated structure forms, if two solubilizing groups of substantially different length are used in an alternating fashion. An indication for the occurrence of interdigitated structures is that only even reflections of higher order (002, 004, 006, ...) are observed.

If the concentration of side groups increases such as in dialkoxy-PPEs **1** or in Bunz' dialkyl-PPEs **3**, generally a lamellar or doubly lamellar structure is assumed. In these lamellar structures, if sufficiently crystalline, a *d*-spacing at low angles is observed which approximately represents double the length of the extended side chain multiplied by sin α. The angle α stands for the tilt angle of the side chain with respect to the main chain. In addition to the larger *d*-spacing, the lamellar phases display well-resolved higher order reflections, but only the uneven, odd ones appear, which is in contrast to the case of the interdigitated phases (001, 003, 005, ...). Bunz, Shimizu, and Enkelmann[124] have carefully analyzed the packing behavior of several dialkyl-substituted PPEs **3** and their monomeric counterparts (Table 15, entries 14–17). Their study fully corroborates and refines Wrighton's model.[32,45] The most important single feature in the packing of both monomers and polymers (most clearly visible in the case of the didodecyl-substituted PPE **3c** and model compound **81c**) is the overwhelming contribution of the alkyl side chains dictating the packing of both monomers **81** and polymers **3**. The monomers were examined by single-crystal X-ray methods, and analysis of the alkyl chain packing reveals that these form a subcell of polyethylene with an excellent match of the cell dimensions.[125] A similar situation will hold in the polymer, in which maximized van der Waals interactions of the side chains force the main chains to stack on top of each other in register. A benzene ring of one polymer chain is positioned over the alkyne unit of the adjacent layer below. This type of packing not only satisfies the side chains but also perfectly takes into account the electrostatic potentials of the main chains, which makes direct, parallel π–π-stacking unfavorable. The distances resulting from this model are in excellent agreement with both those of the monomer structures and the diffraction data obtained from the polymers. Weder[126] demonstrated that several dialkoxy-substituted PPEs **1** dissolve very well in high-molecular-weight polyethylene and can be drawn into very thin films without any phase separation. The observed compatibility was noted with surprise but can be rationalized easily in light of Bunz'[124] finding that long alkyl side chains in PPEs show a perfect polyethylene-type ordering in the solid state. Consequently, PPEs **1** can perform an isomorphic substitution for polyethylene chains in the solid state.

Bis(ethylhexyl)-PPE **3f** was investigated by electron microscopy and shows a distinct fibrous structure in thin, solution-cast films. These fibers are approximately 36 nm wide and at least 5–6 μm long.[124] The origin of this morphology is at the moment not clear, but Swager et al.[47] have produced

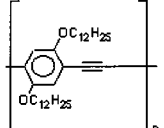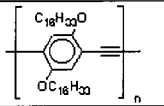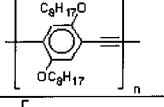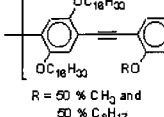**Table 15. X-ray Diffraction Data and Structural Models for PPEs**
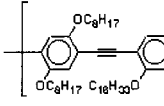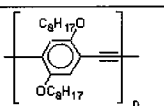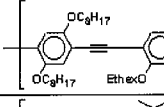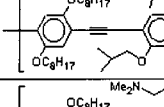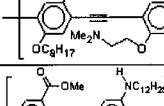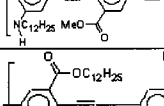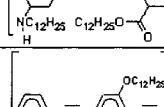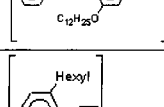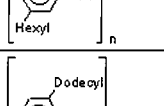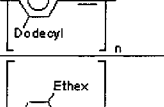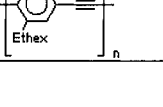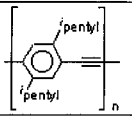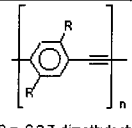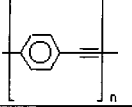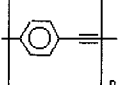
Entry	Structure	Main Diffraction peaks [Å]				Comments
		d	d	d	d	
1[a]	(structure: PPE with $OC_{12}H_{25}$ groups)	29.5		4.2		Lamellar phase.
2[b]	(structure: PPE with $C_{18}H_{33}O$ / $OC_{18}H_{33}$ groups)	33.2	10.9	4.4	4.0, 3.6	Classic lamellar phase with tilted alkoxy chains
3[b]	(structure: PPE with $C_8H_{17}O$ / OC_8H_{17} groups)	25.6	13.1	4.4	4.0	Classic lamellar phase with tilted alkoxy chains; Duran-Wegner model used.
4[b]	(structure: PPE with $OC_{18}H_{33}$, OR groups; R = 50 % CH_3 and 50 % C_8H_{17})	31.4 22.5		4.0		Disordered lamellar structure due to mixed side chains.
5[c]	(structure: PPE with OC_8H_{17}, $OC_{18}H_{33}$ groups)	27.4	6.4	4.4, 4.0		Partially interdigitated, lamellar structure due to differences in chain lengths. Partial interdigitation concluded from the observation of even reflections, which are suppressed in purely lamellar, non-interdigitating structures.
6[c]	(structure: PPE with $C_8H_{17}O$ / OC_8H_{17} groups)	18.2 (24.3 as spun)	6.2 (7.2)	4.1 (4.2)	3.6	Dramatic difference upon annealing.. Phase transition? Layered lamellar structure, tilted side chains
7[c]	(structure: PPE with OC_8H_{17}, OEthex groups)	23.2		4.5		Side chain incompatibility leads to less ordered structure
8[c]	(structure: PPE with OC_8H_{17} and ester groups)			4.5		Side chain incompatibility leads to less ordered structure
9[c]	(structure: PPE with OC_8H_{17}, Me_2N groups)	15.8		4.2	3.7	Side-chain crystallinity observed
10[d]	(structure: PPE with OMe, $NC_{12}H_{25}$ amide groups)	27.1				Surprisngly large spacing. Suggested structure probably not correct
11[d]	(structure: PPE with $OC_{12}H_{25}$, $NC_{12}H_{25}$ groups)	28				Lamellar-layered structure
12[e]	(structure: PPE with $OC_{12}H_{25}$, $C_{12}H_{25}O$ groups)	14.7	7.3	4.2	3.8	Interdigitated phase
13[f]	(structure: PPE with Hexyl groups)	16.2				All dialkyl-PPEs for lamellar or doubly lamellar phases.
14[f]	(structure: PPE with Dodecyl groups)	25.0	8.5	4.2	3.8	
15[f]	(structure: PPE with Ethex groups)	12.4		4.3	4.1	

Table 15 (Continued)

Entry	Structure	Main Diffraction peaks [Å]				Comments
		d	d	d	d	
16[j]	*i*pentyl / *i*pentyl	13.7	6.82	4.4, 4.0	3.4	
17[j]	R / R, R = S-2,7-dimethyloctyl	21.3	7.2			
18[j]		5.83	4.2	3.9	3.1	The parent must display a different packing due to the completely deviant d-spacings of this insoluble material.
19[g]			4.2	3.97	3.1	

[a] Wautelet, P.; Moroni, M.; Oswald, L.; LeMoigne, J.; Pham, A.; Bigot, J.-Y.; Luzzati, S. *Macromolecules* **1996**, *29*, 446. [b] Ofer, D.; Swager, T. M.; Wrighton, M. S. *Chem. Mater.* **1995**, *7*, 418. [c] Weder, C.; Wrighton, M. S. *Macromolecules* **1996**, *29*, 5157. The same data are published in Weder, C.; Wrighton, M. S.; Spreiter, R.; Bosshard, C.; Günter, P. *J. Phys. Chem.* **1996**, *100*, 18931. [d] Moroni, M.; LMoigne, J.; Pham, T. A.; Bigot, J.-Y. *Macromolecules* **1997**, *30*, 1964. [e] Li, H.; Powell, D. R.; Hasyashi, R. K.; West, R. *Macromolecules* **1998**, *31*, 52. [f] Bunz, U. H. F.; Enkelmann, V.; Kloppenburg, L.; Jones, D.; Shimizu, K. D.; Claridge, J. B.; zurLoye, H.-C.; Lieser, G. *Chem. Mater./* **1999**, *11*, 1416. [g] Yamamoto, T.; Muramatsu, Y.; Shimizu, T.; Yamada, W. *Macromol. Rapid Commun.* **1998**, *19*, 266.

similar fibrous structures in a cyclophane-bridged PPE by application of the LB technique. However, Swager attributes the formation of these fibrillar structures to reorganization of PPE layers as a result of an interplay of hydrophilicity and hydrophobicity of surface and polymer in terms of minimization of surface energy. Rabe, Schnablegger et al.[127] investigated the morphology of Heitz' ethylhexyl ester-substituted PPE[30] **2h** by a variety of methods and concluded strong aggregate formation in dilute solution by ultracentrifugation and light scattering. They present the model of a self-assembly process leading via the formation of cylinders to fibrils and later to clusters. These authors examined their PPE by TEM and find similar fibrillar structures as observed in the LB films by Swager[47] and in the bulk by Bunz.[124] The width of the double-stranded fibrils according to TEM is approximately 36 nm, which corresponds nicely to the value for the fibrils found by Bunz et al. It is however not completely clear whether the coincidence is circumstantial or has a common physical origin.

Structure of PPEs on Surfaces, in Films, and LB Preparations. The fact that alkoxy-PPEs **1** can be fabricated into LB films should, according to Swager,[47] allow the size selection of biological molecules and their use in chemical sensors and suggests them as polymeric modules in molecular electronics. All of these exciting morphologies are of fundamental scientific interest. Structures at interfaces are important but not restricted to LB films at the air–water interface. Samori et al.[20] demonstrated that thiocarbamoyl-terminated dihexyl-PPE **3a** forms interesting fibrillar structures on mica with a width of 3 nm and a length of approximately 1 μm. While the width of the fibril approximates the length of one macromolecule, the authors suggest that these PPEs form nanoribbons. These morphologies may be of impor-

tance in molecular electronics to bridge nanogaps,[20] and the best developed nanostructures have been obtained upon slow evaporation of dilute solutions of the PPE onto the surface.

B. Liquid Crystalline PPEs

Thermotropic liquid crystalline behavior has been proposed for PPEs; it was however never conclusively proven in the case of dialkoxy-substituted PPEs **1**.[42] Two main obstacles always remained: It was not possible to obtain isotropic melts for relatively high-molecular-weight materials, and clear-cut liquid crystalline textures had never been observed by polarizing microscopy, despite the observation of "birefringent fluids".[32,45,46] The inability to form an isotropic liquid phase is a consequence of the thermal sensitivity of dialkoxy-substituted PPEs **1** at temperatures above 130–150 °C. The first reported thermotropic LC phases of a PAE thus were derived from the organometallic PAE derivatives **10**,[37] which show either thermotropic nematic or lyotropic smectic ordering[80] depending upon the molecular structure of their respective monomers. The LC behavior was evidenced by a combination of differential scanning calorimetry (DSC), X-ray powder diffraction (XRD), and electron microscopy/diffraction.

In the case of PPEs **1** LC behavior was evidenced by Weder,[34] who observed that concentrated solutions (>11%) of an alternating dialkoxy-PPE (ethylhexyl/ dioctyl) **1l** in 1,2,4-trichlorobenzene were birefringent, showing maltese crosses and Schlieren textures. From these findings the authors concluded the presence of a lyotropic nematic mesophase. While the formation of lyotropic mesophases is of scientific interest, for the fabrication of advanced electrooptical devices, thermotropic LC behavior is much more advantageous.[95,117,120] A combination of high molecular weight, high purity, and absence of cross-links
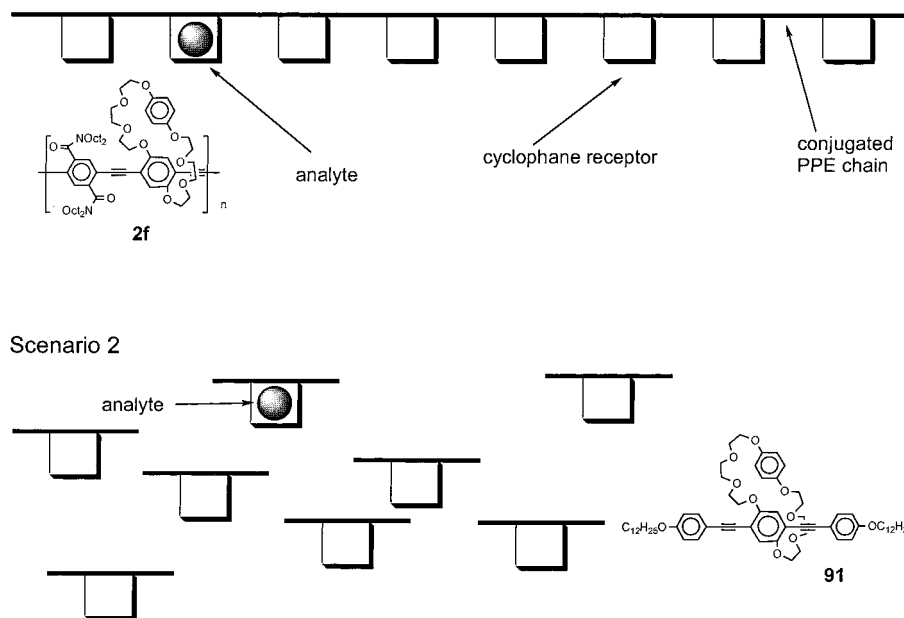
Figure 2. Applications of PPEs as sensory materials.

in combination with thermal stability should give rise to thermotropic LC phases in PPEs **3**. If these prerequisites are combined, it is clear that high-molecular-weight dialkyl-substituted PPEs **3** with long and/or branched side chains would be suitable candidates for thermotropic LC PPEs. Alkyne metathesis furnishes PPEs which exactly match these requirements.[41,96] Examination of didodecyl-PPE **3c** and bis(ethylhexyl)-PPE **3f** by a combination of variable-temperature XRD, polarizing microscopy, and DSC evidenced the occurrence of thermotropic LC phases in PPEs for the first time.[95a] Due to the lamellar ordering of the PPEs in the solid state,[124] the LC phases likewise must reflect some of that ordering. As a consequence, these materials form neither classic nematic nor classic smectic phases, but resemble more so the sanidic phases reported by Ringsdorf.[119] A good indication for this phase behavior is the textures observed by polarizing microscopy. LC PPEs show Schlieren textures or batons. It is possible, due to the enhanced thermal stability of the dialkyl-PPEs **3**, to access these phases from the isotropic melt by cooling. While in some cases classic Schlieren textures can be observed, often nicely developed textures arise, which point to a higher degree of order in these materials. The intermediacy of these lamellar phases between smectic and nematic justifies them to be named. If smectic and nematic are combined, the resulting terms for these phases would be *smatic*, which the author of this review suggests for lamellar PPE phases. Watanabe has employed another strategy for the synthesis of LC PAEs. He attached mesogenic side chains to a PAE backbone and observed thermotropic LC behavior.[95b]

The existence of thermotropic liquid crystalline phases allows the manipulation of morphology and thus their optical properties by external forces,[117] including magnetic fields. Such phases will play a role in future development of aligned layers for polarized emission and other LED-type applications.

V. Applications

In this section applications of PPEs and PAEs will be covered. However, only polydisperse polymeric materials are the focus of this review. Neither the work of Tour[7,19,22] utilizing defined oligomers as molecular wires in nanotechnology applications nor Moore's[21,31] elegant development of folded *m*-oligo-PEs and well-defined PE dendrimers is covered here (see references cited in Tables 1 and 2). However, these topics are sufficiently referenced to allow the interested reader facile access.

A. Molecular Electronics/Wires and Sensors

Swager has pioneered the use of PPEs as sensors[15,33,128] and coined the concept of "molecular wire approach" to sensing. What is the underlying principle? PPEs are very fluorescent in solution, and the incorporation of any binding sites for analytes capable of quenching fluorescence should diminish PPE's emission. This will happen upon exposure of dilute PPE solutions to the quencher (analyte). Any bound analyte works as a low-energy defect site for the polymer. The energy should be funneled to this site and dissipate efficiently. Swager's most efficient "sensing PPEs" **2f** carry one electron-rich oligo-(ethylene glycol) cyclophane per monomer unit. It is a binding site for paraquat (**89**) which acts as fluorescence quencher. One polymer chain carries many of these cyclophane units, but binding of only a percentage of the binding sites with paraquat already will lead to a complete suppression of fluorescence due to conjugation in PPEs. An exciton, which is generated upon irradiation, is delocalized over a substantial part of the polymer chain. It will find the defect site of lowest energy, i.e., the site of the bound analyte, and decay thus radiationless (Figure 3).

To appreciate the signal-enhancing character of this concept (Figure 2, scenario 1), a situation has to be envisaged in which every binding site is an
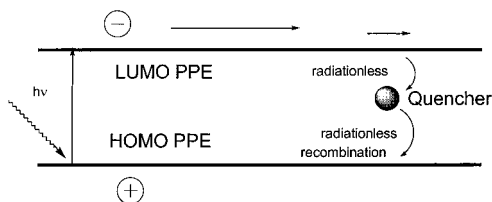
Figure 3. Electronic band structure of PPEs.

isolated molecule and carries its own fluorescent quencher (Figure 2, scenario 2). While in scenario 1 one molecule of analyte bound to the polymer chain completely shuts down the fluorescence of the "wired in series" system, in scenario 2, with the isolated sensor molecules, it would take the binding of eight molecules of analyte to achieve the same effect. Insofar this concept is extremely valuable for a significant enhancement of sensitivity. This effect can be fine-tuned by the structure and topology of the conjugated PPEs.

In an extension of this methodology, Swager recently reported the formation of Langmuir–Blodgett multilayers containing the cyclophane-PPE **2f**.[129] The authors studied PPE multilayers, which were topped by a surface energy trap (acridine orange), and found that rapid inter- and intramolecular energy transfer in these supramolecular systems occurs. The intermolecular energy transport is dominated by dipole–dipole interactions. It is more efficient in multilayer assemblies in which a three-dimensional energy-transfer topology is facilitated by thicker films. This concept works, despite the smaller relative concentration of the surface trap (acridine orange). The primary goal of this investigation was to find the optimum thickness for chemosensory applications of PPEs in films, and the results show that the fluorescence increases in the multilayer device containing up to 25 layers.

Building onto the concept of molecularly wired sensors for signal amplification, Swager reported in 1998[15,49] the synthesis of a series of porous PPE derivatives in which pentiptycene modules are incorporated into the PPE main chain. The incorporation of the pentypticene moieties makes **29** and **30a** (Chart 5) efficient solid-state emitters unaffected by aggregation; i.e., their emission spectra in solution and in the solid state are almost identical. The authors found that thin films of these highly fluorescent PPEs are excellent sensors for the detection of trinitrotoluene and dinitrotoluene. Both aromatics suppress the fluorescence of **29** or **30a** effectively but reversibly. The headspace, i.e., the atmospheric volume above land mines, contains measurable quantities of dinitrotoluene. As a consequence, polymers **29** and **30** coated on top of a fiber optic sensor will allow their simple detection by these very sensitive molecular wire-type materials. This elegant concept should be extendable and applicable to any other analyte, (a) which has the ability to quench fluorescence and (b) for which a receptor can be attached to PPEs.

Chart 5
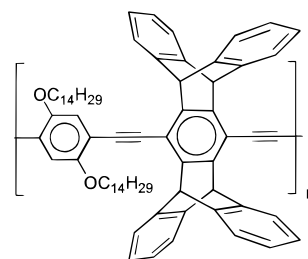
30a
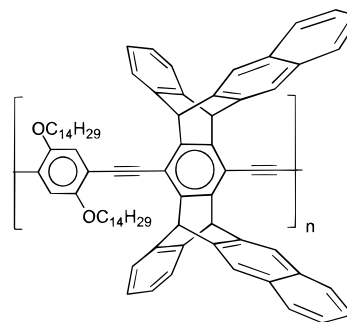
30b

B. Photonic Applications of PAEs

1. Light-Emitting Diodes

In several papers the fabrication of simple single-layer devices with PPEs is mentioned. Heitz et al. report that electroluminescence of carbonyl(2-ethyl-hexyloxy)-PPE **2h** (an ester-substituted PPE) occurs at 557 nm, without providing details of fabrication (Chart 6).[30] Pang[66] showed in a similarly cursory fashion that a m–p-PPE, **15**, shows electroluminescence at 454 nm in a single-layer device. A Japanese group[130] reported electroluminescence of several non-

Chart 6

557 nm   545 nm
Wavelength of Emission in LED

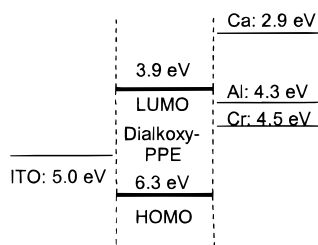**2h**   **15b**

549 nm

1l
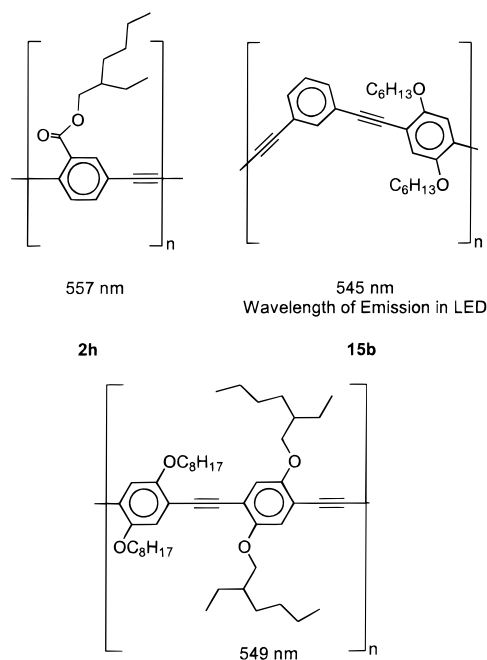
Figure 4. PPEs as light-emitting materials.

descript dialkoxy-PPEs with alternating pyridine, thiophene, and anthracene groups in an Al/PPE/ITO device structure. In the case of their anthracene copolymer, red-orange (590 nm) electroluminescence is observed, while the pyridine-containing copolymer shows blue-green emission (480 nm). Some experimental details are given, and the electroluminescence is determined at low temperature (78 K). Weder[131] published a careful study of electroluminescence in dialkoxy-substituted PPEs, which emit yellow-green light. His experiments show that contrary to PPVs, electron injection into the relatively low-lying LUMO (3.9 eV) of PPEs is no problem and even more efficient with aluminum than with the air-sensitive calcium (Figure 4). However, there is an energy mismatch for hole injection; i.e., the HOMO is too low to efficiently donate electrons into the ITO anode. External quantum efficiencies are up to 0.035%, which leaves much room for improvement. An interesting candidate as emitter may be the hitherto unknown mixed PPV/PPE, which should both show good hole injection and at the same time would still be capable of electron uptake.

2. Sheet Polarizers and Energy-Transfer Materials

Weder[126] has recently shown that dialkoxy-PPEs **1l** carrying alternating ethylhexyl and octyl side chains can be dispersed in high-molecular-weight polyethylene by codissolution (2−25% PPE) in xylenes and subsequent spin-casting. Absorption and emission spectra of the pristine films resemble the ones obtained for pristine films of pure **1l**. These films can be drawn at 110 °C on a hot shoe to 80 times their original length. Films of a thickness of approximately 3 μm are obtained. In these drawn films the emission is still red-shifted from 474 nm (solution) to 496 nm, but is now very narrow. In addition the films do show a dramatic dichroic ratio (emission‖/emission⊥ > 70) parallel to the drawing direction. Typically state-of-the-art polarization ratios in conjugated polymers have not exceeded 10, rendering this result fundamentally important.[132] An interesting question is the structural model for the PPEs in polyethylene. Weder finds that in the drawn films the diffraction peaks due to the PPE moieties have disappeared and only the diffraction of polyethylene is recorded. This finding may be surprising at first, but single-crystal data collected on monomeric model compounds **81** equipped with long hydrocarbon substituents show (vide supra) that (a) side chains dominate the packing of PPEs and (b) the hydrocarbon tails form a polyethylene subcell in the crystalline state![124] This must be the reason Weder's polymer orients perfectly into polyethylene matrices.

Chart 7
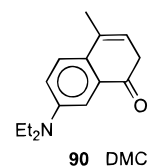
The reported bathochromic shift of 20 nm (solution → solid state) can be explained by a model that sugggests[120] complete planarization of the conjugated PPE backbones in the polyethylene matrix by the draw-induced order. TEM investigations on materials with high PPE content but polyethylene solid-state structure would be extremely interesting.

The high dichroic ratios in the thin PE/PPE film blends not only are of fundamental importance but have immediate practical applications. Weder has shown in two spectacular contributions[17,18] that PPEs **1l** can be used as photoluminescent polarizers in LCD displays. Current LC displays are limited in efficiency and brightness by the fact that absorbing polarizers and color filters have to be used. If the highly polarized, PPE-containing polyethylene films are utilized instead, devices with substantially increased brightness, contrast, and efficiencies are obtained. If a sensitizer, DMC (Chart 7), is used in connection with PPE in polyethylene, the drawn ternary blends, in which DMC is oriented randomly, perform isotropic-to-polarized conversion of light with high efficiencies. The conversion is explained to occur by energy transfer from excited but isotropic DMC molecules to the highly oriented PPE chains. The concept is promising and should have immediate commercial applications.

VI. Conclusion

In this review I attempt to give a comprehensive overview of the field of PAEs with emphasis on the developments during the last four years. Earlier material, covered by Giesa's[26] review, was included where necessary or desirable, presenting important conceptual progress. The field of PAEs has developed rapidly and on different frontiers, including synthesis of new and improved syntheses of known polymer topologies, understanding of structures and phase behavior in the bulk, thin films, or LB assemblies, and tailoring of optical properties in solution/solid state. In addition to fundamental progress, new horizons opened up with spectacular applications of PPEs as chemosensors in land mine detection, as light-emitting devices, or in binary PPE/polyethylene mixtures as sheet polarizers in LC displays. The breadth of the field ranging from hard-core organic synthesis to sophisticated physicochemical and commercial engineering applications makes PAEs a gold mine for the adventurous, interested in crossing borders of conventional areas and combining these into something new. In the future the field of PAEs will rapidly expand; we have barely scratched the surface, and the only thing we are restricted by is our own imagination to expand and conquer this fascinating topic.

VII. Acknowledgments

VIII. References

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