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Poly(arylene ethynylene)s

From Synthesis to Application

Springer

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Volume Editor: Christoph Weder

With contributions by
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177
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Preface

Over the past three decades, π-conjugated semi-conducting polymers have attracted significant interest since these materials combine the processability and outstanding mechanical characteristics of polymers with the readily-tailored electrical, optical, and magnetic properties of functional organic molecules. In particular, the potential use of these materials in light-emitting diodes, field-effect transistors, photovoltaic cells, and other opto-electronic devices has motivated the development of synthesis and processing methods of conjugated polymer materials with unique properties. Among a variety of materials, poly(arylene ethynylene) (PAE) derivatives have attracted the attention of an ever growing number of research groups around the globe. Hundreds of different PAEs have been reported to date and, during the last ten years, this family of conjugated polymers has established itself as an important class of materials with interesting optical and electronic properties. The spectacular progress made on many frontiers has propelled PAEs into the scientific mainstream, and many technologically relevant applications that utilize these polymers have been spurred. In six chapters, which root in the authors' own research experience, this special volume of the series Advances in Polymer Science attempts to capture the most recent phase of this exciting evolution. The book does not claim to be a complete compilation of the extensive literature in this field, but rather attempts to document recent progress on the basis of selected, illustrative examples. On behalf of all the contributors to this volume, I ask for the understanding of those researchers whose work has not been included.

The first chapter, written by *Uwe Bunz*, summarizes the most recent progress in the synthesis of PAEs and covers the literature from 1999 through 2003. In the second chapter, *Elisabeth Klemm, Thomas Pautzsch,* and *Lars Blankenburg* describe current work in the field of organometallic PAEs. The next chapter by *Christian R. Ray* and *Jeffrey S. Moore* focuses on the supramolecular organization of foldable phenylene ethynylene oligomers and polymers. The application of PAEs in bio- and chemosensors is described in the chapter written by *Juan Zheng* and *Timothy M. Swager*. The penultimate chapter, written by *Takakazu Yamamoto, Isao Yamaguchi,* and *Takuma Yasuda* , reviews the synthesis and chemical properties of PAEs based on sulfur-, nitrogen- and silicon-containing heteroaromatic moieties. Finally, a summary of

the electronic properties of PAEs and their potential applications in 'plastic electronic' devices is given in chapter written by *Gabriela Voskerician* and myself.

We hope that this volume will not only become a key reference for those in the field, but also serve its purpose as a source of inspiration for the design of future generations of advanced materials with unique and/or unusual opto-electronic properties.

Shaker Heights, March 2005 Christoph Weder

Contents

Adv Polym Sci (2005) 177: 1–52
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Synthesis and Structure of PAEs

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Abstract This review discusses the progress in the synthesis of poly(aryleneethynylene)s (PAEs). It covers the literature from 1999 through 2003. The last comprehensive review of PAE synthesis appeared in 2000. The present review comprehensively updates the developments in the synthesis of PAEs. Synthetic methods are discussed first, followed by the description of PAEs with novel structures and topologies. Progress has been made in the field of water-soluble and bioavailable poly(*para*-phenyleneethynylene)s (PPEs) and in the field of heterocyclic PAEs. In the last section the polymer-analogous reactions of PAEs are treated. Reduction and metal complexation are discussed. Most of the novel PAEs are proposed for applications in "plastic electronics" and/or in sensors.

Keywords Pd catalysis · Alkyne metathesis · Conjugated polymers · Acetylene chemistry · Alkynes · Arene chemistry

1 Introduction

Poly(aryleneethynylene)s (PAEs) [1] are a class of polymers in which arene groups are separated by alkyne linkers. Figure 1 shows the general structure of a PAE and the structure of the most important representative of this class, the poly(*para*-phenyleneethynylene)s (PPEs), in addition to two classes of structurally related conjugated polymers, the poly(*para*-phenylenevinylene)s (PPVs) [2] and the poly(diacetylene)s (PDAs) [3]. While the structural relationship between the PPEs and both the PPVs and the PDAs is close, their properties are different. PPEs, here as an example for all PAEs, are fluorescent in solution and in the solid state, are often stable up to 300 °C in air, and generally show enhanced photostability when compared to the PPVs. The PAEs show a distinct chromogenic behavior that is expressed in their solvatochromicity, thermochromicity, ionochromicity, surfactochromicity, and biochromicity [4–8] (see also other chapters in this volume) not found in the PPVs, but somewhat reminiscent of the optical properties of the PDAs and of the polythiophenes [9].

This review deals with the synthesis of PAEs. Described are the developments this field has undergone in the last 4 years. A comprehensive review on PAEs appeared in 2000 (Table 1, entry 1) [1]. Several other noteworthy PAE reviews are those of Yamamoto (Table 1, entries 7, 8) that cover mostly heterocyclic representatives and Pinto and Schanze's review (Table 1, entry 6) about water-soluble conjugated polymers. The specific area of dialkyl PPEs and their synthesis by alkyne metathesis has been reviewed recently (Table 1, entries 2–4)

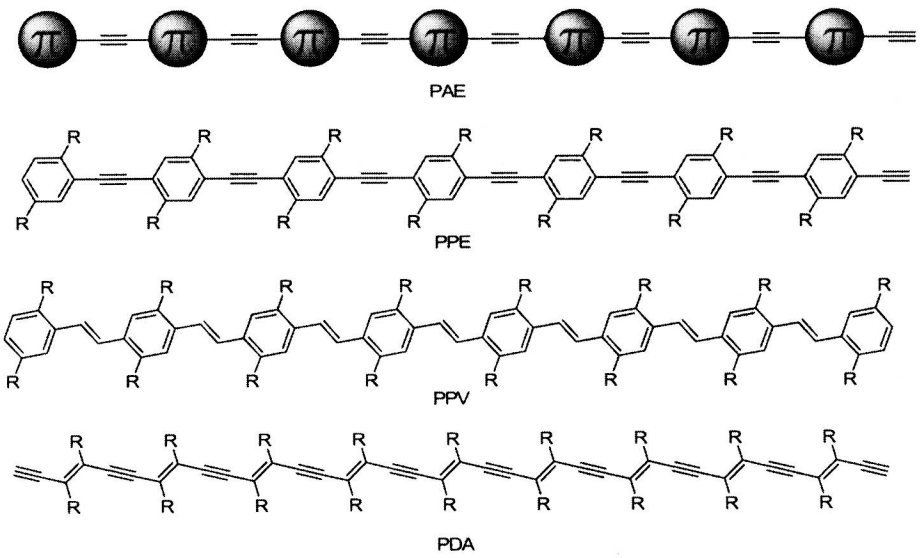


Fig. 1 PAEs, PPEs, and structurally related conjugated polymers PPVs and PDAs

Table 1 Reviews in the area of PAEs

Entry	Author(s)	Citation	Title
1	Bunz UHF	(2000) Chem. Rev. 100:1605–1644	Poly(aryleneethynylene)s: syntheses, properties, structures, and applications
2	Bunz UHF	(2001) Acc. Chem. Res. 34:998–1010	Poly(*p*-phenyleneethynylene)s by alkyne metathesis
3	Bunz UHF	(2002) In: Astruc D (ed) Modern arene chemistry. Wiley-VCH, pp 217–249	The ADIMET reaction: synthesis and properties of poly(dialkyl *para*-phenyleneethynylene)s
4	Bunz UHF	(2003) In: Grubbs RH (ed) Handbook of metathesis. Wiley-VCH, 3:354–370	Acyclic diyne metathesis utilizing in situ transition metal catalysts: an efficient access to alkyne-bridged polymers
5	Rusanov AL, Khotina IA, Begretov MM	(1997) Russ Chem Rev 66:1053–1068	The use of Pd-catalyzed cross coupling for the synthesis of polymers incorporating vinylene and ethynylene groups
6	Pinto MR, Schanze KS	(2002) Synthesis 1293–1309	Conjugated polyelectrolytes: synthesis and applications
7	Yamamoto T	(2003) Synlett 425–450	Synthesis of π-conjugated polymers bearing electronic and optical functionalities by organometallic polycondensations. Chemical properties and applications of the π-conjugated polymers
8	Yamamoto T	(1999) Bull Chem Soc Jpn 72:621–638	π-Conjugated polymers bearing electronic and optical functionalities. Preparation by organometallic polycondensations, properties, and their applications
9	Giesa R	(1996) Rev Macromol Chem Phys C36: 631–670	Synthesis and properties of conjugated poly(aryleneethynylene)s
10	Wosnick JH, Swager TM	(2000) Curr Opinion Chem Biol 4:715–720	Molecular photonic and electronic circuitry for ultrasensitive chemical sensors

and comprehensively. It will therefore be touched upon only cursorily here. If the reader is interested in the early attempts to make PPEs, Giesa's review (Table 1, entry 9) gives a good overview. Table 2 lists reviews that are tangentially important to the field of PAEs and/or deal with the synthesis, properties, and applications of oligomeric aryleneethynylenes (AE). The present review covers the field of *polymeric* AEs and the literature from mid-1999 through 2003. Oligomeric AEs – while interesting in themselves – are not included,

Table 2 Relevant reviews that are related to the field of PAEs

Author	Citation	Title
Negishi EI, Anastasia L	(2003) Chem Rev 103: 1979–2018	Palladium-catalyzed alkynylation
Moore JS	(1997) Acc Chem Res 30: 402–413	Shape-persistent molecular architectures of nanoscale dimension
Hill DJ, Mio MJ, Prince RB, Hughes TS, Moore JS	(2001) Chem Rev 101: 3893–4012	A field guide to foldamers
Swager TM	(2002) Chem Res Toxicol 15:125	Ultrasensitive sensors from self-amplifying electronic polymers
McQuade DT, Pullen AE, Swager TM	(2000) Chem Rev 100: 2537–2574	Conjugated polymer-based chemical sensors
Swager TM	(1998) Acc Chem Res 31: 201–207	The molecular wire approach to sensory signal amplification
Kingsborough RP, Swager TM	(1999) Prog Inorg Chem 48:123–231	Transition metals in polymeric π-conjugated organic frameworks
Marsden JA, Palmer GJ, Haley MM	(2003) Eur J Org Chem 2355–2369	Synthetic strategies for dehydrobenzo[*n*]annulenes
Haley MM, Pak JJ, Brand SC	(1999) Top Curr Chem 101:81–130	Macrocyclic oligo(phenylacetylenes) and oligo(phenyldiacetylenes)
Watson MD, Fechenkötter A, Müllen K	(2001) Chem Rev 101: 1267–1300	Big is beautiful – "aromaticity" revisited from the viewpoint of macromolecular and supramolecular benzene chemistry
Tour JM	(1996) Chem Rev 96: 537–553	Conjugated macromolecules of precise length and constitution. Organic synthesis for the construction of nanoarchitectures
Tour JM	(2000) Acc Chem Res 33:791–804	Molecular electronics. Synthesis and testing of components
Youngs WJ, Tessier CA, Bradshaw JD	(1999) Chem Rev 99: 3153–3180	*ortho*-Arene cyclynes, related heterocyclynes, and their metal chemistry

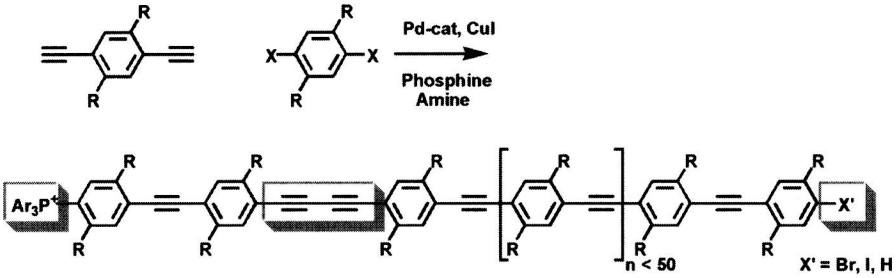
unless their discussion is necessary or useful for the general understanding of the topic, or where they serve as models for PAEs. For more information, Table 3 shows seminal contributions to the field of oligo AEs. The areas of porphyrin-containing ethynylated polymers and AE polymers containing metals *in the main chain* are not covered (see chapter in this volume by E. Klemm).

Table 3 Relevant primary publications in the field of oligomeric AEs

Author	Citation	Title
Zhang JS, Moore JS, Xu ZF, Aguirre RA	(1992) J Am Chem Soc 114:2273–2274	Nanoarchitectures 1. Controlled synthesis of phenylacetylene sequences
Schumm JS, Pearson DL, Tour JM	(1994) Angew Chem 33:1360–1363	Iterative divergent/convergent approach to linear conjugated oligomers by successive doubling of the molecular length
Huang SL, Tour JM	(1999) J Am Chem Soc 121:4908–4909	Rapid solid-phase synthesis of oligo-(1,4-phenyleneethynylene)s by a divergent–convergent tripling strategy
Hwang JJ, Tour JM	(2002) Tetrahedron 58: 10387–10405	Combinatorial synthesis of oligo-(phenyleneethynylene)s
Anderson S	(2001) Chem Eur J 7: 4706–4714	Phenyleneethynylene pentamers for organic electroluminescence
Melinger JS, Pan YC, Kleiman VD, Peng ZH, Davis BL, McMorrow D, Lu M	(2002) J Am Chem Soc 124:12002–12012	Optical and photophysical properties of light-harvesting phenylacetylene monodendrons based on unsymmetrical branching
Peng ZH, Pan YC, Xu BB, Zhang J H	(2000) J Am Chem Soc 122:6619–6623	Synthesis and optical properties of novel unsymmetrical conjugated dendrimers
Kukula H, Veit S, Godt A	(1999) Eur J Org Chem 277	Synthesis of monodisperse oligo-PEs using orthogonal protecting groups with different polarity for terminal acetylene units
Wagner RW, Johnson TE, Lindsey JS	(1996) J Am Chem Soc 118:11166–11180	Soluble synthetic multiporphyrin arrays. 1. Modular design and synthesis

2 Synthetic Methods

There are currently two methods available to make PAEs with significant molecular weights. The classical method, first used by Giesa and Schulz [10], employs the Heck–Cassar–Sonogashira–Hagihara (Table 2, entry 1) coupling to react an aromatic diyne with an aromatic dihalide in an amine solvent (Scheme 1). This method is general and compatible with most functional groups, save the heavier halides and unprotected alkynes. Good results are



Scheme 1 The Pd-catalyzed synthetic method to make PAEs

obtained when diiodoarenes are utilized in piperidine, diisopropylamine (DIPA), or triethylamine as solvent and either $(PPh_3)_2PdCl_2$ or $(PPh_3)_4Pd$ as catalyst in combination with CuI. For an in-depth discussion of the parameters of this coupling and its mechanism see Table 1, entry 1 and Table 2, entry 1. The addition of THF to the reaction mixture, independently described by Thorand and Krause [11] and by LeMoigne et al. [12], increases the molecular weight and yield of the obtained PAEs.

The disadvantage of the Pd-catalyzed couplings is the often (but not always) low molecular weight or degree of polymerization (P_n) of the isolated PAEs. Typical P_n values in these reactions are approx. 20–50, even though independently Swager's and Weder's groups have reported high molecular weight materials when utilizing $(Ph_3P)_4Pd$ as catalyst [13].

A problem in these couplings is the identity of the end groups of the formed polymers. Pd-catalyzed dehalogenation and/or phosphonium salt formation are side reactions that are difficult to avoid. A concern for the structural integrity of the backbone is the formation of butadiyne defects. While there is no direct measure to determine the amount of butadiyne defects in PAEs, the numbers are estimated to range from 1 to 10% of all repeat units.

The formation of butadiyne defect structures in PAEs is always observed, even if Pd(0) catalysts are used. It is not clear where the necessary oxidant comes from. Often a small excess of diyne is utilized, and such preparations seem to give higher molecular weight materials [14]. In the process of the formation of the final PAE, very large oligomers or small polymers with alkyne end groups could be intermediates. These intermediates would oligomerize via a Pd-catalyzed variant of a Hay-type coupling [15] to give the observed high molecular weight PAEs. This is a hypothesis that could explain Swager's results in the formation of high molecular weight PPEs. The butadiyne defect structures would only have to occur every other 50–100 repeat units and would not be detected by ^{13}C NMR spectroscopy. Fortunately, the butadiyne defects do not seem to have a large influence on the optical and electronic properties of the PAEs, yet it would be desirable to have a more controlled way of making defect-free PAEs.