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Alkyne Metathesis with Simple Catalyst Systems: Efficient Synthesis of Conjugated Polymers Containing Vinyl Groups in Main or Side Chain

Glen Brizius, Neil Gregory Pschirer, Winfried Steffen, Katherine Stitzer, Hans-Conrad zur Loye, and Uwe H. F. Bunz*

Contribution from the Department of Chemistry and Biochemistry, The University of South Carolina, Columbia, South Carolina 29208

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Abstract: The synthesis of novel conjugated polymers by acyclic diyne metathesis (ADIMET) is reported. These polymers are hybrids between poly(*p*-phenylenevinylene) and poly(*p*-phenyleneneethynylene) (PPE). They contain phenylene, ethynylene, and vinylene groups (−≡−Ph−=−Ph−, PPVE). Simple in situ catalysts formed from $Mo(CO)_6$ and 4-chlorophenol were used to metathesize the dipropynyl(tetraalkyl)stilbene monomers. The monomers are made by a combination of Horner reactions and Heck-type couplings. The PPVEs form in high yields and are structurally defined. They show degrees of polymerization (P_n) of 30−220 repeating units (i.e. 60−450 benzene rings), demonstrating that the presence of the double bonds does *not* interfere with alkyne metathesis. The PPVEs were structurally characterized by XRD and electron microscopy. They show fibrillar and network-type morphologies, which should make them interesting for applications in molecular electronics. Solid samples of PPVEs display powder XRD patterns almost identical to those of the PPEs. PPVEs thus assume similar doubly lamellar structures as the PPEs. The aggregation behavior of PPVEs was studied. In addition, ADIMET to a poly(2,7-fluorenyleneethynylene) carrying unsaturated side chains is reported. In this case the presence of unsaturation does neither interfer with efficient alkyne metathesis.

Introduction

Herein is described the following: (a) "Instant" catalysts formed from $Mo(CO)_6$ and 4-chlorophenol in off-the-shelf 1,2-dichlorobenzene perform clean alkyne metathesis of propynylated substrates in the presence of double bonds.[1] (b) The catalysts allow the synthesis of alkyl-substituted poly(*p*-phenyleneethynylene)/poly(*p*-phenylenevinylene) hybrids (PPVE, **3**) and the preparation of poly(2,7-fluorenyleneethynylene)s (**29**) decorated with unsaturated citronellyl side chains. (c) The solid-state structure, aggregation, and supramolecular ordering of the PPVEs **3** was determined by powder XRD, electron microscopy, and UV−vis spectroscopy.

Conjugated polymers are organic semiconductors and as such are important as active layers in light emitting diodes (LED),[2] "plastic" lasers,[3] light emitting electrochemical cells,[4] thin film transistors,[5] and the growing area of chemical sensing.[6,7] While heterocyclic polymers have certainly played an important role in these applications[8−10] the hugely popular poly(*p*-phenylenevinylene)s (PPV, **1**) and the polyfluorenes dominate the field of LEDs[2] and similar applications, while the poly(*p*-phenyleneethynylene)s (PPE, **2**) are increasingly important in diverse sensing applications.[6,7] However, the hybrid of these two structure types, i.e., PPV and PPE, **3**, which could be termed PPVE, has, surprisingly, never been reported.

We have successfully exploited alkyne metathesis[11] with simple catalyst systems for the preparation of high-molecular-weight dialkyl-PPEs **2**[12] and polynaphthyleneethynylene-PPE copolymers[13] and in the ring-closing metathesis[1] of dipro-

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[1] (a) Independently of us, Fürstner has recently reported the tolerance of double bonds in the metathesis of alkynes: Fürstner, A.; Guth, O.; Rumbo, A.; Seidel G. *J. Am. Chem. Soc.* **1999**, *121*, 11108. (b) For related work of this group see: Fürstner, A.; Seidel, G. *Angew. Chem.* **1998**, *37*, 1734. Fürstner, A.; Mathes, C.; Lehmann, C. W. *J. Am. Chem. Soc.* **1999**, *121*, 9453. (c) For high yield ring closing alkyne metathesis of 2,*n*-diyne hydrocarbons see: Weiss, K. Universität Bayreuth, unpublished results.

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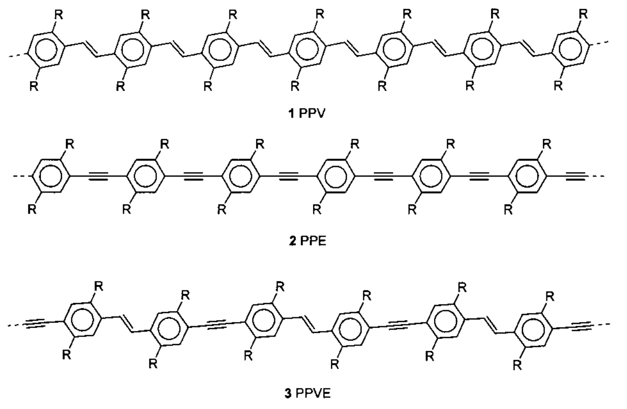

1 PPV

2 PPE

3 PPVE

Substitutent Key for **1**-**3**: **a**, R = (*S*)-3,7-Dimethyloctyl; **b**, 2-Ethylhexyl; **c**, Dodecyl; **d**, Octyl

pynylated phenyl ethers,[14] and planned to use ADIMET for the synthesis of PPVEs **3**.

Results and Discussion

Synthesis. At the outset[1] of the investigation we were skeptical if the "instant" catalysts would metathesize propynylated substrates in the presence of double bonds. A series of propynylated stilbene model compounds **7** (Scheme 1) was prepared via a combination of organolithium, Heck, and Horner chemistries. To our pleasant surprise, treatment of **7** with $Mo(CO)_6$ and 4-chlorophenol under standard metathesis conditions (150 °C, 16−24 h) in off-the-shelf 1,2-dichlorobenzene (ODCB) furnished the dimers **8b**,**c** and the organometallic representative **8e**. Pure dimers **8** were obtained in almost quantitative yield after acid and base wash of the reaction mixture, which was followed by removal of the solvent. Neither chromatography nor crystallization was necessary for the purification of these dimers. This result demonstrates that metathesis of alkynes proceeds smoothly if alkenes are present in the same molecule. This is remarkable, because the opposite, i.e., undisturbed olefin metathesis of vinylated, alkyne-containing substrates, is not common. Instead, alkynes actively participate and enyne metathesis is observed, as was elegantly shown by Grubbs and Zuercher.[15]

These intriguing results prompted us to explore the limits of tolerance of the simple metathesis catalysts with respect to vinyl groups. As a consequence we prepared the propynylated substrates **10**, **12**, **14**, **16**, **18**, **20**, and **22**, which we subjected to the standard metathesis conditions (Scheme 1). To our great surprise, all of the monomers underwent alkyne metathesis under standard conditions. Even unsupported styrenes in the *meta* or *para* position (**11**, **13**) are not polymerized but remain untouched and perform well. Likewise the *o*-styryl-substituted propynyl benzene **14** undergoes clean dimerization to **15** in a respectable 84% yield. To prove the structure of the dimer **15** unequivocally, we performed a single-crystal X-ray study (for details including packing diagrams see the Supporting Information), which is shown in Figure 1. The molecule of **15** is Z-shaped and assumes a fully planar extended conformation in the solid state (see Supplementary Information). The bond lengths and angles are in excellent agreement with the expected values.

If butadiene groups or heterocylces are present in the precursors, the yield of the dimerized diphenylacetylenes (**17**, **19**, and **23**) drops to 37−45%, due to either the presence of the sensitive butadiene group or the limited compatibility of heterocyclic building blocks such as thiophene to the relatively harsh metathesis conditions employed here. Side products could not be identified and starting material was not recovered. However, this series of experiments shows that alkyne metathesis with simple catalyst systems has substantial potential in small molecule organic chemistry.

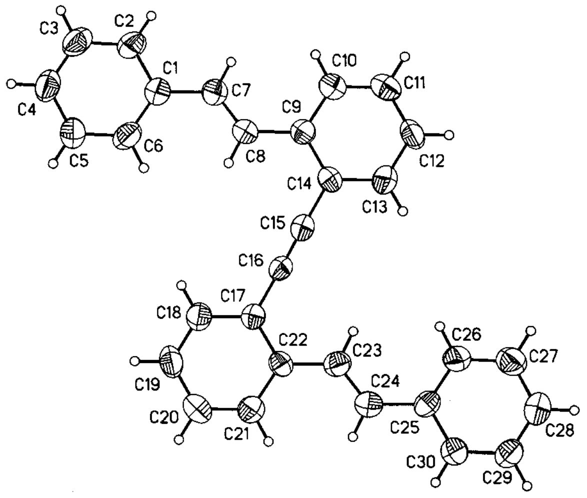

Figure 1. ORTEP of dimer **15**.

With these encouraging results in hand, a series of PPVEs **3** was synthesized. Scheme 2 shows the preparative route to the monomers **25** and their polymerization to **3**. A McMurry reaction of **6** accessed **25** directly, but in very low yields. Instead an in situ Horner approach, described by Smith and Salvatore, was used.[16] Reduction of **6** (Scheme 2) with $LiAlH_4$, followed by in situ reaction with methanesulfonyl chloride and Arbuzov reaction delivers the phosphonates **24** in good-to-excellent yields. Horner reaction of **24** with **6** in the presence of an excess of NaH in dimethoxyethane leads to the monomers **25** in yields of 70% starting from **6**. The use of a Horner reaction, performed at high temperature in the polar solvent DME, leads to monomers **25** in which the double bond is solely trans-configured. According to ^{1}H NMR analysis the trans/cis ratio is >100 in **25a**−**d**. The monomers **25a**−**d** are colorless powders or almost colorless oils and are subjected to alkyne metathesis under standard conditions in ODCB at 140−150 °C. The bright yellow polymers **3a**−**d** are isolated in high yield after acid and base wash of the reaction mixtures followed by precipitation into methanol (Scheme 3). Table 1 shows yield, degree of polymerization (P_n), polydispersity (M_w/M_n), and optical properties (discussion vide infra) of **3a**−**d**. Both yields and P_n are substantial for **3** and reinforce that alkyne metathesis with the instant catalyst is effective in the presence of double bonds. The polymers **3** were characterized by high-temperature NMR spectroscopy and their P_n and polydispersity obtained by GPC. The ^{1}H NMR spectrum of dodecyl-PPVE (**3c**) shows only three signals in the aromatic region, assigned to the protons residing on the trans double bond at δ 7.40 (s, 2 H) and the two different aromatic protons at δ 7.28 and 7.48 (2s, 2 H each, total of 4 H). In the ^{13}C NMR spectrum of **3c** seven signals in the region of δ 120−145 are observed for the stilbene core and one signal at δ 92.7 representing the alkyne group.

The higher P_n of the polymer **3c** when compared to its congeners **3a**,**b**,**d** can be explained by the superior purity of

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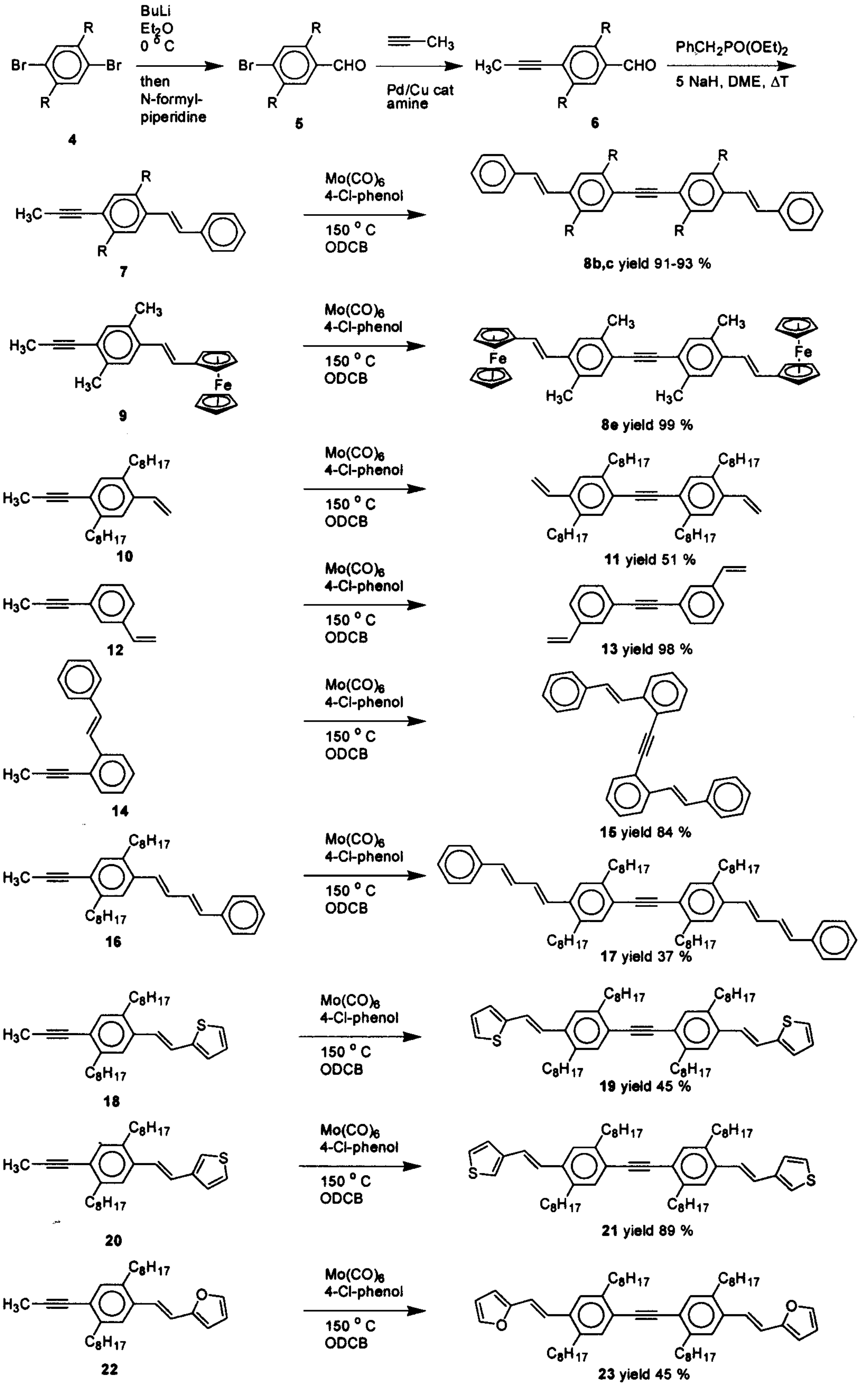
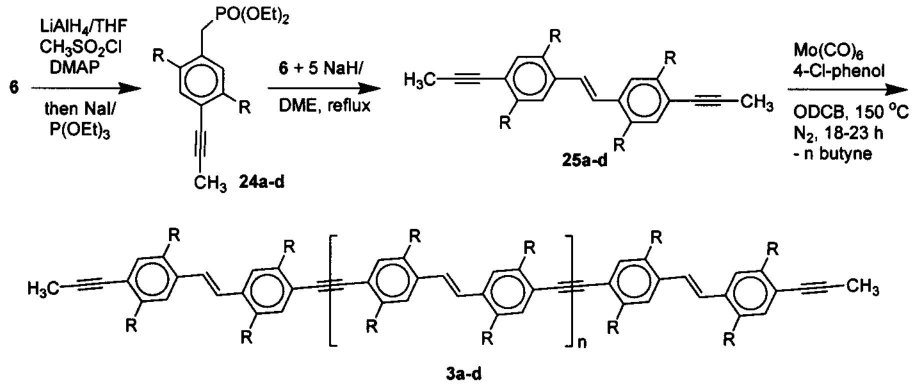
Scheme 1



substituent pattern: **4-8**: **a** R = (*S*)-3,7-Dimethyloctyl, **b** R = 2-Ethylhexyl, **c** R = Dodecyl, **d** R = Octyl

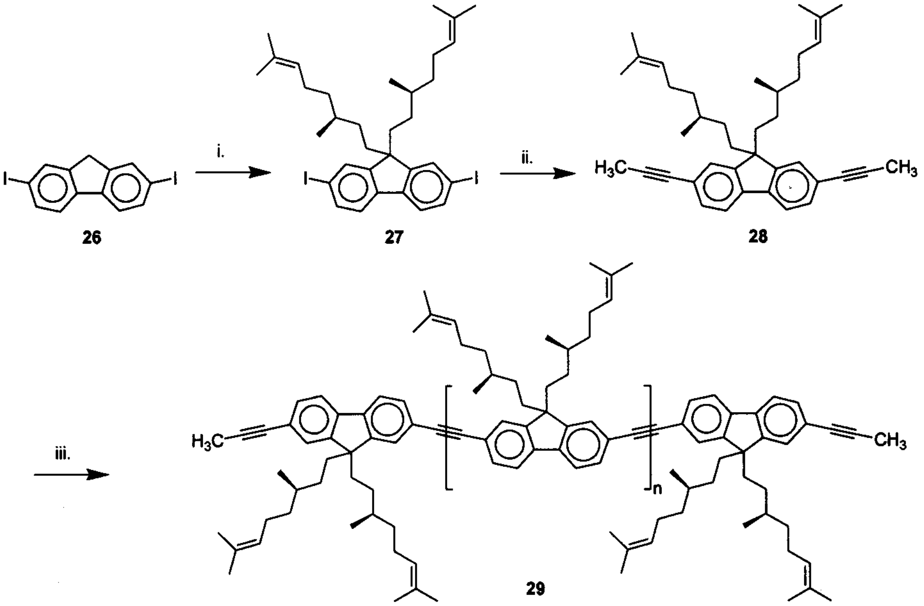
the corresponding monomer **25c**. This monomer was available on a 2−3 g scale and was multiply recrystallized. The removal of trace impurities, often hard to detect by NMR, is important if very high molecular weights are to be obtained in ADIMET. That is not too surprising, since ADIMET is a polycondensation process and sensitive to the purity of the utilized monomer. Still, if only moderately pure monomers are used, PPVEs **3a**,**b**,**d** of substantial molecular weights were obtained. This demonstrates

Scheme 2. Substituent Pattern of **3**, **6**, and **24**



Substitutent Key for 3, 6, 24: a, R = (*S*)-3,7-Dimethyloctyl; **b**, 2-Ethylhexyl; **c**, Dodecyl; **d**, Octyl

Scheme 3[a]



[a] Reagents and conditions: (i) (*S*)-(+)-citronellyl bromide, $BnNMe_3^+Cl^-$, DMSO, 18 h, 80%; (ii) propyne, $(PPh_3)_2PdCl_2$, CuI, piperidine, 16 h, 84%; (iii) $Mo(CO)_6$, 4-chlorophenol, ODCB, 150 °C, 22 h, 89%.

Table 1. Yield, Molecular Weight, Polydispersity, UV/Vis, and Fluorescence of PPVEs **3a**–**d**

			P_n			UV/Vis [nm]		fluorescence [nm]	
3	substituents	yield (%)	NMR	GPC	M_w/M_n	solution	film	solution	film
a	3,7-dimethyloctyl	78	43	152	3.43	405	425, 456 sh	457, 482	481, 514
b	ethylhexyl	92	38	77	2.09	397	445	458, 485	471, 500
c	dodecyl	96	>150	685	4.29	403	419, 460 sh	455, 485	488, 518
d	octyl	98	60	100	2.54	399	413, 458 sh	455, 484	496, 513

that ADIMET is a sufficiently robust process to furnish PPVEs in a straightforward manner.

To further explore the tolerance of the metathesis catalysts for double bonded functionalities, monomer **28** was prepared according to Scheme 3 and subjected to the conditions of the alkyne metathesis. Polymer **29** formed in 52% yield (soluble fraction, some insoluble material) and with a substantial degree of polymerization ($P_n = 82$; $M_w/M_n = 5.3$). ^1H and ^{13}C NMR spectroscopy show that the double bond is intact in **29**. From the results gathered for both the dimers (Scheme 1) as well as for the polymers **3** and **29** we can conclude that vinylic functionalities do not interfere with the conditions of alkyne metathesis when utilizing simple in situ catalysts formed from $Mo(CO)_6$ and 4-chlorophenol in off-the-shelf ODCB. This makes ADIMET a very convenient tool for organic and polymer synthesis.

Characterization, Optical Behavior, Aggregation, and Supramolecular Ordering of PPVEs 3. We have recently investigated aggregation,[17] phase behavior,[18] and solid-state structure[19] of PPEs (**2**). PPEs show doubly lamellar liquid

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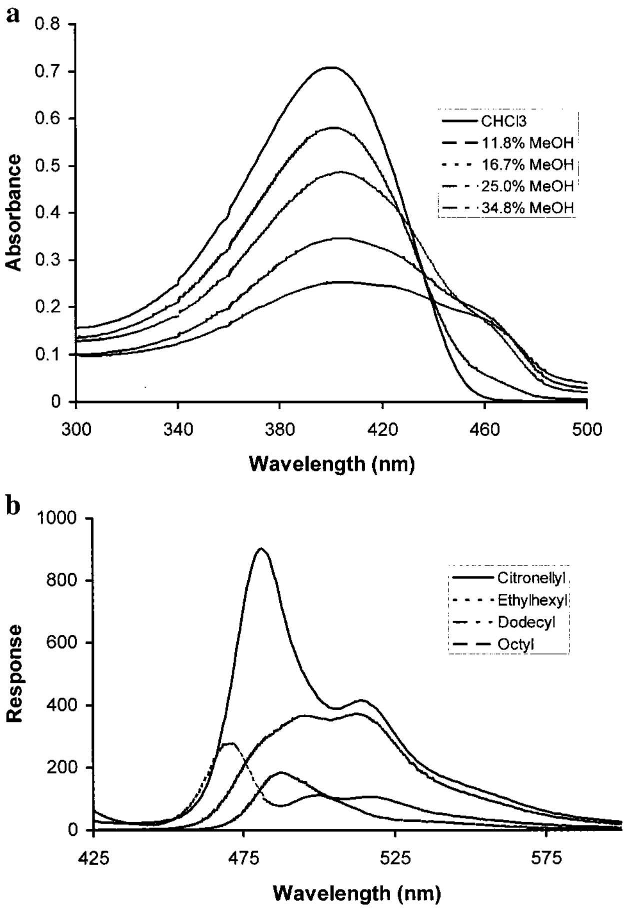

Figure 2. (a) UV−vis spectra of polymer **3d** in chloroform and after addition of increasing amounts of methanol. (b) Solid-state emission spectra of **3a**−**d** (thin films).

crystalline phases,[18,19] in which aggregation, phase behavior, and optical properties go hand in hand.[17c] It was attractive to compare the PPVEs **3** to the PPEs **2**. How does the presence of a vinylene group in PPVEs change the optical properties and the morphology? The solution UV−vis spectra of **3a**−**d** are broad and unstructured but bathochromically shifted by 11−16 nm when compared to those of identically substituted PPEs. Upon addition of methanol the PPVEs **3** show the development of a second, red-shifted transition (460 nm, **3d**), which is broad and featureless (see Figure 2a). This second transition is attributed to aggregation, induced by the addition of the nonsolvent methanol. No vibronic fine splitting is observed, contrary to the case of the PPEs.[17] At the moment it is not clear if the red-shifted aggregate band is due to planarization of the polymer backbone[17c] or the formation of ground-state aggregates.[20]

In solution all PPVEs **3** show emission at 460 nm, with photoluminescence quantum yields ranging from 28 to 34%. In the solid state (drop-cast films, slow evaporation) emission of **3** is dependent on the side chains (Figure 2b, Table 1), with photoluminescence quantum yields of approximately 5%. Dodecyl and octyl-PPVE (**3c**,**d**) show the most red-shifted, broad emissions (525 nm), suggesting the formation of solid-state excimers.[20] Substituent branching in **3** probably leads to increased distances between the polymer chains and thus to emission which is blue shifted and less disturbed by interchain interactions. The 3,7-dimethyloctyl substituents in **3a** are moderately effective in this regard, but bisethylhexyl-PPVE **3b** shows a strong blue solid-state emission at 470 nm (Figure 2b). A second much weaker emission is observed at 500 nm, suggesting diminished interchain interactions.

Table 2. X-ray Data of **3a**−**d** (Values for the Corresponding PPEs Are Given in Parentheses)

3	substituents	2Θ (deg)	*d* (Å)	area percent
a	3,7-dimethyloctyl	4.149	21.3 (*21.3*)	100.0
		12.342	7.17 (*7.2*)	7.2
		20.451	4.34	3.5
b	2-ethylhexyl	7.002	12.6 (*12.4*)	100.0
		18.147	4.88	17.5
		20.902	4.25 (*4.3*)	4.1
		21.144	4.20 (*4.1*)	3.8
c	dodecyl	3.701	23.9 (*25.0*)	100.0
		11.052	8.00 (*8.5*)	5.3
d	octyl	4.351	20.3	100.0
		12.800	6.91	9.9
		21.904	4.05	2.2

In the powder-XRD (see Table 2) of the PPVEs **3** one diffraction peak at low angles is visible for each of the polymers **3a**−**d**. The low angle diffraction peak has *d* values from 12.6 (**3b**) to 23.9 Å for **3c** and represents the lateral distance between chains. Molecular modeling (MM2, Spartan Pro) of an oligomeric subunit of **3d** shows that the wing span of the side chains matches this 20.3 Å distance interpreted to be the interchain distance in **3d**. We have recently analyzed the packing behavior and the solid-state structure of the dialkyl-PPEs **2**.[19] We find that the powder X-ray diffraction patterns of **2** and **3** are almost superimposable, with **2** having better developed and sharper diffraction peaks. The close match in powder diffraction data witnesses the structural similarity of **3** to the respective PPEs **2**. Vinylene groups can isomorphically substitute alkyne linkages in an organic solid-state structure. The slight length mismatch and their out-of-plane rotation (according to MM2 calculations) to avoid intramolecular steric repulsion does not seem to disrupt packing. From these data, we conclude that PPVEs **3** form lamellar phases similar to those observed in the PPEs **2**.[19,21]

High molecular weight PPVEs **3a**−**d** do not melt undecomposed according to DSC and variable-temperature polarizing microscopy data, probably due to the decrease in stability brought along by the vinylene groups. However, lyotropic liquid crystalline (LC) phases form as evidenced by polarizing microscopy. The lyotropic textures observed for **3b** are indistinguishable from the textures seen for bisethylhexyl-PPE **2b**.[18] The notion that side chains critically influence solid-state structures of rigid rods is supported by the similarity of lyotropic LC phases of **2** and **3**.

Electron microscopy of thin films of **3a**,**b**,**d** are shown in Figure 3a−c. Lamellar-fibrillar supramolecular structures form (**3a**,**d**). These are quite similar to structures (nanowebs) observed by Rabe and Müllen[22] and us[19b] in the self-assembly of dihexyl-PPEs on mica or graphite. Independently, Swager[20b] found that self-assembly of PPEs on the air−water interface gives fibrillar morphologies. Bisethylhexyl-PPVE **3b** on the other hand displays more of a crystalline, star-shaped morphology (Figure 3b) where several lamellae originate from the same center. These

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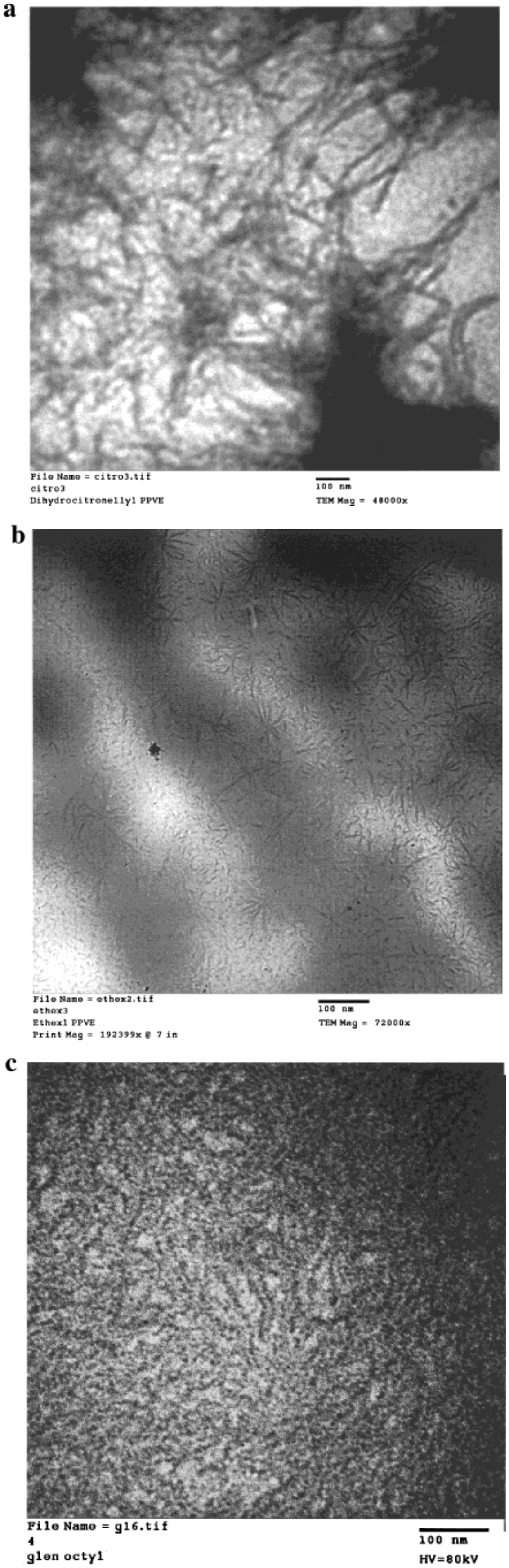

Figure 3. Transmission electron micrographs of polymer **3**. Films were obtained by spreading a diluted solution of the respective polymer in dichloromethane onto a water surface. The films were lifted off by an immersed copper TEM grid. Scale bars are shown. (a) TEM picture of **3a**. (b) TEM picture of **3b**. (c) TEM picture of **3d**.

stars correspond nicely to disclinations found in polarizing micrographs of the lyotropic LC-preparations of **3b**.

In the examined cases of **3** all of the observed fibrils are wire-like approximately 6−27 nm wide and 80−250 nm long. The width of the fibrils suggests that the long axes of the PPVE molecules are arranged along the long axis of the fibril, because in **3b** as well as in **3d** the length of a single rigid PPVE chain considerably extends the width of one lamella. The values obtained for the width of the lamellae from our fibrous PPVE networks coincide nicely with the ones found by Rabe, who interprets these features as fibrillar double ribbons of PPEs.[20b,22c] At the same time our PPVE fibrils resemble the lamellar structures we have recently observed in dialkyl-PPEs **2**.[20] From the available evidence the formation of fibrillar-lamellar, wire-like nanostructures seems a general feature for PPEs, a scheme into which the related PPVEs **3** fit nicely.

Conclusion

Olefins are noncompetent substrates for alkyne metathesis catalysts formed from mixtures of $Mo(CO)_6$ and 4-chlorophenol. On the basis of these finding, two novel types of conjugated polymers were synthesized, viz. PPVEs **3** and the citronellyl-substituted poly(fluorenylyeneethynylene)s **14**.[23] Optical properties, aggregation behavior, and supramolecular structure/morphology were examined for **3a**−**d**. While the optical behavior of **3** is quite different from that of dialkyl-PPEs **2**, their solid-state structure must be isomorphous to that of the PPEs, according to the powder XRD data. This conclusion is supported by electron microscopy of thin films of **3** where formation of fibrous-lamellar structures, closely related to those observed for PPEs,[20,22] was evidenced. We plan to investigate PPVEs as active layers in light-emitting diodes, organic semiconductor, and self-assembled nano-devices.

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Supporting Information Available: Detailed experimental and procedural details including spectroscopic characterization for **3**−**29** and details of the solution of the single-crystal structure of **15** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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