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One-Step Synthesis of Low Molecular Weight Poly(*p*-phenyleneethynylenevinylene)s via Polyaddition of Aromatic Diynes by Catalysis of the [Ru(*p*-cymene)Cl_2]$_2$/AcOH System

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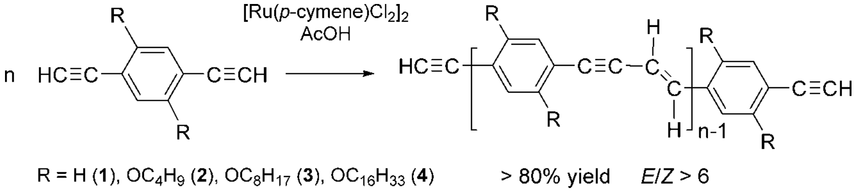

π-Conjugated low molecular weight polymers characterized by regio- and stereoregular alternation of phenylene and (*E*)-1-en-3-yne moieties have been synthesized by polyaddition of 1,4-diethynylbenzene or of 2,5-diethynyl-1,4-alkoxybenzene monomers, employing the commercially available di-μ-chlorobis[(*p*-cymene)chlororuthenium(II)] complex as the metal catalyst source, under homogeneous, atom-economical, amine- and phosphine-free conditions. Bulk materials of poly(*p*-phenyleneethynylenevinylene) derivatives are obtained with yields larger than 80%, from which polymers readily soluble in chlorinated solvents and in tetrahydrofuran are extracted in 60−75% yields. The polymers with average degrees of polymerization in the range $n_{AV} = 4-8$ display optical properties in solution similar to those of the higher molecular weights analogues.

Introduction

Organic conjugated polymers and oligomers display remarkable optoelectronic properties which have opened the way to several applications in material science.[1] These carbon-rich extended π-electron systems consist of aromatic rings conjugated with double or triple bonds, the most typical structures being the poly(*p*-phenylenevinylene)s (PPV) and the poly(*p*-phenyleneethynylene)s (PPE). The common synthetic strategies toward these materials imply the repetitive formation of carbon−carbon double bonds or single bonds for PPV[1b,2] and cross-coupling reactions of dihalogenated electrophilic arenes with diethynyl nucleophilic derivatives for PPE.[1b,3,4a] Two different partners and the formation of stoichiometric byproduct are involved in all cases (Scheme 1).

Synthetic efficiency and novel structural features are constantly pursued in order to improve reaction conditions and properties of the conjugated polymers. Recently, processes based on metathesis reactions with significantly improved atom-economy characteristics were employed in the synthesis of conjugated polymers containing double or triple bonds.[3b,4] In these respects, the catalytic polyaddition of aromatic diethynyl derivatives appears a simple and straightforward method for the preparation of the class of π-conjugated polymers characterized by the alternation of arene and C-4 enyne units (−Ar−C≡C-

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(1) (a) Müller, T. J. J., Bunz, U. H. F., Eds. *Functional Organic Materials. Synthesis, Strategies and Applications*; Wiley-VCH: Weinheim, Germany, 2007. (b) Haley, M. M., Tykwinski, R., Eds. *Carbon-Rich Compounds. From Molecules to Materials*; Wiley-VCH: Weinheim, Germany, 2006. (c) Tour, J. M. *J. Org. Chem.* **2007**, *72*, 7477–7496. (d) McQuade, D. T.; Pullen, A. E.; Swager, T. M *Chem. Rev.* **2000**, *100*, 1605–1644.

(2) Bao, Z.; Chen, Y.; Cai, R.; Yu, L. *Macromolecules* **1993**, *26*, 5281–5286.

(3) (a) Mori, A.; Ahmed, M. S. M. In *Comprehensive Organometallic Chemistry III*; Mingos, D. M. P., Crabtree, R. H., Hiyama, T., Eds.; Elsevier: Oxford, UK, 2007; Vol. 11, Chapter 19. (b) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605–1644.

(4) (a) Babudri, F.; Farinola, G. M.; Naso, F. *J. Mater. Chem.* **2004**, *14*, 11–34. (b) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565–1604.

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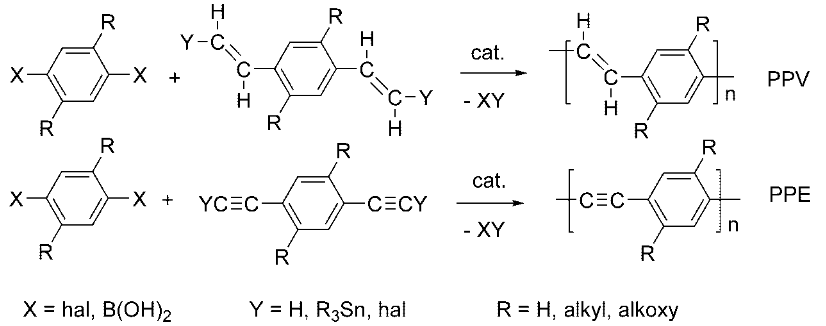
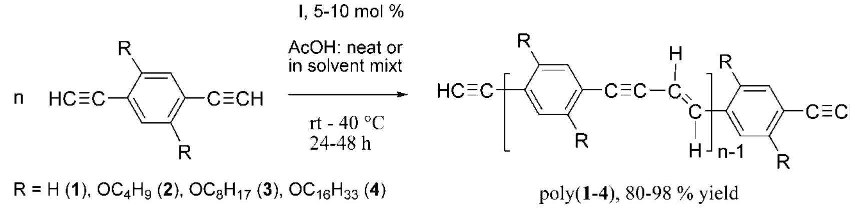
SCHEME 1. Representative C−C Coupling Reactions for the Synthesis of Poly(*p*-phenylenevinylene) and Poly(*p*-phenyleneethynylene) Derivatives



SCHEME 2. Regio- and Stereoselective One-Step Synthesis of (*E*)-Poly(*p*-phenyleneethynylenevinylene) Derivatives, Catalyzed by the [Ru(*p*-cymene)Cl$_2$]$_2$(I)/Acetic Acid System



CH=CH−). The few examples reported in the literature of poly(*p*-phenyleneethynylenevinylene) derivatives (PPEV)[5] obtained by this approach are based on the extension of the dimerization of terminal alkynes to aromatic diynes upon use of appropriate catalysts. According to the regio- and stereoselective features of the dimerization process,[6] materials with *E*, *Z*, or *gem*-vinylene linkages were obtained under catalysis by organometallic complexes of the platinum group,[7] of the lanthanide series,[8] or by a low-valent titanocene complex.[9]

We recently reported on a novel, simple, and *E*-stereoselective procedure for the dimerization of aromatic alkynes.[10] The reaction performed at rt in neat acetic acid, or in aqueous or nonaqueous mixtures, proceeds by ruthenium catalysis starting from the commercially available ruthenium complex [Ru(*p*-cymene)Cl$_2$]$_2$ (**I**), is compatible with aryl ring substituents of different electronic and steric features, and affords the corresponding (*E*)-1,4-diarylenyne products with high stereoselectivity. It is worth mentioning that the *E*/*Z* stereoisomeric ratio is a structural feature affecting the luminescence properties of PPV,[11] or the white electroluminescence of aromatic enynes.[12] In addition, the introduction of C-4 unsaturated bridges between aromatic moieties, with increased relative distance with respect to PPV and PPE, is currently seen as a convenient approach for favoring the coplanar arrangement of the adjacent repeat units and hence the π-delocalization and communication properties of the polymers.[13] We wish to report now on the application of our procedure to the regio and stereo controlled synthesis of a series of low molecular weight poly(*p*-phenyleneethynylenevinylene)s.

Results and Discussion

An outline of the reactions carried out in this work is shown in Scheme 2.

Synthesis and Characterization of (*E*)-Poly(*p*-phenyleneethynylenevinylene) P1. In order to ascertain the applicability of our dimerization procedure to a polyaddition process, we investigated first the reactivity of 1,4-diethynylbenzene (**1**). When a degassed solution of **1** in glacial acetic acid (0.18 M) was stirred under nitrogen in the presence of 10 mol % of complex **I**, precipitation of a brown powder was observed during the course of the reaction. A brown solid was collected after 48 h (80% yield), which was sparingly soluble in organic solvents, as expected for a polymeric derivative of **1**. Therefore, this material was characterized in the solid state by ^{13}C NMR and FT-IR spectroscopy. The assignments of the ^{13}C NMR signals were obtained by the CP-SPI sequence which allowed a full spectral editing of the CP-MAS spectrum. The benzene quaternary carbon atoms show signals at 122.9 and 135.9 ppm, the benzene CH atoms at 127.0 and 132.0 ppm, and the chain double bond carbons at 109.8 and 141 ppm. The internal −C≡C− groups display a broad signal at 92 ppm, while the terminal triple bond carbons appear at 84.2 (−*C*≡CH) and 80.5 (−C≡*C*H) ppm. The assignments were further confirmed by comparison with the literature data of (*E*)-1,4-diphenylbut-1-ene-3-yne in solution.[10] The FT-IR spectrum (KBr) shows the characteristic bands of *p*-phenylene groups at 1597, 1501, 1408,

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[5] Hybrid polymers of PPV and PPE, characterized by phenylene units interspaced with alternate double and triple bonds, e.g., −C≡C-Ar-C=C-Ar−, were also reported and indicated as poly(p-phenyleneethynylenevinylene)s. (a) Brizius, G.; Pschirer, N. G.; Steffen, W.; Stitzer, K.; zur Loye, H.-C.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2000**, *122*, 12435–12440. (b) Ramos, A. M.; Rispens, M. T.; Hummelen, J. C.; Janssen, R. A. J. *Synth. Met.* **2001**, *119*, 171–172.

[6] (a) Bustelo, E.; Dixneuf, P. H. In *Handbook of C-H Transformations*; Dyker, G., Eds.; Wiley-VCH: Weinheim, 2005; Vol. 1, Chapter II, pp 62−72. (b) Wakatsuki, Y. *J. Organomet. Chem.* **2004**, *689*, 4092–4109.

[7] Katayama, H.; Nakayama, M.; Nakano, T.; Wada, C.; Akamatsu, K.; Ozawa, F. *Macromolecules* **2004**, *37*, 13–17.

[8] Nishiura, M.; Hou, Z. *J. Mol. Catal. A* **2004**, *213*, 101–106.

[9] Ueda, M.; Tomita, I. *Polym. Bull.* **2004**, *51*, 359–364.

[10] Bassetti, M.; Pasquini, C.; Raneri, A.; Rosato, D. *J. Org. Chem.* **2007**, *72*, 4558–4561.

[11] (a) Son, S.; Dodabalapur, A.; Lovinger, A. J.; Galvin, M. E. *Science* **1995**, *269*, 376–378. (b) Liao, L.; Pang, Y.; Ding, L.; Karasz, F. E. *Macromolecules* **2001**, *34*, 6756–6760. (c) Pang, Y.; Li, J.; Hu, B.; Karasz, F. E. *Macromolecules* **1999**, *32*, 3946–3950. (d) Katayama, H.; Nagao, M.; Nishimura, T.; Matsui, Y.; Umeda, K.; Akamatsu, K.; Tsuruoka, T.; Nawafune, H.; Ozawa, F. *J. Am. Chem. Soc.* **2006**, *127*, 4350–4353.

[12] Liu, Y.; Nishiura, M.; Wang, Y.; Hou, Z. *J. Am. Chem. Soc.* **2006**, *128*, 5592–5593.

[13] Taylor, M. S.; Swager, T. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 8480–8483.

TABLE 1. Reaction Conditions and Yields of (*E*)-Poly(*p*-phenyleneethynylenevinylene) Derivatives P1−4, by Catalysis of [Ru(*p*-cymene)Cl_2]$_2$/AcOH at rt

product	substrate/M	solvent mixture	time/h	% yields	color
P1[a]	**1**/0.18	AcOH	48	80	brown ochre
P2[b]	**2**/0.09	AcOH/CH_2Cl_2 (3:2)	24	96(69)[c]	deep orange
P3[b]	**3**/0.09	AcOH/CH_2Cl_2 (3:2)	24	98(60)[c]	brown-red
P4[a,d]	**4**/0.018	AcOH/CH_2Cl_2/THF (1:1:2.5)	48	95(75)[c]	pale orange

[a] **I**, 10 mol %. [b] **I**, 5 mol %. [c] Extracted by Soxhlet and soluble in chlorinated solvents and in tetrahydrofuran. [d] 40 °C.

1014, 838 cm^{-1}, and of the internal and terminal triple bonds at 2184 and 2054 cm^{-1}, respectively. The presence of a strong absorption at 946 cm^{-1}, due to the CH out-of-plane bending of *trans*-CH═CH−,[2] and the absence of bands near 720 cm^{-1} which is characteristic of corresponding *cis*-CH═CH− moieties in poly(*p*-phenyleneethynylenevinylene),[14] indicate a material with high *E*-stereoselectivity. Therefore, these spectra of **P1** are consistent with a polymeric structure characterized by a benzene-enyne repeat unit with terminal triple bonds HC≡C-[(*p*-C_6H_4)-C≡C-CH═CH]$_n$-(*p*-C_6H_4)-C≡CH. A soluble fraction of **P1**, extracted with chloroform at rt, shows a UV−vis spectrum characterized by λ_{max} = 373 nm, which is red-shifted by 55 nm with respect to the monomeric enyne system of (*E*)-1,4-diphenylbut-1-en-3-yne (λ_{max} = 318 nm), and a fluorescence spectrum with λ_{em} values at 418 and 442 nm. Poly(*p*-phenyleneethynylenevinylene), containing a mixture of *E* and *Z* double bond moieties, was previously reported, as the result of a two-step sequence involving the palladium-catalyzed coupling polymerization of *p*-diiodobenzene, norbornadiene, and 1,4-bis(trimethylstannilethynyl)benzene (2 days, 100 °C), followed by a retro-Diels−Alder reaction carried out at 165 °C.[14] Our methodology yields a material with high *E* content under milder experimental conditions.

Synthesis and Solid-State Characterization of (*E*)-Dialkoxypoly(*p*-phenyleneethynylenevinylene)s P2−4. In order to improve the solubility in organic solvents and to impart different optical properties to the polymerization products, the coupling reactions were performed on diynes **2-4** bearing alkoxy chains of different length (OC_4H_9, **2**; OC_8H_{17}, **3**; $OC_{16}H_{33}$, **4**; Scheme 2), in the presence of 5−10 mol % of complex **I**. Dichloromethane or tetrahydrofuran, which are compatible with the dimerization reaction,[10] were used as cosolvents, and the initial concentration of **2**−**4** was 0.09 M or lower, in order to assist the solubility in the reaction mixture of both the diynes and the expected polymers. Since compound **4** bearing the long 16-carbon chains did not dissolve easily into acetic acid/dichloromethane mixtures, THF was added and the temperature raised to 40 °C in order to obtain a clear reaction solution. The reactions of **1**−**4** started from intense orange clear solutions from which solid material precipitated with time passing. Although the starting materials could no longer be detected by TLC after 5 h, the reactions were allowed to proceed further in order to favor the self-coupling of the initially formed oligomers. Powders of different colors were separated from the reaction mixture by filtration, with yields higher than 80%. Representative experimental conditions used in the preparation of **P1**−**4** are reported in Table 1.

The solid products **P2**−**4** were characterized by ^{13}C NMR and FT-IR measurements in the solid state, which were performed in order to assess the chemical composition of the bulk material. The ^{13}C CP-MAS spectrum of **P2** and the corresponding CP-SPI trace are shown in Figure 1 (including a template with atom numbering used throughout the text). The spectrum exhibits the double bond carbons at 108.8, 105.9 (C-9) and 134.5 (C-10) ppm, the internal triple bond carbons at 96.3 (C-7) and 90.9 (C-8) ppm, and those of the C≡CH groups as a broad signal at 82 ppm. The aryl carbon atoms are found at 154.6 and 150.7 ppm (C-1, C-4), 126.2 and 114.0 (C-5 and C-2), and 116 ppm (C-3, C-6 as shoulder). The FT-IR spectra of **P2**−**4** exhibit the (*E*)-CH═CH out of plane bending as a strong band at 955 cm^{-1} and the chain triple bonds absorption

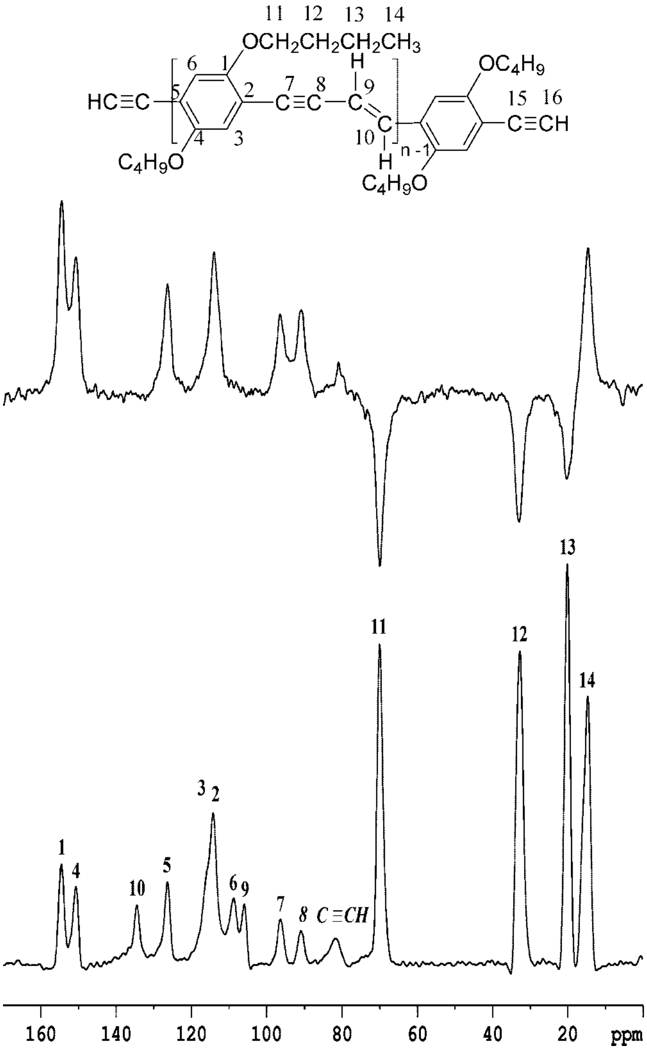

FIGURE 1. ^{13}C CP-MAS NMR spectrum (bottom trace) of P2. In the ^{13}C CP-SPI spectrum (top trace), the methine carbon resonances are zeroed, the methylene carbon resonances are inverted, and those due to quaternary and methyl carbon atoms are intense and positive.

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[14] Choi, C.-K.; Tomita, I.; Endo, T. *Macromolecules* **2000**, *33*, 1487–1488.

[15] In addition to the typical CO_2 absorptions, we could not detect any C═C stretching band at 2360 cm^{-1}, which is the value reported for the polyaddition products of 2,7-diethynyl-9,9-dioctylfluorene in ref 7.

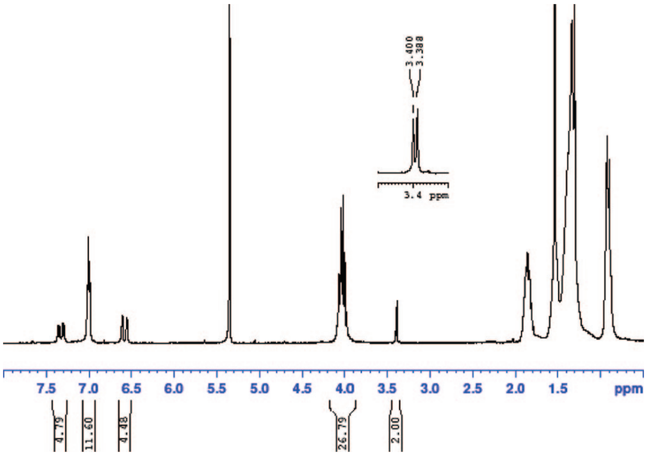

FIGURE 2. ^{1}H NMR spectrum of the soluble fraction of **P3**, obtained by chromatographic separation from chloroform/silica (300.13 MHz, in CD_2Cl_2).

at 2185 cm^{-1}.[15] Evident NMR signals or IR absorptions due to carbonyl groups, which accounted for consistent amounts of byproduct as acetate adducts or formal hydration of the triple bond in the dimerization of aryl alkynes,[10] were not observed in the ^{13}C NMR or FT-IR spectra of these unsaturated systems, indicating that the polymerization proceeds with higher chemical selectivity than the dimerization process. Although we have found this outcome rather surprising, it is not uncommon for polymerization reactions to exhibit improved yields and selectivity with respect to the model coupling reactions.[8,16]

We have performed a quantitative analysis of the ^{13}C CP-MAS spectrum of **P2**, by comparing the areas of the resonances at 96.3 or at 90.9 ppm due to the triple bond carbons C-7 and C-8, respectively, and the area of the broad resonance at 81.8 ppm, due to the four carbons of the two terminal C≡CH groups, thus obtaining an estimated average number of repeat units, $n_{\mathrm{av}} = 8$.[17]

Characterization and Solution Properties of (*E*)-Dialkoxy-poly(*p*-phenyleneethynylenevinylene)s P2−4. Soluble fractions of the polymers were obtained from the bulk materials either by simple solvent extraction at rt, continuous extraction with chloroform in a Soxhlet apparatus (24 h) or by separation with column chromatography. The Soxhlet extractions afforded bright colored powders, which were redissolvable in halogenated solvents, tetrahydrofuran and toluene, in 60−75% yields (Table 1). Chromatographic separations using chloroform as eluent gave fractions accounting for about 20% yields with respect to compounds **2**−**4**. The ^{1}H NMR spectrum of the eluted fraction of **P3**, reported in Figure 2, shows, in addition to the arylene and the alkoxy chain protons, two groups of superimposed doublets at δ 7.3 and 6.6 (^3J = 16 Hz) ppm, due to the two olefinic protons of the enyne repeat units (−Ar-CH═CH−), and two near singlets at δ 3.40 and 3.39 ppm, due to the C≡CH protons, while peaks attributable to either cis-substituted or vinylidene double bonds, expected around 6 ppm, were not detected.[7] Similar features were observed in the ^{1}H NMR spectra of the soluble fractions of **P2** and **P4**, indicating excellent *E*-stereoselectivity.

One regioselectivity constraint implicit in the dimerization-polyaddition process regards the sequential arrangement of the double and triple bonds of the enyne units between the aryl groups, which can give either a regioregular alternation, as in −(Ar-CH═CH-C≡C-Ar-CH═CH-C≡C)$_n$−, or a more random sequence depending on whether one terminal triple bond of a growing chain converts into a double or a triple bond upon further coupling.[7] The presence of two distinct well resolved and equally intense singlets in the ^{1}H NMR region of the alkynylic protons suggests a regular alternation of the three unsaturated moieties along the oligomeric chains of **P2**−**4**, yielding two different C≡CH terminal groups (Scheme 2). Alternatively, a rather broad or a multiple peak absorption would be expected.

The stereoselectivity issue regarding the olefin moieties in these polymeric compounds was properly addressed from analysis of the soluble materials obtained by Soxhlet extraction. The ^{1}H NMR spectra of these samples exhibit additional multiplet signals in the ranges 6.03−5.94 and 7.17−7.08 ppm, attributable to the (*Z*)-CH═CH-C≡C− protons, and accounting for relative *E*/*Z* ratios of 7.3, 15 and 6.2 for **P2** (*E* 88%), **P3** (*E* 94%), and **P4** (*E* 86%), respectively. Impurities corresponding to ca. 5% of the aromatic protons were found as broad signals near 8.2 ppm.

A high-field NMR study of **P2** dissolved at rt in 1,1,2,2-tetrachloroethane(TCE)-d_2 was also performed. A full characterization was obtained by means of 2D experiments, namely ^{1}H−^{1}H COSY, ^{1}H−^{13}C HSCQ, and ^{1}H−^{13}C HMBC, which allowed us to obtain the assignments of the skeleton carbon atoms, and, in addition, to confirm those of the ^{13}C solid state spectra (the full list of ^{1}H and ^{13}C chemical shifts, the corresponding long-range correlations and assignments are reported in the Supporting Information). The HMBC experiment displays the connection of different spin systems (Figure 3). In particular, the vinylic H-10 shows long-range couplings with the C-7 ethynyl carbon and the C-6 and C-4 carbons of the aromatic ring, whereas H-9 shows couplings with the aromatic C-5 quaternary carbon. The ethynyl CH hydrogen is long-range coupled with the aromatic C-2 and C-3 carbons of terminal aryl moieties.

The average degree of polymerization (n_{AV}) values and the number-average molecular weights (M_{n}) of **P2**−**4** were determined by ^{1}H NMR spectroscopy upon integration of the terminal ethynyl peaks with respect to the olefinic −C≡C-CH═ signal, and by gel permeation chromatography (GPC) using polystyrene as the standards. These values along with the optical data of the polymers are summarized in Table 2. In spite of the different molarity scale of the two techniques and of the overestimation by GPC resulting from structures with rigid-rod moieties,[7,18] the ^{1}H NMR and GPC measurements gave n_{AV} values in reasonable agreement. The MALDI-TOF spectrum of a sample of **P3** eluted from column chromatography showed different

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(16) (a) Note 17 in: Micozzi, A.; Ottaviani, M.; Giardina, G.; Ricci, A.; Pizzoferrato, R.; Ziller, T.; Compagnone, D.; Lo Sterzo, C. *Adv. Synth. Catal.* **2005**, *347*, 143–160. (b) Dutta, T.; Woody, K. B.; Watson, M. D. *J. Am. Chem. Soc.* **2008**, *130*, 452–453.

(17) Caution must be used in the quantitative evaluation of the intensity and/or the area of the C resonances of ^{13}C CP-MAS spectra. In fact, these values depend on the CP rates which can be different for different carbon atoms. In simple cases, the problem can be solved by investigating the CP dynamic which allows one to chose the suitable contact time for quantitative measurements. The CP dynamic of the P2 sample was investigated by performing a series of experiments with a contact time τ ranging from 0.05 to 22 ms and reporting the area of the C-7 and C-8 resonances as well as those of the terminal methine groups as a function of τ. The results (data not reported) suggest that a contact time of 15 ms allows one to obtain suitable integral values. Harris, R. K. Multinuclear Magnetic Resonance in Liquids and Solids - Chemical Applications; Granger, P., Harris, R. K., Eds.; *NATO ASI Series, Ser. C, Vol. 322*; Kluwer: Dordrecht, The Netherlands, 1990; p 291.

(18) Ricks, H. L.; Choudry, U. H.; Marshall, A. R.; Bunz, U. H. F. *Macromolecules* **2003**, *34*, 1424–1425.

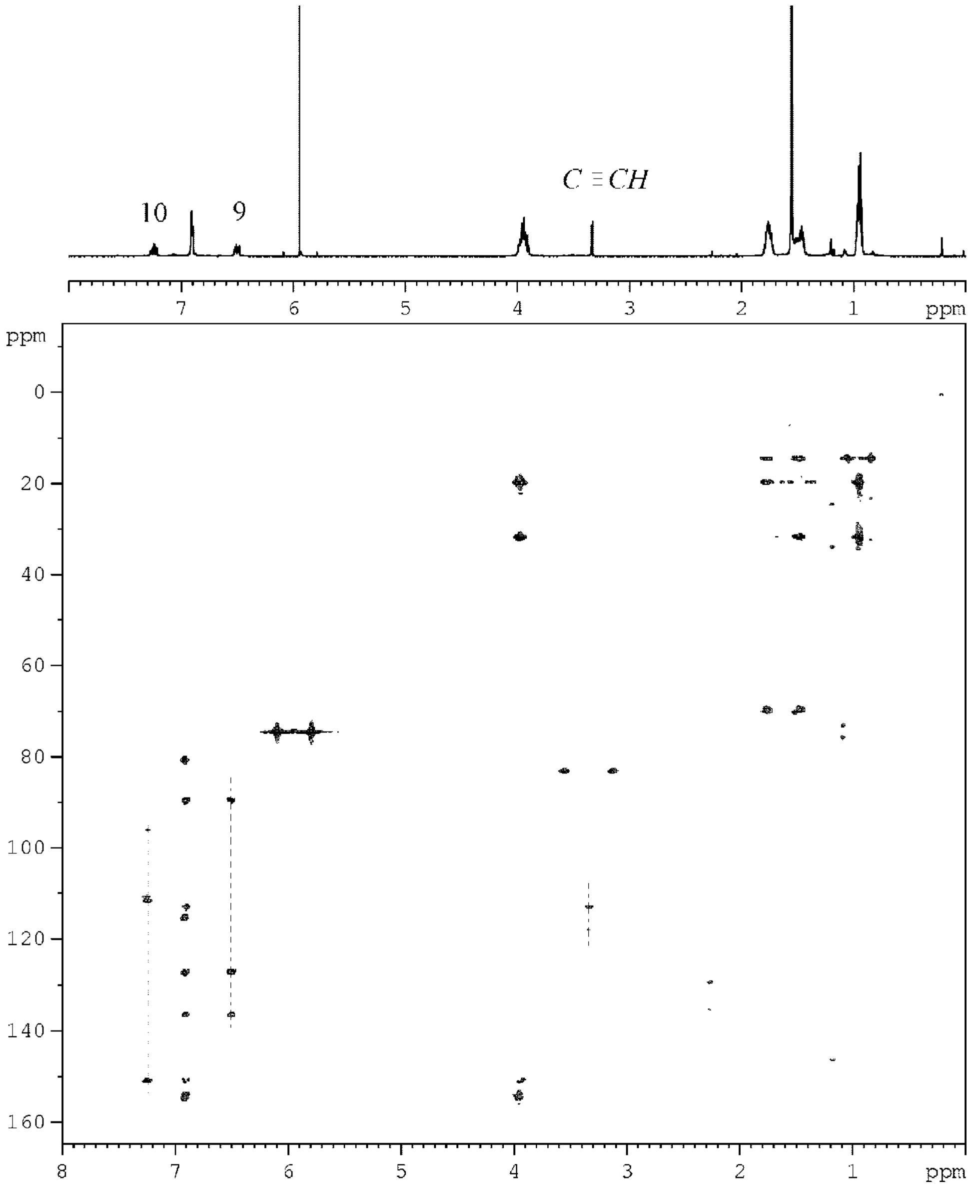

FIGURE 3. ^{1}H−^{13}C HMBC map of **P2** (TCE-d_2, 27 °C) and the corresponding 600.13 MHz ^{1}H NMR spectrum (top). The long-range couplings of H-16, H-10, and H-9 are highlighted with a dotted line. The soluble fraction of P2 was obtained by extraction and filtration in the deuterated solvent from the solid material, at rt.

TABLE 2. Molecular Weights and Optical Data of the PPEV Derivatives

entry	polymer	n_{AV}[a]	n_{AV}[b]	$M_{n,GPC}$[c]	M_w/M_n[d]	λ_{abs} (nm)[e]	λ_{em} (nm)[f]
1	**P1**	4.2	5.4	680	3.0	373	418, 442
2	**P2**	5.1	6.2	1670	2.5	432	474, 491
3	**P3**[g]	5.5	7.4	2840	2.6	431	475, 499
4	**P3**[h]	7.2	10.2	3920	2.6	448	510
5	**P4**	4.8	4.5	2720	2.1	432	495

[a] Average degree of polymerization, determined by ^{1}H NMR spectroscopy (CD_2Cl_2). [b] Average degree of polymerization determined by GPC based on polystyrene standards ($CHCl_3$, ca. 10^{-6} M). [c] Number-average molecular weight. [d] Molecular weight distribution, by GPC (M_w: weight-average molecular weight). [e] Wavelenght of absorption maximum ($CHCl_3$). [f] Wavelenght of emission maximum (<0.1 A; $CHCl_3$). [g] Reaction conditions: [**3**] = 0.064 M, AcOH/CH_2Cl_2 (2:1), 24 h. [h] Reaction conditions: [**3**] = 0.077 M, AcOH/CH_2Cl_2 (1:5), 3 h.

oligomers with increasing repeat unit from $n = 3$ (m/z = 1147.68) up to $n = 7$ (m/z = 2678.36). The molecular weights of these polymers appear comparable to those of the analogous (*E*)-rich polymer formed from 2,7-diethynyl-9,9-dioctylfluorene, by catalysis of the $Pd(OAc)_2$/1,3-dimesitylimidazolinium chloride/Cs_2CO_3 system,[7] while they are significantly smaller than that of the **P3** polymer obtained from **3** by catalysis of the praseodymium complex $[(C_5Me_5)_2PrCH(SiMe_3)_2]$.[8]

Upon changing the reaction conditions of substrate **3**, it was found that solvent mixtures with higher dichloromethane content (e.g., [**3**] = 0.09 M; acetic acid/dichloromethane, 1:5) caused the formation of gels after about 4 h of reaction, either at rt or at 35 °C. This material did not redissolve easily upon further heating and stirring, indicating the existence of stable self-assembled structures. Formation of gels is known to occur in solutions of PPEs[19] and to hinder the synthesis of soluble PPVs.[20] Although conditions favoring gel formation were avoided at this stage of the work, it is worth mentioning that a

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(19) Swager, T. M.; Gil, C. J.; Wrighton, M. S. *J. Phys. Chem.* **1995**, *99*, 4886–4893.

(20) Hsieh, B. R.; Yu, Y.; VanLaeken, A. C.; Lee, H. *Macromolecules* **1997**, *30*, 8094–8095.

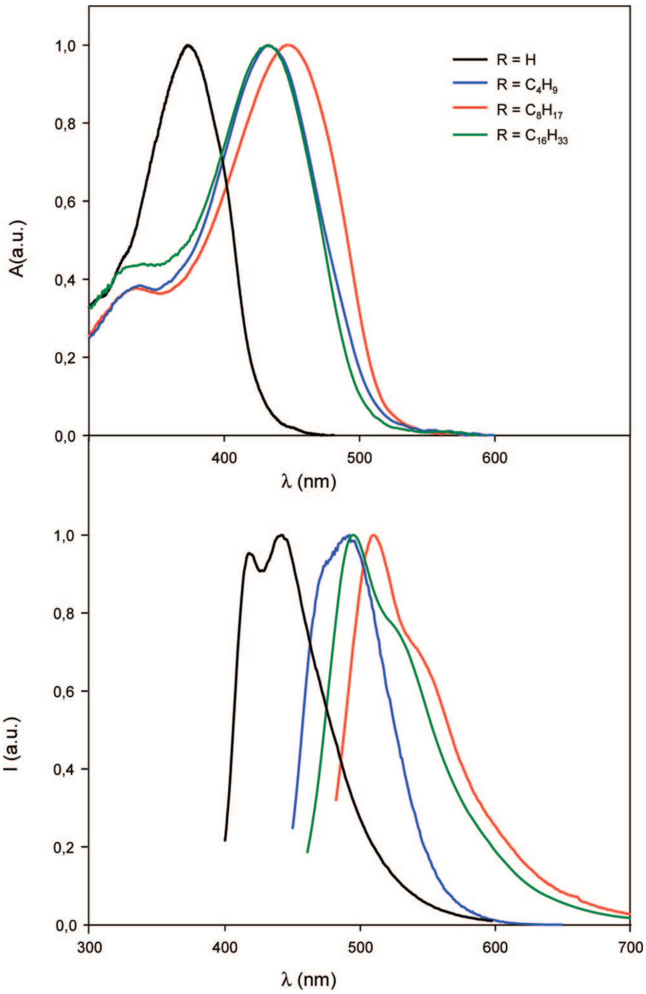

FIGURE 4. Normalized UV−vis (top) and emission (bottom) spectra of **P1** (black), **P2** (blue), **P3** (red), and **P4** (green) in air-equilibrated chloroform solutions at 25 °C.

sample obtained by pouring into methanol the reaction solution at 3 h reaction time and extracted with chloroform exhibited different n_{AV} value and UV−visible absorption maximum with respect to those obtained from the reaction performed in acetic acid/dichloromethane 2:1 (Table 2, entries 3 and 4).

The UV−visible absorption and fluorescence spectra of **P1−4**, obtained at rt in chloroform solutions, are shown in Figure 4. Beer's Law was maintained over the concentration range used in these measurements, indicating the absence of aggregation phenomena. Compared with the poly(*p*-phenylethynylenevinylene) **P1**, compounds **P2−4** presented significantly red-shifted absorption and emission maxima, due to the electronic effects of the alkoxy groups, as in the case of PPV polymers.[2] The absorptions correlate to some extent with the n_{AV} values of these polymers, while the emission bands, which exhibited two main features in the 468−474 and 491−510 nm ranges, were less sensitive and independent of the excitation wavelength. The emission bands of **P2−4** are red-shifted of 10−20 nm from those of analogous alkoxy substituted PPE, in spite of the higher n_{AV} (20−100) of the latter polymers,[19] while analogous PPV polymers show various features in the range 500−600 nm.[1b,2] The fluorescence quantum yield of the eluted fraction of **P3** was estimated by using quinine sulfate in 0.5 M H_2SO_4 as standard. The measured value of 40% is within the range of the quantum efficiencies reported in the literature for alkoxy substituted PPEs[19,21] and PPVs,[11b,c] and similar to those reported for the poly(aryleneethynylenevinylene)s derived from 2,7-diethynyl-9,9-dioctylfluorene.[7]

High molecular weight dialkoxypoly(phenyleneethynylenevinylene)s were reported by Ueda, obtained by polycondensation of diethynyl aromatic compounds with *trans,trans*-1,4-bis(β-bromovinyl)benzene, under the typical conditions of the palladium catalyzed Heck coupling procedure.[22] The weight-average molecular weights were in the range 30000−56000. These polymers exhibited $\pi-\pi^*$ absorptions in the visible region with maxima at 430−440 nm, and fluorescence spectra in solution with main bands at 490 nm. These data indicate that the π-conjugation of polymers **P2−4** is extended enough as to exhibit absorption and emission features similar to those of polymers with much higher molecular weights.

Formation and Activity of the Catalytic System. The dichloro(*p*-cymene)ruthenium(II) dimer is the starting material for a large variety of organometallic complexes, among which the most active in ruthenium based homogeneous catalysis.[23] It is a saturated 18 electron complex and as such unable to interact properly with organic substrates. Due to the lability of the μ-chloro bridges favoring the formation of monometallic derivatives, the complex can be efficiently used to generate in situ the active species of various organic catalytic processes.[24] In the present case, acetic acid promotes the solvolysis of the dimer and yields mono and bis-acetato complexes via ligand exchange processes.[25] The switch of the acetate ligands between bidentate or monodentate modes, corresponding to 18e or unsaturated 16e species, allows the metal center to bind the bis-ethynyl substrate and to initiate the catalytic cycle (Scheme 3).

On the basis of the accepted mechanism of the dimerization of terminal alkynes catalyzed by ruthenium complexes,[6,10] the polyaddition process of the diethynyl monomers **1−4** can be regarded as a step-growth polymerization reaction, in which the key C−C coupling step involves a ruthenium(II) complex bearing alkynyl and vinylidene moieties in mutually cis positions. The vinylidene ligand is formed via a 1,2-hydrogen shift in a π-bonded η^2-alkyne, while the alkynyl group arises by transmetalation with an acetate ligand.[6] The subsequent catalytic steps of this process, based on ruthenium(II) intermediates, can be depicted as shown in Scheme 4.

The 1−2 migration step (*i*) of the alkynyl ligand to the vinylidene α-carbon atom affords a σ-enynyl complex. The release of an oligomeric molecule and a ruthenium(II) species (*ii*) available for further catalytic steps occurs by transmetalation with acetic acid acting as proton donor.[10,26] The preference for vinylidene or alkynyl coordination modes between monomeric or oligomeric diethynyl molecules, or their relative migratory aptitudes in *i*, may affect the

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(21) Pizzoferrato, R.; Berliocchi, M.; Di Carlo, A.; Lugli, P.; Venanzi, M.; Micozzi, A.; Ricci, A.; Lo Sterzo, C. *Macromolecules* **2003**, *36*, 2215–2223.

(22) Venkatesan, D.; Yoneda, M.; Ueda, M. *React. Func. Polym.* **1996**, *30*, 341–352.

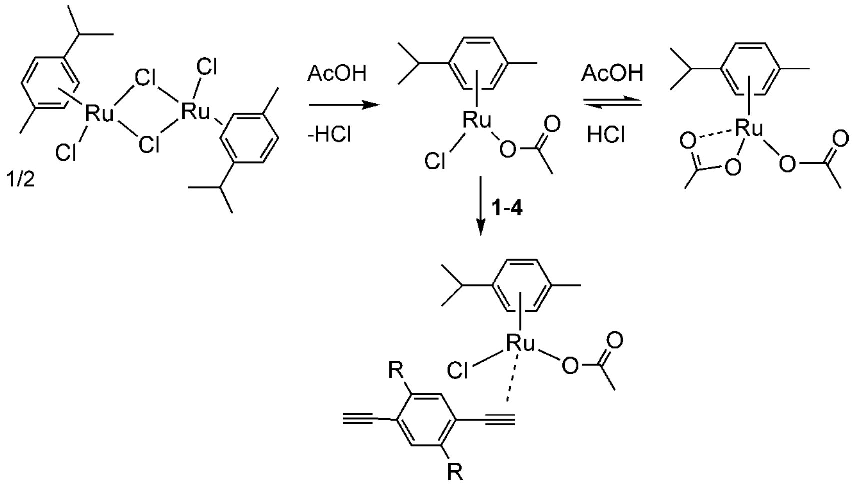
(23) Bruce, M. I. *Comprehensive Organometallic Chemistry III*; Mingos, D. M. P., Crabtree, R. H., Hiyama, T., Eds.; Elsevier: Oxford, UK, 2007; Vol. 6.

(24) For specific examples, see: (a) Transfer hydrogenation of ketones: Västilä, P.; Zaitsev, A. B.; Wettergren, J.; Privalov, T.; Adolfsson, H. *Chem. Eur. J.* **2006**, *12*, 3218–3225. Noyori, R.; Yamakawa, M.; Hashiguchi, S. *J. Org. Chem.* **2001**, *66*, 7931–7944. Palmer, M.; Walsgrove, T.; Wills, M. *J. Org. Chem.* **1997**, *62*, 5226–5228. (b) Hydrosilylation of alkynes: Na, Y.; Chang, S *Org. Lett.* **2000**, *2*, 1887–1889. (c) The Kharasch reaction: Quebatte, L.; Solari, E.; Scopelliti, R.; Severin, K. *Organometallics* **2005**, *24*, 1404–1406. (d) Olefin metathesis: Fürstner, A.; Ackerman, L. *Chem. Commun.* **1999**, *9*, 5–96.

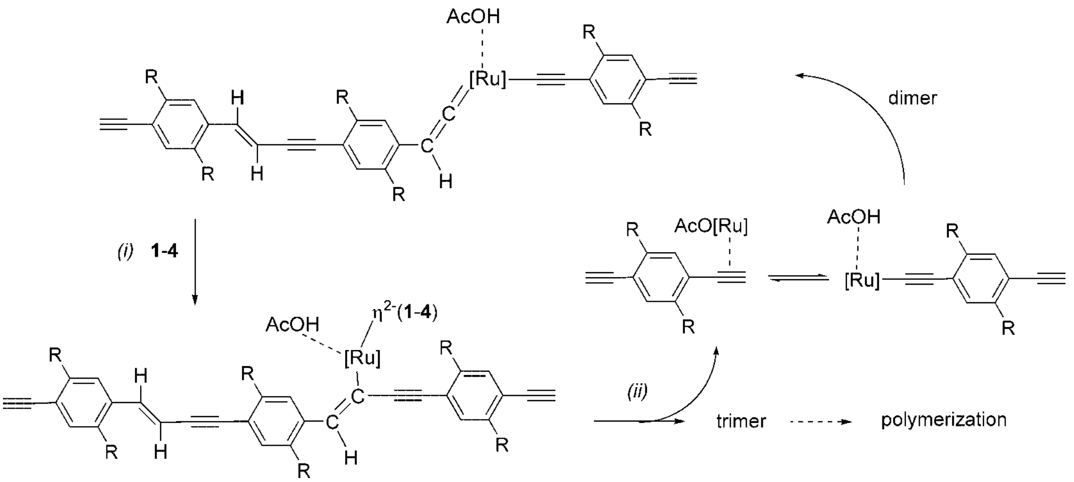
(25) Tocher, D. A.; Gould, R. O.; Stephenson, T. A.; Bennett, M. A.; Ennett, J. P.; Matheson, T. W.; Sawyer, L.; Shah, V. K. *J. Chem. Soc., Dalton Trans.* **1983**, 1571–1581.

(26) Melis, K.; De Vos, D.; Jacobs, P.; Verport, F. *J. Organomet. Chem.* **2002**, *659*, 159–164.

SCHEME 3. Activation Steps of Complex [Ru(*p*-cymene)Cl$_2$]$_2$ in Acetic Acid



SCHEME 4. Key Steps of the Polyaddition Catalytic Cycle Forming Trimeric Species ([Ru] = (*p*-Cymene)RuCl or Solvated RuCl)



regio and stereoregularity of the polyaddition C−C bond-forming process. It is worth mentioning that the other ruthenium based catalytic systems employed in the dimerization of terminal alkynes[6,10] or in a corresponding polyaddition process give preferentially enynes with *Z* geometry.[7]

Conclusions

We have shown that the dimerization of terminal alkynes catalyzed by the [Ru(*p*-cymene)Cl$_2$]$_2$/acetic acid system can be conveniently extended to the preparation of low molecular weight poly(phenyleneethynylenevinylene) derivatives, under mild conditions, in the absence of phosphine or amine additives. With the exception of the polymerization processes based on olefin or alkyne metathesis,[3b,4] this method represents the first case of ruthenium catalysis in which a commercially available metal source is employed for the synthesis of conjugated polymers. Acetic acid plays a role in both the activation and the propagation stages of this catalytic process. The extension of the procedure to the preparation of copolymers and the introduction of specific optically active moieties are in progress.

Experimental Section

Polymerization of 1,4-Diethynylbenzene (P1). [Ru(*p*-cimene)Cl$_2$]$_2$ (61 mg, 0.10 mmol) was introduced into a Schlenk tube equipped with a magnetic bar and a rubber septum, and three argon/vacuum cycles were performed under stirring. A solution of 1,4-diethynylbenzene (117.5 mg, 0.932 mmol) in acetic acid (5.2 mL) was degassed three times under vacuum/argon and then transferred via cannula into the tube. The amber solution (**I**, 1.9×10^{-2} M; **1**, 0.18 M) was kept under stirring at room temperature for 48 h, which caused consistent precipitation of a brown powder. The precipitate was allowed to deposit in the flask upon standing in the refrigerator. The mother liquor was separated via cannula from the precipitate, which was washed with small portions of acetic acid (×3), and once with pentane. The residue was dried under vacuum and collected as a yellow-brown solid (95 mg, yield 80%) showing spectroscopic data in agreement with the structure proposed for **P1**. ^{13}C CP-MAS NMR (50.13 MHz): δ 80.5 (C16), 84.2 (C-15), 95 (C7−8), 109.8 (C-9), 122.9, 127.0, 132.0, 135.9, 141 (C-10) ppm. FT-IR (KBr pellet, cm^{-1}): 3032, 2184 (C≡C), 2054 (C≡CH), 1979, 1640, 1597, 1501, 1408, 1384, 946 (*trans*-CH=CH), 838, 814, 547 cm^{-1}. **P1** decomposes above 185 °C. The elemental analyses gave lower carbon content than that calculated according to its molecular formula, which may be due to the coprecipitation of metal containing intermediates (Scheme 4). Due to the low solubility of the polymer, column chromatography, or Soxhlet extraction were not valuable methods for purification.

Polymerization of 2,5-Diethynyl-1,4-dibutyloxybenzene (P2). [Ru(*p*-cimene)Cl$_2$]$_2$ (30.5 mg, 0.0498 mmol) and 2,5-diethynyl-1,4-dibutyloxybenzene (246 mg, 0.912 mmol) were introduced into a Schlenk tube equipped with a magnetic bar and a rubber septum, and three argon/vacuum cycles were performed under stirring. A solution mixture of dichloromethane/acetic acid (10 mL, 2:3, v/v) was degassed rapidly under vacuum/argon and then transferred via cannula into the reaction tube. The amber solution (**I**, 4.5 × 10^{-3} M; **2**, 0.09 M) was kept under stirring at room temperature for 24 h. Consistent precipitation of a red-brown powder was observed during the course of the reaction. After TLC analysis (silica, hexane/dichloromethane, 1:1), the reaction mixture was filtered and the solid washed thoroughly with methanol, dried in air under suction and then under vacuum. The red solid (237 mg, yield 96%) showed spectroscopic data in agreement with the structure of **P2**. ^{13}C CP-MAS NMR (50.13 MHz): $\delta = 154.6$ (C-1), 150.7 (C-4), 134.5 (C-10), 126.4 (C-5), 114.2 (C-2), 108.8 (C-6), 105.9 (C-9), 96.3 (C-7), 90.9 (C-8), 81.8 (C-15,16), 70.0 (C-11), 32.7 (C-12), 20.1 (C-13), 14.6 (C-14) ppm. FT-IR (KBr pellet, cm^{-1}): 2957, 2866, 2185 (C≡C), 1638, 1494, 1467, 1412, 1384, 1207, 1039, 1010, 955 (*trans*-CH=CH−), 860, 744, 603. FT-IR ($CHCl_3$, cm^{-1}): 3300. ^{1}H NMR (sample extracted at rt in CD_2Cl_2, 300.13 MHz, 35 °C): $\delta = 7.37-7.28$ (m, 4H, −C*H*=CH-C≡C−), 7.04−6.98 (m, 10H, aromatic), 6.58 (broad d, $J = 16.26$ Hz) and 6.57 (d, $J = 16.36$ Hz) (superimposed doublets, 4H, −CH=C*H*-C≡C−), 4.12−3.98 (m, 20H, OCH_2), 3.40 and 3.39 (two s, 2H, C≡CH), 1.92−1.77 (m, 20H, OCH_2CH_2−), 1.66−1.50 (m, CH_2), 1.10−0.98 (m, 30H, CH_3) ppm. A portion of the solid material (61 mg) was extracted with chloroform in a Soxhlet apparatus, evaporated slowly from an acetone/chloroform solution and vacuum-dried, affording a bright red solid (42 mg). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 154.17 and 153.77−153.31 (C-1), 150.64 and 150.37 (C-4), 136.31−135.86 (C-10), 127.21 and 126.58 (C-5), 117.86−116.60 (C-3), 112.47, 111.09−108.99 (C-6,9), 95.42 (C-7), 89.21 (C-8), 82.28, 82.02, 80.23, 80.05 (C-15−16), 69.66−68.85 (C-11), 31.42−31.30 (C-12), 19.34−19.18 (C-13), 13.88 (C-14) ppm. A sample suitable for elemental analysis was obtained by column chromatography using chloroform as eluent. Mp: 121.5−122.8 °C. Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 78.88; H, 7.86.

Polymerization of 2,5-Diethynyl-1,4-dioctylyloxybenzene (P3). $[Ru(p\text{-cimene})Cl_2]_2$ (38.1 mg, 0.0622 mmol) and 2,5-diethynyl-1,4-dioctyloxybenzene (448 mg, 1.17 mmol) were introduced into a Schlenk tube equipped with a magnetic bar and a rubber septum, and three argon/vacuum cycles were performed under stirring. A solvent mixture composed of dichloromethane/acetic acid (13 mL, 2:3, v/v) was degassed rapidly under vacuum and transferred via cannula into the tube. The amber solution (**I**, 4.5 × 10^{-3} M; **3**, 0.09 M) was kept under stirring for 25 h at rt. The consumption of the starting material was checked by TLC analysis (hexane/dichloromethane, 1:1). The dark orange fine solid, which formed during the reaction, was collected by filtration, thoroughly washed with methanol, dried in air under suction, and vacuum-dried overnight. The brown red solid (438 mg, yield 98%) showed spectroscopic data in agreement with the structure of **P3**. ^{13}C CP-MAS NMR (50.13 MHz): $\delta = 154.5$ (C-1), 150.5 (C-4), 133.6 (C-10), 126.7 (C-5), 115.6 (C-2), 106.6 (C-6), 95.5 (C-7), 91.2 (C-8), 82.6−81.1 (C-15,16), 69.8 (C-11), 33.2 (C-12), 28.7, 26.1, 23.7 (C-13−C-16), 16.6, 15.1 (C-17,18) ppm. FT-IR (KBr pellet, cm^{-1}): 3314 (C≡C−H), 3054 (aromatic CH), 2924, 2852, 2184 (C≡C), 2106 (C≡CH), 1639, 1495, 1468, 1411, 1386, 1274, 1210, 1038, 955 (*trans*-CH=CH), 857, 726, 637, 600. Elution by column chromatography with chloroform as eluent afforded readily soluble material. Mp: 99.0−102.2 °C. ^{1}H NMR (CD_2Cl_2, 300.13 MHz, 35 °C): $\delta = 7.38-7.25$ (m, 4.5H, −C*H*=CH-C≡C−), 7.03−6.97 (m, 11H, aromatic), 6.58 (d, $J = 16.36$ Hz) and 6.57 (d, $J = 16.39$ Hz) (two superimposed doublets, 4.5H, −CH=C*H*-C≡C−), 4.10−3.95 (m, 22H, OCH_2), 3.40 and 3.39 (two s, 2H, C≡CH), 1.94−1.76 (m, 22H, OCH_2CH_2−), 1.46−1.25 (m, $-(CH_2)_5-$), 0.97−0.85 (m, 33H, CH_3) ppm. MALDI-TOF (*m/z*): calcd for $[C_{26}H_{38}O_2]_3H^+$ 1147.8694, found 1147.6869; calcd for $[C_{26}H_{38}O_2]_4$ 1529.1487, found 1529.8454; calcd for $[C_{26}H_{38}O_2]_5H^+$ 1912.4437, found 1911.9741; calcd for $[C_{26}H_{38}O_2]_6H^+$ 2294.7309, found 2295.0841; calcd for $[C_{26}H_{38}O_2]_7H^+$ 2677.0181, found 2678.3632. Anal. Calcd for $C_{26}H_{38}O_2$: C, 81.62; H, 10.01. Found: C, 79.40; H, 10.41. A portion of the solid material (100 mg) was extracted with chloroform in a Soxhlet apparatus, the solution concentrated slowly from acetone/chloroform and vaccuum-dried, yielding a bright red solid (60 mg). ^{13}C NMR ($CDCl_3$, 75.5 MHz): $\delta = 154.34-153.30$ (C-1), 150.36 (C-4), 136.05 and 135.89 (C-10), 117.79−116.58 (C-3), 112.36 and 111.01−108.96 (C-6,9), 95.17 (C-7), 89.37 (C-8), 82.31, 82.05, 80.24, 80.05 (C-15,16), 69.89−69.16 (C-11), 31.83 (C-12), 29.32, 29.25, 26.06, 25.96, 22.68 (C-13−C-17), 14.13 (C-18).

Polymerization of 2,5-Diethynyl-1,4-dihexadecyloxybenzene (P4). $[Ru(p\text{-cymene})Cl_2]_2$ (5.2 mg, 0.0085 mmol) and 2,5-diethynyl-1,4-dihexadecyloxybenzene (102 mg, 0.168 mmol) were introduced into a Schlenk tube. After argon/vacuum cycles were performed under stirring, a solvent mixture composed of dichloromethane/acetic acid (4 mL, 1:1, v/v) and previously degassed rapidly under vacuum was transferred via cannula into the tube. To obtain a clear solution, 5.0 mL of THF was added to the reaction mixture. The amber solution (**I**, 0.93 × 10^{-3} M; **4**, 0.019 M) was kept under stirring at 40 °C for 48 h. Consistent precipitation of an orange powder was observed with time passing. After TLC analysis (silica, hexane/dichloromethane, 1:1), an orange fine solid was collected by filtration, thoroughly washed with methanol, dried in air under suction, and allowed to dry under vacuum overnight (96 mg, yield 95%). ^{13}C CP-MAS NMR (50.13 MHz): $\delta = 154.6$ (C-1), 150.7 (C-4), 134.5 (C-10), 126.4 (C-5), 114.2 (C-2), 108.8, 105.9 (C-6), 96.3 (C-7), 90.9 (C-8), 81.8 (C15,16), 70.0 (C-11), 32.7 (C12), 20.1 (C-13 - C-25), 14.6 (C-26) ppm. FT-IR (KBr pellet, cm^{-1}): 2919, 2845, 2108, 1637, 1499, 1471, 1406, 1388, 1274, 1223, 1041, 1028, 957, 858, 718, 651, 628. ^{1}H NMR (CD_2Cl_2, 300.13 MHz, 35 °C, saturated solution extracted at rt): δ = 7.32 and 7.31 (two superimposed d, $J = 16$ Hz, 2.8H, C*H*=CH-C≡C−), 7.06- 6.94 (m, 7.6H, aromatic), 6.58 and 6.57 (two superimposed d, $J = 16.3$ Hz, 3.8H, CH=C*H*-C≡C−), 4.08−3.96 (m, 16H, OCH_2), 3.40 and 3.38 (two s, 2H, C≡CH), 1.94−1.82 (m, 16H, OCH_2CH−), 1.46−1.22 (m, $-(CH_2)_{13}-$), 0.91 (t, $J = 6$ Hz, 23H, CH_3) ppm. Elution by column chromatography with chloroform afforded readily soluble material. Mp: 84.1−86.9 °C. Anal. Calcd (%) for $C_{42}H_{70}O_2$: C, 83.10; H, 11.62. Found: C, 81.40; H, 12.88.

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Supporting Information Available: General experimental section, experimental procedures for the solid state and solution high field NMR measurements, charts of ^{1}H and ^{13}C NMR spectra of **P1−4** in solution and in the solid state, FT-IR spectrum of **P1**, table of ^{1}H and ^{13}C NMR assignments and long-range correlations of **P2**, and MALDI-TOF analysis of **P3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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