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Homo- and Copolymerization of Aromatic Diynes by Ruthenium/Acid-Promoted (RAP) Catalysis

Chiara Pasquini,[a,b] Ilaria Fratoddi,[b] and Mauro Bassetti*[a]

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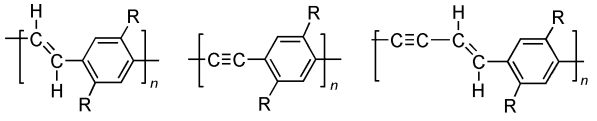
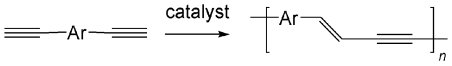
9,9-Bis(2′-ethylhexyl)-2,7-diethynylfluorene (**1**) or 1-(2′-ethylhexyloxy)-2,5-diethynyl-4-methoxybenzene (**2**) react in the presence of the [{RuCl(μ-Cl)(*p*-cymene)}]$_2$/AcOH catalytic system to yield the corresponding poly(aryleneethynylenevinylene) π-conjugated homopolymers, featuring the areneenyne repeat unit (Ar–C≡C–CH=CH–) and characterized by high regio- and stereoselectivity [(*E*) > 93 %]. The copolymerization of **1** and **2** affords poly-(*E*)-FL-ethynylenevinylene-*co*-(*E*)-MEH-ethynylenevinylene [FL = fluorene; MEH = 1-(2′-ethylhexyloxy)-4-methoxybenzene], as the first example of a random copolymer derived from the polyaddition process of aromatic diynes. The catalytic system of this atom-economic polyaddition process is formed in situ from the commercially available ruthenium dimer and acetic acid and promotes the C–C coupling at room temperature. The branched 2-ethylhexyl chains in the arene moiety assist the formation of polymers with degrees of polymerization in the range of 9–20 repeat units. The optical properties of the new polymers were studied in chloroform solution and in film and compared to those of the main classes poly(arylenevinylene) and poly(aryleneethynylene) conjugated polymers.

Introduction

Conjugated polymers (CP) are materials of choice in the field of organic electronics, due to their electroluminescent properties.[1] The development of efficient and selective synthetic methodologies is fundamental in order to achieve materials with advanced optical and mechanical properties.[2] Poly(*p*-phenylenevinylene) (PPV) and the related poly(*p*-phenyleneethynylene) (PPE) polymers are among those classes of CP initially developed and extensively used nowadays for applications in materials science.[1,2]



One interesting structural variation with respect to PPV and PPE is represented by the introduction of C_4 unsaturated carbon spacers between the aromatic units. Benefits are expected regarding the coplanar arrangement of the aromatic skeleton and hence the delocalization of electron density along the conjugated backbone, as in the case of the –C≡C–C≡C– bridge.[3] In this respect, poly(*p*-phenyleneethynylenevinylene)s (PPEVs), featuring arene-enyne repeat units (–C≡C–C=C–Ar), represent a relatively unexplored class of π-conjugated polymers. Following from the early reports on the preparation of poly(aryleneenyne)s by the palladium-catalyzed coupling of aromatic diynes with vinyl bromides,[4] the synthetic route adopted in recent years is the metal-catalyzed polyaddition reaction of the sole aromatic diynes, which allows a step-growth polymerization process to proceed on both sides of the reactive monomers, thus yielding the expected unsaturated chain.[5] The single C–C bond-forming step is based on the catalytic dimerization of terminal alkynes.[6] This approach is appealing due to its characteristics of atom economy and lack of waste materials, except for those derived from product or catalyst decomposition.



We recently reported on a novel catalytic system, which mediates the dimerization of aromatic terminal alkynes and affords 1,4-disubstituted enynes with high (*E*) stereoselectivity, through C(sp)–C(sp^2) bond formation. The catalytic system is formed in situ by the combination of the commercially available ruthenium complex [{RuCl(μ-Cl)(*p*-cymene)}]$_2$ (**I**) with acetic acid and is compatible with various cosolvents and with aryl substituents of different electronic properties.[7] The extension of the procedure to aromatic diynes, namely to 1,4-diethynylbenzene and to 1,4-dialkoxy-2,5-diethynylbenzene monomers (alkyl = C_4H_9,

[a] CNR, Istituto di Metodologie Chimiche, Sezione Meccanismi di Reazione, Dipartimento di Progettazione Molecolare, P.le A. Moro 5, 00185 Roma, Italy
Fax: +39-06-490421
E-mail: mauro.bassetti@uniroma1.it
[b] Department of Chemistry, University "La Sapienza", P.le A. Moro 5, 00185 Roma, Italy
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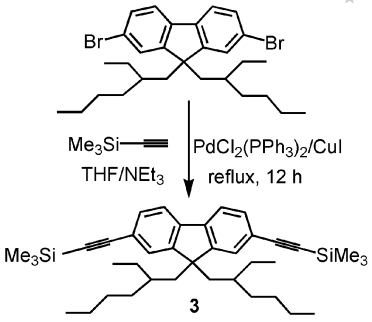
C_8H_{17}, $C_{16}H_{33}$), afforded a series of low molecular weight PPEVs.[8] The dialkoxy derivatives showed good solubility in organic solvents and optical properties analogous to those of the corresponding higher molecular weight polymers.[4b]

Due to the potential of this C–C bond-forming process for the synthesis of π-conjugated polymers, we intended to expand the scope of this catalytic system. Polymers incorporating fluorene or MEH [MEH = 1-(2′-ethylhexyloxy)-4-methoxybenzene] segments are known for their exceptional optoelectronic and processibility properties.[1] Poly(*p*-phenylene) (PP) and PPV systems based on these subunits have been extensively investigated and successfully used in optoelectronic devices,[9,10] whereas some examples are also known among the class of PPE polymers.[11,12] Broadening the structures of these polymers to include the enyne linkage between the aromatic moieties was then felt as a potential advancement in the field. Therefore, the compounds 9,9-bis(2′-ethylhexyl)-2,7-diethynylfluorene (**1**) and 1-(2′-ethylhexyloxy)-2,5-diethynyl-4-methoxybenzene (**2**) were chosen as the diyne starting materials for the synthesis of the corresponding PPEV homopolymers. Moreover, the presence of the 2-ethylhexyl substituents in **1** and **2** allowed us to test the compatibility of the polyaddition process with the presence of sterically hindered side chains, since only PPEVs with linear alkyl chains have been described so far.[4–6,13] Alkyl branching in the backbone of CP is known to affect both aggregation and electronic properties and to improve solubility and processibilty with respect to those polymers bearing linear alkyl or alkoxy side chains.[1,11,12a,14] Compounds **1** and **2** were also copolymerized in the presence of the $[\{RuCl(\mu\text{-}Cl)(p\text{-cymene})\}]_2$/AcOH catalytic system, thus affording the first example of a random copolymer obtained from the polyaddition process of two diethynyl substrates. The combination of two or more chromophores along the unsaturated backbone represents a powerful tool for band-gap and energy-level engineering of conjugated polymers, especially in the case of fluorene-based systems.[9d–9f,15]

Results and Discussion

The known compound 9,9-bis(2′-ethylhexyl)-2,7-diethynylfluorene (**1**)[9d] was obtained upon desilylation of 9,9-bis(2′-ethylhexyl)-2,7-bis(trimethylsilylethynyl)fluorene (**3**) by using sodium hydroxide in water/methanol/tetrahydrofuran (95%). The (trimethylsilyl)ethynyl derivative **3** was prepared by reaction of 2,7-dibromo-9,9-bis(2′-ethylhexyl)fluorene with (trimethylsilyl)acetylene under the conditions of the Sonogashira coupling (87%, Scheme 1).

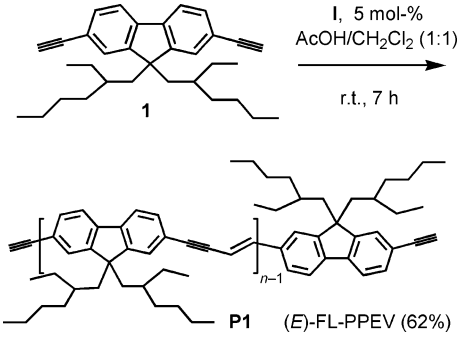
Complexity and multiple signals were observed in the ^1H and ^{13}C NMR spectra of these fluorene derivatives. Specifically, triple signals are exhibited by the aromatic carbon atoms and by the protons of the C≡CH (**1**) and C≡C$SiMe_3$ (**3**) groups, and split signals are given by the carbon atoms of the 2-ethylhexyl chains (see Experimental Section and Supporting Information). These features, which were not



Scheme 1. Synthesis of 9,9-bis(2′-ethylhexyl)-2,7-bis(trimethylsilylethynyl)fluorene (**3**).

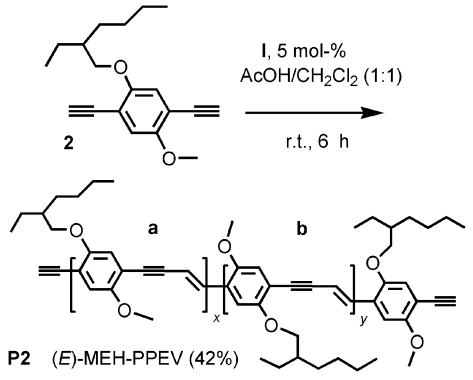
previously commented in the literature, are consistent with the existence of diastereoisomers arising from the presence of the two CH stereogenic centers in the alkyl chains of the fluorene moiety.

The polyaddition process requires the use of a cosolvent, with respect to the dimerization reaction performed in acetic acid, in order to avoid the precipitation of the firstly formed oligomers in the reaction mixture and to allow the extension of the ensuing chain in solution.[8] Test experiments performed in the presence of various cosolvents showed the compatibility of the **I**/AcOH catalytic system with tetrahydrofuran, dioxane, toluene, chloroform and dichloromethane. The reactions of **1** appeared slower in the cyclic ethers, as judged by analysis of the products at comparable reaction times, whereas the formation of a gel was observed in toluene and in chloroform. Raising the temperature to 35–40 °C reduced the stereoselectivity of the (*E*)-CH=CH composition in the polymer to below 90%. The reactions of **1** and **2** were performed in dichloromethane/AcOH in nearly equivalent volumes at room temp. (Schemes 2, 3, and 4). Number- and weight-average molecular weights (M_n and M_w) and molecular-weight distributions (M_w/M_w) of polymers **P1**–**3** were determined by gel permeation chromatography (GPC). Yields and characterization data of the polymers are reported in Table 1.

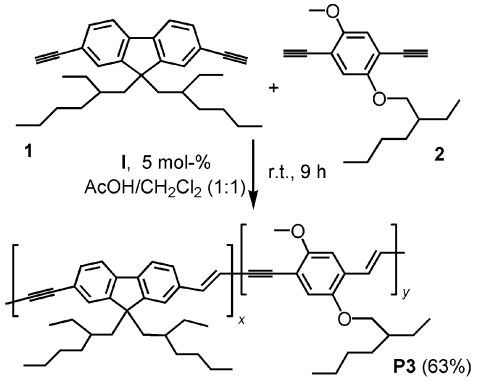


Scheme 2. Synthesis of (*E*)-polyfluoreneethynylenevinylene.

The diethynyl monomer **1** was allowed to react in the presence of complex $[\{RuCl(\mu\text{-}Cl)(p\text{-cymene})\}]_2$ for 7 h (Scheme 2). Longer reaction times resulted in the formation of stable gels from which soluble materials could no longer be extracted. The polymeric bulk material was obtained



Scheme 3. Synthesis of (*E*)-MEH-polyphenyleneethynylenevinylene (only one of the four isomers involving terminal **a** and **b** units is represented).



Scheme 4. Copolymerization of diynes **1** and **2** (end groups omitted for clarity).

Table 1. Characterization of poly(aryleneethynylenevinylene)s.

Polymer	Yield [%]	n_{AV}[a]	M_n[b] (M_w/M_n)[c]	(*E*)/(*Z*)/*gem*	T_d [°C][d]
P1	62	20	5400 (1.1)	93:3:4	366
P2	42	13	5830 (1.1)	>98:<1:<1	360
P3	63	9	5380 (1.2)	97:1:2	375

[a] Number-average repeat units, determined by ^{1}H NMR spectroscopy. [b] Number-average molecular weight, determined by GPC based on polystyrene standards. [c] Polydispersity index (number-average molecular weight/weight-average molecular weight). [d] Decomposition temperature (5% weight loss) determined by TGA.

from the reaction mixture by precipitation in MeOH, and isolated as a brownish powder (95%). The FTIR spectrum of the solid showed absorptions characteristic of the enyne moiety at 2109 (w, $\nu_{C\equiv C}$) and 952 [m, (*E*)-CH=CH] cm^{-1}.

Insoluble material in the bulk product was separated by filtration through silica using chloroform as eluent, and the **P1** polymer obtained in 62% yield, as wholly soluble material after reprecipitation from methanol. The ^{1}H NMR spectrum (CD_2Cl_2) displayed (i) the (*E*) geometry of the vinylene linkages [δ = 7.19 and 6.53 (d, ^3J = 16 Hz) ppm], (ii) the vinylic (*E*)/(*Z*)/*gem* isomeric ratio, by integration with the resonances at δ = 6.01 [^3J = 11.5 Hz, (*Z*)-CH=CH] and 5.85/5.58 (C=CH_2) ppm, and (iii) the average number of repeat units (n_{AV}), obtained as the *n*–1 value by integration of the enyne resonances with the proton signals of the terminal triple bonds at δ = 3.21 ppm (see Supporting Information).

The ^{13}C{^{1}H} NMR spectrum showed the signals of the internal triple bonds at δ = 92.9 and 89.4 (FL–C≡C) ppm, of the terminal C≡CH groups at δ = 84.3, and of the vinylic moieties (FL-CH=CH) at δ = 141.6 and 107.4 ppm, respectively, as well as the remaining carbon resonances. The presence of resolved ^{13}C NMR signals suggests that the [{RuCl(μ-Cl)(*p*-cymene)}]$_2$/AcOH system affords a polymer with high regioregularity. Although incorporation of substructures of the type (–C≡C–Ar–C≡C–CH=CH–Ar–CH=CH–)$_n$ cannot be excluded, large contributions from these should result in broadening of both the ^{1}H and ^{13}C NMR spectra.

The UV/Vis absorption and photoluminescence spectra of the fluorene-(*E*)-PPEV polymer, obtained in dilute chloroform solutions and in thin film, are shown in Figure 1. The absorption spectrum arises from the π–π* transition of the conjugate polymer backbone, with a λ_{max} value (414 nm, ε = 44500 M^{-1} cm^{-1}, chloroform) that is redshifted by 84 nm with respect to the diethynyl monomer **1**. The fluorescence spectrum possesses a vibronic structure, with emissions at 451 (λ_{max}), 482, and 520 (shoulder) nm. Comparisons of the optical data of this polymer, in solution and in film, with those of 9,9-dialkyl derivatives of polyfluorenes (PFs), of poly(fluoreneethynylene)s, and of poly(fluorenevinylene)s are reported in Table 2.

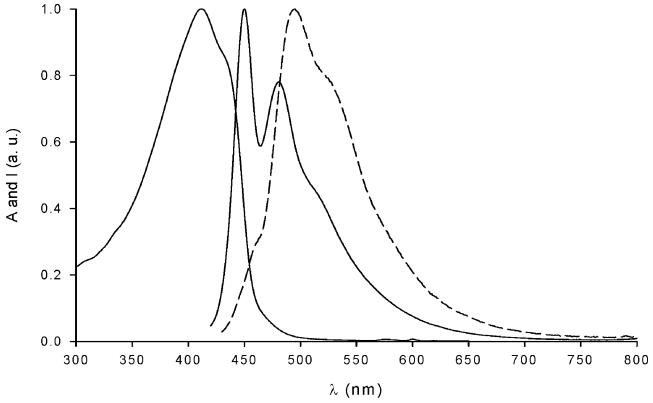


Figure 1. Normalized absorption and photoluminescence (λ_{exc} = 410 nm) spectra of (*E*)-FL-PPEV (**P1**) in chloroform solution (6.6×10^{-7} M, solid line) and film (dashed line).

Table 2. Optical data of fluorene-based polymers.[a,b]

Polymer	λ_{abs} ($CHCl_3$)	λ_{abs} (film)	λ_{ems} ($CHCl_3$)	λ_{ems} (film)
PF[c]	386	372	418,[d] 440, (475)	426,[d] 446, 485
PPE[e]	394, 412[d]	392, 416	426,[d] 446	434,[d] 452
PPV[f]	417	419	463	478, 507,[d] 543
PPEV **P1**	414, (440)[g]	415, (440)	451,[d] 482, (520)[g]	458, 495,[d] (526)

[a] Values in nm. [b] Numbers in parentheses represent the location of shoulders. [c] Ref.[9a,9b] [d] λ_{max}. [e] Ref.[11] [f] Ref.[9e] [g] See also ref.[5a]

The data show progressive redshifts on going from PF to PPE and to (*E*)-PPEV, which may be due to improved π-overlap upon increased relative distance between the fluorene moieties, whereas the PPV polymers exhibit absorption and emissions at the longest wavelength. The redshifts in the emission spectra of the thin films are known to arise from the interchain contacts in the solid state.[9b,11]

1-(2′-Ethylhexyloxy)-2,5-diethynyl-4-methoxybenzene (**2**) reacted in the presence of the **I**/AcOH catalytic system to afford the desired polymer **P2** (Scheme 3), obtained as wholly soluble material in 42% yield.[16] The presence of insoluble material, which accounts for the difference with respect to the yield of the bulk (92%), may be due to reduced solubility upon increasing chain length, as we observed for the dialkoxy derivatives,[8] and as reported for those PPE polymers exhibiting a solubility limit around 20 repeat units.[11,12a,14a] Furthermore, the formation of stable gels, which occurred upon increasing the reaction time and/or the relative volume content of the halogenated solvent vs. acetic acid (e.g., dichloromethane/AcOH, 5:1, v/v) indicates the attainment of supermolecular networks by interchain cross-linking, a common phenomenon in the synthesis or in the manipulation of the MEH-PPV polymers as well.[10b,17]

The FT-IR spectrum of **P2** exhibited the absorption bands of the H–C≡C end groups at 3310 and 2183 (w) cm^{-1}, of the arene at 1604 cm^{-1}, and of the (*E*)-CH=CH segment at 954 cm^{-1}. Typical features in the ^1H NMR spectrum are the pseudo doublet of (*E*)-CH=CH groups at δ = 6.61 (^3J = 16 Hz) ppm and four singlets at δ = 3.43, 3.42, 3.41, and 3.39 ppm, due to the terminal triple bonds. The observed resonances are in agreement with the presence of four different C≡CH groups, which can be envisaged in the polymeric structure depicted in Scheme 3 by assuming a random alternation of the isomeric **a** and **b** repeat units ($x + y = n–1$).[18] Signals attributable to double bonds of either (*Z*) geometry or *gem* configuration, expected in the range δ = 6.2–5.8 ppm, are not appreciable above the spectrum baseline, which indicates a material with high (*E*) stereoselectivity (>98%).

The UV/Vis spectrum of **P2** in chloroform solution is characterized by a broad absorption at λ_{max} = 452 nm (ε = 19560 $M^{-1} cm^{-1}$). The fluorescence spectrum shows an emission maximum at 513 nm and a vibronic component at 542 nm (Figure 2). These values are redshifted compared to those of the symmetric dialkoxy derivatives (λ_{abs} = 432–448 nm; λ_{ems} = 491–510 nm), an effect that is associated with the longer chain length of the MEH-enyne polymer.[8] The corresponding MEH-PPE polymer, with comparable molecular weight characteristics (n_{AV} = 13, M_n = 6600), exhibits blueshifted values in both absorption and emission (Table 3).[12a] MEH-PPV polymers absorb near 500 nm and emit at 558 nm in chloroform.[19] Since the PPVs are characterized by much higher molecular weights, this comparison may not be viewed as strictly pertinent. However, it is worth noting that the chains of MEH-PPVs are known to consist of hundreds of quasi-localized chromophores with conjugation lengths ranging from 10 to 17 repeat units, due to the presence of tetrahedral carbon defects.[20] Therefore, the fluorescence emission bands of the MEH-enyne polymer **P2** fall into an intermediate range between the corresponding PPV and PPE polymers, a feature that may be useful for the fine tuning of the optical properties. It is worth noting that **P2** is characterized by a significantly higher Stokes' shift with respect to both PPE and PPV.

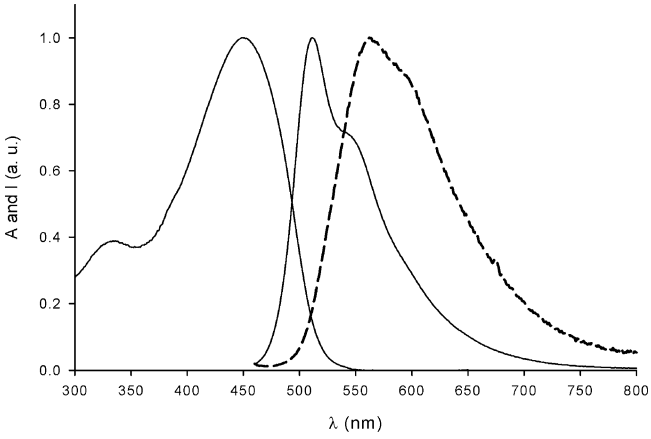


Figure 2. Normalized absorption and photoluminescence (λ_{exc} = 450 nm) spectra of (*E*)-MEH-PPEV (**P2**) in chloroform solution (1.25×10^{-6} M, solid line) and film (dashed line).

Copolymers composed of fluorene subunits in the conjugated backbone and incorporating a second chromophore display the most interesting optoelectronic properties.[9c–9f,15] In order to test the potential of this methodology for the synthesis of copolymers, of which there are no previous examples based on the polyaddition process, compound **1** was allowed to react in the presence of 20 mol-% of **2** (Scheme 4). The soluble random copolymer (*E*)-FL-PPEV-*co*-(*E*)-MEH-PPEV (**P3**) was obtained in 63% yield and characterized by FT-IR, ^1H and ^{13}C NMR, GPC, and MALDI-TOF data.[21]

Table 3. Optical data of MEH-based polymers.[a,b]

Polymer	λ_{abs} ($CHCl_3$)	λ_{abs} (film)	λ_{ems} ($CHCl_3$)	λ_{ems} (film)	Stokes' shift [cm^{-1}][c]
PPE[d]	442	–	477	–	1930
PPV	494[e]	505[f]	558 (607) [e]	590[f]	2322
PPEV **P2**	452	446	513 (542)	562	2631
PPEV **P3**	417	410	(450), 482	534	3230

[a] Values in nm. [b] Numbers in parentheses represent the location of shoulders. [c] Calculated from the λ_{max} values, in chloroform. [d] Ref.[12a] [e] Ref.[19] [f] Ref.[10d]

Incorporation of the dialkoxy moiety into the fluorene backbone is evidenced by the phenylene IR band at 1605 cm^{-1}, by the ^1H and ^{13}C NMR signals of the OCH_2 and OMe groups, at δ = 3.95 (^1H) and 72.1, 71.6 (^{13}C) ppm, as well as by a double set of ^{13}C NMR resonances in the region of the alkyl chain carbon atoms. The integration of the NMR signals indicates a content of the MEH unit (ca. 30%) higher than that expected from the molar ratio employed in the synthesis, suggesting the incorporation of the dialkoxy fragment in the longer oligomers and the loss of material with larger fluorene content in the reaction washings, which were in fact yellowish. The MALDI-TOF spectra clearly indicate the combination of the two components in **P3** and highlight the formation of the shorter and more volatile cooligomers in 3:1, 4:1, 5:1 and 3:2 molecular ratios of **1/2**.

The most interesting evidence of the presence of the two chromophores along the unsaturated chain comes from the observation of the absorbance/fluorescence spectra of **P3** in chloroform (Figure 3, Table 3). Whereas the absorption spectrum (λ_{max} = 417 nm, ε = 23760 $M^{-1}cm^{-1}$) exhibits only a small redshift with respect to **P1**, the fluorescence spectrum is markedly different from that of the fluorene-enyne homopolymer and is characterized by an emission maximum at 482 nm.

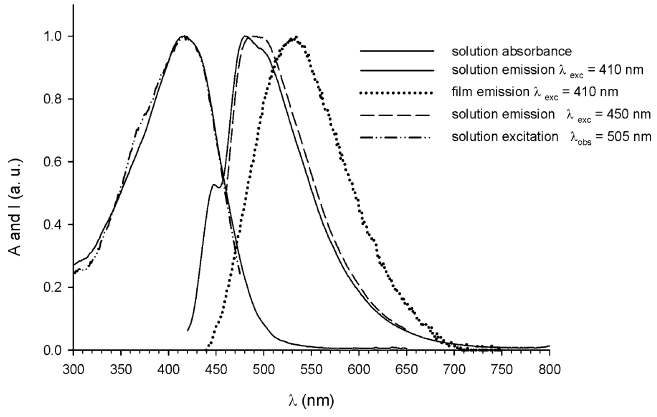


Figure 3. Normalized absorption and photoluminescence spectra of poly-(*E*)-FL-PPEV-*co*-(*E*)-MEH-PPEV (**P3**) in chloroform solution (9.1×10^{-7} M) and film (dashed line).

Accordingly, the Stokes' shift changes from $\Delta\tilde{\nu}$ = 1980 cm^{-1} in the homopolymer **P1** to $\Delta\tilde{\nu}$ = 3230 cm^{-1} in **P3**. The emission spectrum is the result of an efficient resonance energy transfer process occurring along the copolymer backbone as highlighted by the minor spectral variations observed upon changing the excitation wavelength.[22] Energy transfer from the high band gap fluorene moieties to the small band gap MEH subunits was observed in films of poly(fluorenevinylene)-*co*-(MEH-phenylenevinylene)s copolymers, with significant implications for the properties of light-emitting devices.[9e] Indeed, the energy transfer displayed by the **P3** copolymer in dilute solution has a pure intramolecular nature, devoid of any interference from intermolecular interactions typical of the solid state.

The number-average degrees of polymerization (n_{AV}) of **P1**–**3**, as determined by end group analysis of the ^1H NMR spectra, fall in the range 9–20, indicating a larger extent of polymerization with respect to the polymers derived from the 1,4-dialkoxy-2,5-diethynylbenzene derivatives, whose n_{AV} data varied in the range 4–7, under analogous reaction conditions.[8] This indicates that the lower symmetry of the aromatic moieties in **1** and **2** enhances the solubility of the ensuing polymer in the reaction medium, thus assisting more extensive chain formation.[23] One apparent feature of these polymers is the low polydispersity of both the soluble fractions extracted at room temp. from the bulk, with M_w/M_n values in the range 1.1–1.4, and of the materials filtered through silica, in the range 1.1–1.2, whereas the M_w/M_n values of the dialkoxy-PPEVs were in the range 2.1–3.0,[8] as typical cases of stepwise polymerization processes.[9a,9d,9e,11,24] Although the GPC peaks of **P1**–**3** are rather narrow, in particular in the high molecular weight region, it is possible that the observed values arise from an underestimation of the molecular weight distribution. Such cases are described in detail in the literature and are known to arise from changes in chain conformation or relative solubility of the analyte polymer with respect to the polystyrene standards,[25] properties which may have been affected by the presence of the branched alkyl chains in **P1**–**3**. These aryleneenyne polymers show thermal stability, as assessed by TGA, with decomposition temperatures (T_d, at 5% weight loss) in the range 360–375 °C (Table 1), which are comparable to those of the poly(fluoreneethynylene)s (388 °C, M_w = 19200)[9d] and of the poly(fluorenevinylene)-*co*-(MEH-phenylenevinylene)s (355–415 °C).[9e]

Conclusions

9,9-Bis(2′-ethylhexyl)-2,7-diethynylfluorene (**1**) and 1-(2′-ethylhexyloxy)-2,5-diethynyl-4-methoxybenzene (**2**) served to test the compatibility of the catalytic polyaddition process with the presence of sterically hindered side chains in the monomer. Homopolymers and the first copolymer of aromatic diynes were obtained from the [{RuCl(μ-Cl)(*p*-cymene)}]$_2$/AcOH catalytic system under mild conditions. The fluorene- and MEH-based PPEVs display optical properties different and complementary to those of the main class PPV and PPE polymers. We propose this ruthenium acid promoted (RAP) polyaddition process featuring a *one-metal* catalyst as a simple and stereoselective methodology for the synthesis of conjugated (*E*)-aryleneenynes.

Experimental Section

General: The ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance II 300 spectrometer operating in the FT mode at 300.13 MHz (^1H) and 75.5 MHz (^{13}C), respectively. The ^1H chemical shifts are referenced to the residual proton peaks of $CDCl_3$ at δ = 7.27 ppm and of CD_2Cl_2 at δ = 5.35 ppm (vs. TMS). The ^{13}C resonances are referenced to the central peak of $CDCl_3$ at δ = 77.0 ppm and of CD_2Cl_2 at δ = 53.4 ppm, vs. TMS. The FT-IR spectra were recorded with a Nicolet 510 or a Bruker Vertex 70

spectrometer as neat thin films deposited from chloroform or dichloromethane solutions on KBr or ZSM5 disks. Number- and weight-average molecular weights (M_n and M_w) and molecular weight distributions (polydispersity index, PDI = M_w/M_w) were determined by gel permeation chromatography (GPC) with an Perkin–Elmer instrument equipped with a UV detector set at 390 nm. Chloroform (HPLC grade) was used as eluent, pumped at a flow-rate of 0.8 mL min^{-1} by a binary LC pump, and monodispersed polystyrene standards were used for calibration. The absorption and photoluminescence spectra were recorded with a Perkin–Elmer Lambda18 UV/Vis spectrophotometer and a Horiba Jobin Yvon Fluoromax-4 spectrofluorometer, respectively, in dilute chloroform solution (< 0.1 A) at 25 °C. Absorption and photoluminescence spectra were recorded in freshly prepared chloroform solutions in the concentration range of (6–9)×10^{-7} M (< 0.1 A) at 25 °C. Concentrations of **P1** and **P2** are given with respect to the repeat unit, concentrations of **P3** are given with respect to a molecular weight calculated on the basis of the ratio observed in the ^{1}H NMR spectrum for the relative amounts of the two repeat units (FL/MEH = 7:3). The absorbance and the photoluminescence properties of **P3** were tested in a control experiment against a solution of equal concentration of chromophores prepared by mixing **P1** and **P2** in this ratio (see Supporting Information). The molar extinction coefficients (M^{-1} cm^{-1}) were measured in chloroform solutions in the concentration range of (0.6–15)×10^{-6} M, with ± 5% experimental error. The thin films used in the absorbance and fluorescence measurements were spin-deposited (300 rpm) onto quartz plates from chloroform solutions (1 mg/1 mL). Thermogravimetric analyses (TGA, 10 °C/min) were performed with a Stanton Redcroft model STA-781 analyzer under N_2 (0.05 L/m). Elemental analyses were provided by the "Servizio di Microanalisi" of the Department of Chemistry. High-resolution ESI-TOF mass spectra were obtained with a Waters Micromass instrument from a methanolic solution of compound **3** in the presence of silver nitrate. MALDI-TOF-MS measurements were performed with an Applied Bio-System instrument equipped with a 337 nm nitrogen laser for ion desorption. Samples were prepared by adding a solution of **P1**–**3** (chloroform, 1.6 × 10^{-4} M, 1 mL) to a saturated solution of the Dithranol matrix (toluene, 1 mL) loaded on the target, and then transferred to the mass spectrometer for analysis (3 ns pulse width, 68% grid voltage, delay time 100 ns). Mass assignments were performed on un-manipulated spectra, obtained in the reflective mode, for optimal correlation between observed and calculated mass. Flash chromatography was performed on silica gel 60 (0.040–0.063 mm) for the purification of compounds **1**–**3**, and on silica gel 60 (0.063–0.200 mm) in the filtration of **P1**–**3**. Dichloromethane was distilled from P_2O_5, and THF from Na/K alloy under argon. Glacial acetic acid (reagent grade) was used without further purification. 1-(2′-Ethylhexyloxy)-2,5-diethynyl-4-methoxybenzene (**2**) was prepared according to published procedures.[26] The polymerization reactions were carried out under argon by using Schlenk-line techniques.

9,9-Bis(2′-ethylhexyl)-2,7-bis(trimethylsilylethynyl)fluorene (3): 2,7-Dibromo-9,9-bis(2′-ethylhexyl)fluorene (3.0 g, 5.5 mmol), CuI (0.217 g, 1.14 mmol) and $PdCl_2(PPh_3)_2$ (0.53 g, 0.55 mmol) were placed in a Schlenk tube, and vacuum/Ar cycles were performed. After addition of THF (3 mL), triethylamine (5.5 mL) and (trimethylsilyl)acetylene (1.29 g, 13.1 mmol), the mixture was stirred at reflux overnight. The volatile components of the mixture were removed under vacuum, and the residue was dissolved in dichloromethane. The organic phase was washed with an aqueous solution of ammonium chloride, dried with sodium sulfate, filtered and concentrated. Purification by chromatography (SiO_2; hexanes) afforded the desired product as a yellowish oil (2.8 g, 87% yield), which crystallized upon standing, m.p. 60–62 °C. FT-IR (neat): $\tilde{\nu}$ = 3026, 2959, 2925, 2858, 2156, 1463, 1421, 1378, 1249, 887, 844, 759, 701, 647 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε) = 309 (40070), 326 (52270), 341 (82900 M^{-1} cm^{-1}) nm. Photoluminescence ($CHCl_3$, λ_{exc} = 303 nm): λ = 343, 362, 377 (sh) nm. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 7.61–7.58 (m, 2 H, aromatic), 7.49–7.42 (m, 4 H, aromatic), 1.95 (br. d, J = 5.5 Hz, 4 H, FL-CH_2CH), 0.98–0.63 (m, 18 H, alkyl chains), 0.53 (br. t, J = 7.1 Hz, 12 H, CH_2CH_3), 0.283, 0.274, 0.267 (s, 18 H, $SiMe_3$) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 150.9, 150.84, 150.77, 140.84, 140.8, 140.7, 131.2, 131.0, 130.9, 127.5, 127.4, 127.3, 121.5, 121.40, 121.36, 119.7, 106.0, 94.0, 54.8, 44.4, 34.6, 33.3, 33.2, 27.91, 27.89, 27.1, 27.0, 22.7, 14.1, 10.4, 10.3, 0.0 ppm. ESI-TOF-MS: calcd. for $C_{39}H_{58}AgSi_2$ 691.3125; found 691.3085 [M + Ag$^+$].

9,9-Bis(2′-ethylhexyl)-2,7-diethynylfluorene (1): The desilylation reaction was performed according to a protocol described in the literature.[27] An alkaline water/alcoholic mixture (0.6 mL of 5 M aqueous NaOH and 1.8 mL of methanol) was added dropwise to a stirred solution of 9,9-bis(2′-ethylhexyl)-2,7-bis(trimethylsilylethynyl)fluorene (**3**, 0.73 g, 1.25 mmol) in THF (1.8 mL). The mixture was stirred at room temp. for 2 h. Then water was added, and the mixture was extracted with hexanes. The organic layers were washed to neutrality and dried with sodium sulfate. The solution was filtered and the solvent removed under vacuum at room temp. The residue was purified by chromatography (SiO_2; hexanes) to afford the desired product as a colourless oil (0.52 g, 95% yield). FT-IR (neat): $\tilde{\nu}$ = 3305, 3065, 3031, 2958, 2916, 2107, 1897, 1785, 1608, 1462, 1414, 1378, 1216, 892, 823, 762, 650, 609 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε) = 303 (33600), 316 (26800), 323 (26300), 330 (49400 M^{-1} cm^{-1}) nm. Photoluminescence ($CHCl_3$, λ_{exc} = 303 nm): λ = 404, 421, 436 (sh) nm. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 7.69–7.61 (m, 2 H, aromatic), 7.55–7.45 (m, 4 H, aromatic), 3.13, 3.12, and 3.11 (s, C≡CH), 1.96 (br. d, J = 7.4 Hz, 4 H, FL-CH_2CH), 0.99–0.44 (m, alkyl chains) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 150.91, 150.86, 150.80, 141.1, 141.05, 141.01, 131.2, 131.14, 131.08, 127.74, 127.66, 120.5, 120.4, 120.3, 119.9, 84.52, 84.46, 84.40, 54.9, 44.4, 34.6, 33.52, 33.50, 27.98, 26.97, 22.7, 14.0, 10.3 ppm.

Synthesis of Polymers, General Procedure: The diethynyl substrate and [{RuCl(μ-Cl)(*p*-cymene)}]$_2$ (**I**) (5 mol-%) were introduced into a Schlenk tube, degassed by argon/vacuum cycles, and dissolved in a solvent mixture of CH_2Cl_2/AcOH (1:1), previously degassed and then transferred through a cannula. The solution was stirred at room temp., and then poured into an MeOH/AcOH mixture (95:5; 300 mL), which was kept under vigorous stirring overnight. The resulting solid was filtered, washed with methanol and dried to afford the bulk product. The bulk dissolved in $CHCl_3$ was eluted through a short silica gel column to remove insoluble materials, and the final product was recovered after reprecipitation from methanol, and dried under vacuum.

(*E*)-Polyfluoreneethynylenevinylene (P1): 1 (186 mg, 0.426 mmol), **I** (14.2 mg, 0.023 mmol), CH_2Cl_2/AcOH (4.6 mL); 7 h; bulk (179 mg). **P1** (115 mg, brownish powder, yield 62%). M.p. 87.8–90.0 °C. FT-IR (neat): $\tilde{\nu}$ = 3307, 3028, 2956, 2922, 2871, 2854, 2182, 2106, 1697, 1604, 1463, 1416, 1378, 1290, 1130, 1005, 944, 890, 811 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 300.13 MHz): δ = 7.80–7.65 (m, aromatic), 7.60–7.42 (m, aromatic), 7.19 (br. d, J = 15.4 Hz, 19 H, -CH=C*H*-FL-), 6.53 [br. d, J = 16.1 Hz, 19 H, -(*E*)-C*H*=CH-FL-], 6.01 [d, J = 11.5 Hz, 0.7 H, -(*Z*)-C*H*=CH-FL-], 5.85 [s, 0.9 H, -FL-C(=C*H*H)-], 5.58 [s, 0.9 H, -FL-C(=CH*H*)-], 3.21 (m, 2 H, -FL-C≡CH), 2.22–1.95 (m, FL-CH_2CH-), 1.08–0.68 [br. m,

-(CH_2)-], 0.65–0.45 (m, Me) ppm. ^{13}C NMR (CD_2Cl_2, 75.5 MHz): δ = 151.5, 151.2, 141.6, 135.3, 131.0, 127.8–127.1, 125.7, 119.8, 107.4, 92.9, 89.4, 84.4, 54.9, 44.4, 34.7, 33.7, 33.5, 28.0, 27.0, 22.7, 13.8, 10.1 ppm. The ^{13}C NMR signals were assigned according to the template shown in Figure 6 of the Supporting Information, on the basis the DEPT experiment and of the literature data.[9a] TGA: T_d = 366 °C. HRMS (MALDI-TOF): calcd. for $[C_{33}H_{42}]_3$ 1315.9893; found 1316.0409 $[M]^+$; calcd. for $[C_{33}H_{42}]_5$ 2192.6461; found 2192.5272 $[M]^+$; calcd. for $[C_{33}H_{42}]_6$ 2631.9781; found 2631.7626 $[M]^+$.

Poly-(*E*)-{5-[(2′-ethylhexyl)oxy]-2-methoxy-1,4-phenyleneethynylenevinylene} (P2): 2 (200 mg, 0.703 mmol, 0.09 M); **I** (22 mg, 0.036 mmol, 0.0045 M); CH_2Cl_2/AcOH (8 mL); 5 h; bulk (185 mg). **P2** (84 mg, yield 42%, bright red solid). FT-IR (neat): $\tilde{\nu}$ = 3310, 3026, 2957, 2924, 2858, 2183, 2104, 1678, 1604, 1495, 1462, 1408, 1213, 1038, 954, 863 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 300.13 MHz): δ = 7.45–7.26 (m, 11 H, -MEH-C*H*=CH-), 7.10–6.96 (br. s, 24 H, aromatic), 6.61 [br. d, J = 16 Hz, 11 H, -(*E*)-C*H*=CH-MEH-], 4.03–3.80 (m, 65 H, OMe and OCH_2-), 3.43, 3.42, 3.41, 3.39 (4 s, 2 H, -MEH-C≡CH), 1.90–1.77 (br. m, 12 H, -OCH_2C*H*-), 1.70–1.33 (m, -CH_2-), 1.11–0.80 (m, Me) ppm. ^{13}C NMR (CD_2Cl_2, 75.5 MHz): δ = 153.7, 151.3, 136.0, 117.7–114.9, 110.4–108.7, 95.1, 88.8, 82.3, 82.1, 72.1, 71.7, 56.3, 46.2, 45.5 39.6, 30.6, 29.7, 29.1, 27.7, 27.3, 24.1, 23.0, 21.2, 20.5, 19.4, 13.8, 10.9 ppm. TGA: T_d = 360 °C. HRMS (MALDI-TOF): calcd. for $[C_{19}H_{24}O_2]_5$ 1421.8916; found 1421.8178 ($[M]^+$); $[C_{19}H_{24}O_2]_6$ 1706.0692; found 1705.9023 $[M]^+$; calcd. for $[C_{19}H_{24}O_2]_{10}$ 2844.7854; found 2845.1928 $[M]^+$.

(*E*)-Polyfluoreneethynylenevinylene-*co*-(*E*)-poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenyleneethynylenevinylene] (P3): 1 (175 mg, 0.401 mmol, 0.067 M); **I** (16 mg, 0.026 mmol); **2** (29 mg, 0.103 mmol, 0.017 M) in CH_2Cl_2/AcOH (6 mL), transferred through cannula into the reaction tube; 9 h; bulk (138 mg). **P3** (130 mg, yield 63%, brown-red solid). FT-IR (neat): $\tilde{\nu}$ = 3310, 2957, 2924, 2870, 2856, 2189, 2106, 1605, 1497, 1464, 1414, 1378, 1210, 1038, 953, 890, 821, 753 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 300.13 MHz): δ = 8.0–7.0 (m, Ar and Ar-C*H*=CH-), 6.67–6.49 (m, 8 H, *E*-C*H*=CH-Ar), 6.02 [d, J = 10 Hz, 0.1 H, (*Z*)-C*H*=CH-Ar], 5.86 and 5.58 [2 s, 0.4 H, Ar-C(=CH_2)-], 3.95 (m, 15 H, OMe and OCH_2-), 3.44 (m, 0.3 H, MEH-C≡CH), 3.21 (br. s, 1.7 H, FL-C≡CH), 2.3–0.95 (m, alkyl protons) ppm. ^{13}C NMR (CD_2Cl_2, 75.5 MHz): δ = 151.5, 151.1, 141.6, 135.8, 131.0, 130.5, 127.7, 127.2, 125.7, 121.7, 120.0, 116.8, 109.1, 107.4, 92.8, 89.5, 84.4, 72.1, 71.6, 56.3, 56.1, 44.3, 39.6, 34.7, 33.7, 33.4, 30.6, 29.7, 29.1, 28.0, 26.9, 24.0, 23.1, 22.7, 13.8, 10.9, 10.0 ppm. TGA: T_d = 375 °C. HRMS (MALDI-TOF): calcd. for $[C_{33}H_{42}]_3[C_{19}H_{24}O_2]$ 1599.1630; found 1599.1705 $[M]^+$; calcd. for $[C_{33}H_{42}]_3[C_{19}H_{24}O_2]_2$ 1884.3441; found 1884.2603 $[M]^+$; calcd. for $[C_{33}H_{42}]_4[C_{19}H_{24}O_2]$ 2038.4951; found 2038.4104 $[M]^+$; calcd. for $[C_{33}H_{42}]_5[C_{19}H_{24}O_2]$ 2476.8238; found 2476.5895 $[M]^+$.

Supporting Information (see footnote on the first page of this article): Table of synthetic optimization data of **P1**–**2**. Copies of ^{1}H and ^{13}C NMR spectra of **1**, **3** and **P1**–**3**. GPC profiles, and MALDI-TOF spectra of **P1**–**3**.

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[22] In order to exclude that the photoluminescent spectrum of **P3** is merely due to the linear combination of the emission spectra of the homopolymers, a chloroform solution of **P1** and **P2** in a 7:3 molar ratio was studied as a control experiment. The resulting sample exhibited an emission spectrum markedly dependent on the chosen excitation wavelength, as expected for a solution containing two independent chromophores (see Figures in the Supporting Information), in contrast with the behaviour of **P3**. This confirms that the **P3** sample is formed by molecular species including the fluorene and the MEH subunits in the same chain. The absence of intramolecular and intermolecular energy transfer between the two chromophores in the control sample further confirms that intramolecular resonance energy transfer processes are involved in the photoluminescence of **P3**.
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