

Acyclic Diene Metathesis Polymerization of Divinylarenes and Divinylferrocenes with Grubbs-Type Olefin Metathesis Catalysts

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1,4-Di(2-ethylhexyl)2,5-divinylbenzene, 1,4-di(2-ethylhexyloxy)-2,5-divinylbenzene, and 9,9-di(2-ethylhexyl)-2,7-divinylfluorene were synthesized from the respective dialdehydes and ADMET polymerized using Grubbs II or Grubbs–Hoveyda–Grela-type olefin metathesis catalysts. The continuous removal of ethene under a dynamic vacuum of 20 mbar at elevated temperatures in high boiling solvents (1,2-dichlorobenzene) resulted in the formation of long-chain poly[2,5-di(2-ethylhexyl)-*p*-phenylenevinylene] ($M_n > 100$ kDa, $P_n = 330$, $M_w/M_n = 3.1$) and poly[9,9-di(2-ethylhexyl)fluorenyl-2,7-vinylene] ($M_n > 70$ kDa, $P_n = 178$). The PPV forms a free-standing film after evaporation of a toluene solution. 1,3-(Diisopropenyl)ferrocene could not be polymerized in this manner; ferrocene-containing polymers were obtained with 1,1'-di(4-vinylphenyl)-3,3',4,4'-tetramethylferrocene.

Introduction

Organic polymers such as poly(*p*-phenylenevinylenes) (PPVs) are important materials with an excellent perspective toward applications in organic light emitting diodes (OLED) and organic photoconductors.^{1,2} Numerous polymerization procedures, such as, for example, the Wessling,³ Gilch,⁴ Wittig and Wittig–Horner,^{5,6} Heck,^{7–9} Suzuki,^{10,11} Stille,¹² and ROMP reactions,¹³ have been applied in the synthesis of such polymers, and none of them is entirely free from problems such as the incomplete elimination of precursor functional groups. The Heck coupling suffers from undesired 1,1-coupling reactions and an ill-defined stereochemistry at the double-bond 1,2-cis/trans mixtures.¹⁴ Problems in controlling chain architecture and molecular mass result in chain defects and large polydispersities in Gilch reaction derived PPVs.⁴ Those problems are critical in device applications,¹⁵ and further advances in polymerization methodology are required.

The ADMET (acyclic diene metathesis) polymerization^{16,17} has rarely been used to synthesize conjugated polymers¹⁸ or PPV-type polymers.¹⁹ Advantages of the ADMET approach are the absence of problematic end groups, the typical trans-configuration of the metathetically generated double bonds, and the absence of branching within the polymer structure. Pioneering work from Thorn–Csányi utilized Schrock-type olefin metathesis catalyst for the PPV synthesis from the respective substituted divinylbenzenes. However, only short-chain oligomeric PPV were formed.^{20–22} Nomura et al. tested Grubbs-type catalysts to obtain extended chain PPV,²³ but this approach critically relies on the removal of ethene by repeatedly cooling the reaction mixture to -30 °C every 60 min, followed by evacuation and reheating to the ADMET reaction temperature. Such heat–cool–vacuum cycles were repeated during 5–24 h to effect the PPV synthesis using Grubbs II or Grubbs–Hoveyda catalysts. On the other hand, Harper et al. reported on the formation of PPV oligomers when using Grubbs II catalyst.²⁴

The significant progress in olefin metathesis catalyst development in the last few years^{25–34} prompted us to study ADMET

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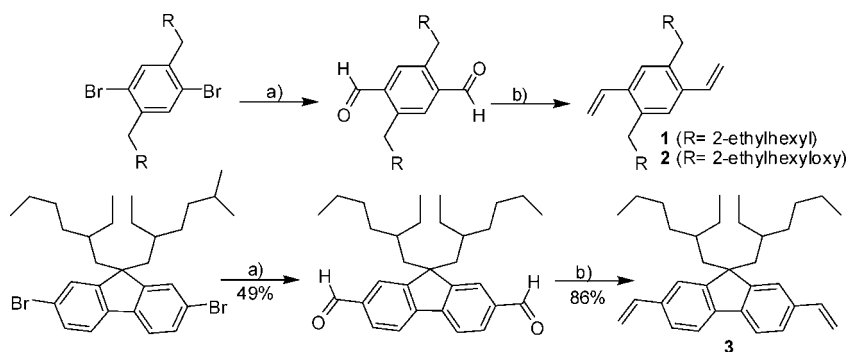
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Scheme 1. Synthesis of the Monomers 1–3^a

^a Reagents and conditions: (a) *n*-BuLi, DMF, Et₂O, -78 °C then aq HCl; (b) (Ph₃PCH₃)⁺I⁻, *n*BuLi, THF, rt.

polymerization of various divinylarenes, including ferrocene-containing monomers.³⁵ The organometallic building block could serve as a redox-switch to reversibly alter the optical and conductivity properties for sensor devices.³⁶ We wish to report here on the synthesis of the respective high molecular weight polymers via ADMET utilizing Grubbs-type olefin metathesis catalysts.

Results and Discussion

In order to improve the efficiency of the ADMET polymerization, the continuous removal of ethene from the reaction flask appears to be a more convenient strategy compared to a discontinuous heat-cool-vacuum sequence. This approach requires high boiling solvents and catalysts, which need to be stable for long periods of time at elevated temperatures. Various Grubbs-type catalysts are fairly robust and were tested in combination with solvents such as 3,4-dichlorotoluene (bp 210 °C), 1,2,4-trichlorobenzene (bp 213 °C), 1,2-dichlorobenzene (bp 180 °C), and 4-chloroanisol (bp 202 °C).

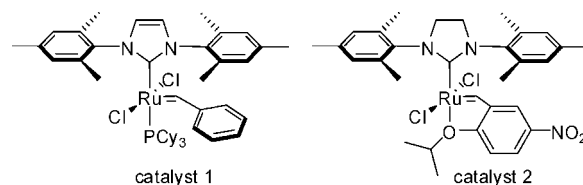
Monomer Synthesis. The three divinyl monomers **1**,²³ **2**, and **3** were synthesized by converting the respective dibromides into the dialdehydes^{4,23,37,38} and then into the desired divinyls using (Ph₃PCH₃)⁺I⁻ (Scheme 1). The advantage of this synthetic route is the facile separation of the desired products (dialdehyde and divinyl species) from monoaldehyde impurities, which may result from the incomplete conversion of the dibromide (Scheme 1, a) or the incomplete Wittig reaction to the divinyl monomers (Scheme 1, b). The strong polarity change of the reactants in each conversion step (Scheme 1) facilitates the chromatographic separation of the respective monofunctional species. 1,4-Bis[(2-ethylhexyl)oxy]-2,5-divinylbenzene has previously been synthesized via Stille coupling of the respective diiodide with Sn(vinyl)₄.³⁷ However, this approach inevitably produces small amounts of monovinylated products, which are difficult to remove from the divinylbenzene product. However, in order to enable the efficient polymerization of the monomers to a high molecular weight PPV, high-purity starting materials are mandatory.

Table 1. ADMET Polymerization of 1,4-Di(2-ethylhexyl)-2,5-divinylbenzene^a

solvent	<i>T</i> (°C)	<i>M_n</i> (10 ³)	<i>M_w</i> / <i>M_n</i>	<i>P_n</i>
3,4-dichlorotoluene ^c	45	24.9	2.4	76
3,4-dichlorotoluene ^c	55	47.4	2.8	145
3,4-dichlorotoluene ^c	65	56.7	3.2	174
3,4-dichlorotoluene ^c	75	67.8	3.3	207
1,2,4-trichlorobenzene ^c	45	26.8	2.4	81
1,2,4-trichlorobenzene ^c	55	44.6	2.6	136
1,2,4-trichlorobenzene ^c	65	55.5	3.0	169
1,2,4-trichlorobenzene ^c	75	74.2	3.0	227
4-chloroanisol ^c	45	7.3	3.4	22
4-chloroanisol ^c	55	16.3	6.6	50
1,2,4-trichlorobenzene ^b	45	33.7	3.2	104
1,2,4-trichlorobenzene ^b	55	42.2	3.3	129
1,2,4-trichlorobenzene ^b	65	63.9	3.4	196
1,2,4-trichlorobenzene ^b	75	66.5	3.6	204
1,2-dichlorobenzene ^{b,d}	45	53.8	2.8	165
1,2-dichlorobenzene ^{b,d}	55	54.7	2.8	167
1,2-dichlorobenzene ^{b,d}	65	77.9	3.0	240
1,2-dichlorobenzene ^{b,d}	75	107.3	3.1	330

^a Conditions: 1 mol% catalyst, initial monomer concentration 0.2 M, reaction time 3 d. ^b Catalyst 1. ^c Catalyst 2. ^d Slow evaporation of solvent. Optimized reaction conditions but with very slow evaporation of solvent (*p* = 20 mbar).

Scheme 2. Catalysts Used for ADMET Polymerization



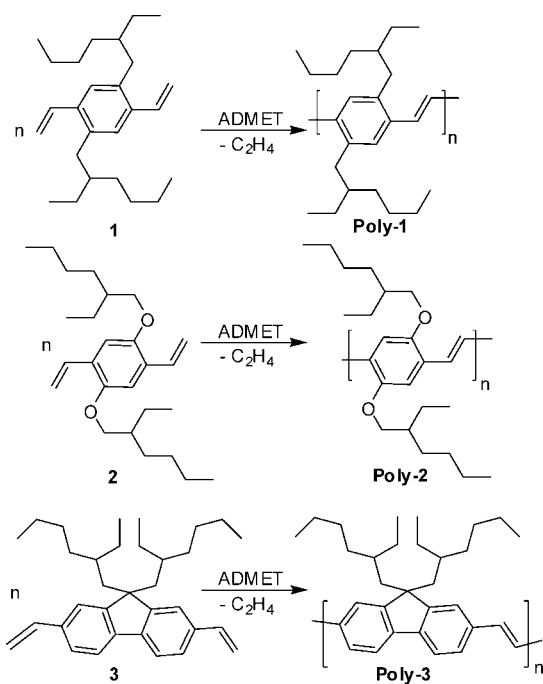
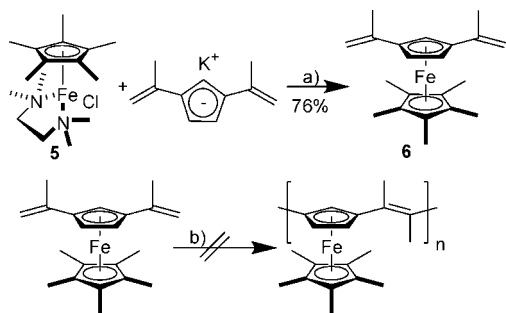
PPV via ADMET Polymerization. We tested several solvent/catalyst combinations for the ADMET polymerization of the divinyl monomer **1** (Table 1). In order to drive olefin metathesis to completion the continuous removal of ethene appears to be very helpful; this is best done by performing the reaction under mild vacuum. Consequently, high boiling solvents are required. The four solvents, 1,2-dichlorobenzene, 3,4-dichlorotoluene, 1,2,4-trichlorobenzene, and 4-chloroanisol, and the Grubbs I and the Grubbs–Hoveyda–Grela complex³⁹ (Scheme 2) were tested in the ADMET polymerization of 9,9-di(2-ethylhexyl)fluorenyl-2,7-vinylene (Scheme 3). Reactions were carried out under a dynamic vacuum of 20 mbar pressure.

The course of the condensation reaction can be followed by monitoring the fluorescence of the reaction mixture, which

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Scheme 3. Synthesis of the ADMET Polymers

Scheme 4. Synthesis of a 1,3-(Diisopropenyl)ferrocene^a

^a Reagents and conditions: (a) THF, $-78\text{ }^{\circ}\text{C}$; (b) optimized ADMET conditions.

initially is pink and then changes to blue and green and finally yellow, indicative of the growing polymer chain. During the reaction, the viscosity of the reaction mixture changes, turning oily on the second day and highly viscous on the third day, so stirring became difficult. This is due to partial loss of solvent as well as to the formation of polymers. After the reaction, dilution with toluene, quenching of the catalyst with ethylvinylether and filtration of the solution into acetone led to the precipitation of the yellow polymer, which was finally filtered off and dried. Following this procedure, a number of polymerization experiments using different catalysts and solvents were performed and the resulting polymers analyzed by GPC (Table 1).

Both catalysts produce high molecular weight polymers with dispersities of close to 3 in 3,4-dichlorotoluene, 1,2,4-trichlorobenzene, and 1,2-dichlorobenzene. This is slightly higher than the theoretical M_w/M_n of 2 expected for this polycondensation reaction.¹⁶ The ADMET results in the various solvents do not differ drastically; the only exception is 4-chloroanisole in which much shorter chain length ($P_n = 50$) and very high polydispersities were produced. The reason for this is unclear, but it has been reported that Grubbs-type olefin metathesis catalysts in ethereal solvents (Et_2O , THF) are less efficient. Catalyst 2 (Scheme 3) initiates more quickly (rapid ethene evolution) but,

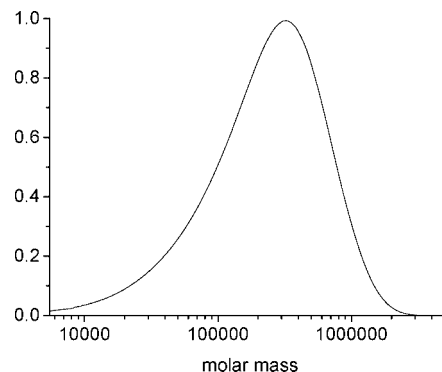


Figure 1. GPC trace of **poly-1**.

as can be seen in Table 1, in the long run both catalysts produce roughly the same polymers. Given the identity of the active species this is hardly surprising.

Initially, we tried to avoid the evaporation of the solvents by applying a $-15\text{ }^{\circ}\text{C}$ cooled reflux condenser on top of the reaction flask. However, we later realized that the very slow evaporation of the solvent during a few days poses no problem. On the contrary, the use of the comparatively volatile solvent (1,2-dichlorobenzene, bp $180\text{ }^{\circ}\text{C}$) led to the formation of very high molecular weight polymers, even though a viscous solution was already formed during the first day, while on the third day a yellow gumlike solid remained in the flask. This material was dissolved in CH_2Cl_2 , and following the normal workup, very high molecular weight polymers were isolated. The polymer produced at $75\text{ }^{\circ}\text{C}$ using catalyst 2 has a M_n in excess of 100000 corresponding to a 330-mer.

PPV Polymer Properties. In the vinylic region of the ^1H NMR spectra of **poly-1**, **poly-2**, and **poly-3**, only a single signal at 7.27 ppm is visible. Peaks at 6.65 ppm, corresponding to the *cis*-vinyl-H,⁴⁰ are not observed. In our ADMET polymers, the α -methylene protons display only one signal, which is indicative of a highly ordered structure. It was reported that poly[2,5-diheptyl-*p*-phenylenevinylene] synthesized via the Wessling route displays two signals for the inequivalent α -methylene protons at 2.77 and 2.43 ppm.⁴¹ The second signal was assigned to a less ordered structure. Obviously, the ADMET polymers reported here are all-*trans* and defect-free within the sensitivity of the NMR experiment.

A high degree of polymerization and the resulting morphology changes are required to enable the efficient formation of polymer films, which is of decisive importance for OLED applications. The morphology of the PPV **poly-1** changes drastically upon chain elongation; with $P_n = 22$ a yellow powder is formed, while simple evaporation of a toluene solution of the long chain **poly-1** with $P_n = 227$ or $P_n = 330$ (Figure 1) gave a mechanically stable, yellow foil (Figure 2).

ADMET Polymerization of 1,4-Di(2-ethylhexyloxy)-2,5-divinylbenzene. Next we applied the optimized ADMET conditions to 4-di(2-ethylhexyloxy)-2,5-divinylbenzene **2** to produce **poly-2**. However, in the polymerization reaction this monomer performed poorly. Table 2 summarizes the data; even at elevated temperatures the degree of polymerization is modest. The likely reason for this failure is that *o*-vinyl ethers are able to act as bidentate ligands to Ru forming inhibited Grubbs–Hoveyda type species with chelating monomers, such as **2**.

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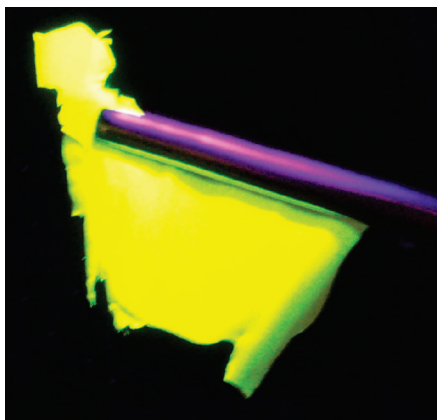


Figure 2. Free-standing film of **poly-1** ($P_n = 330$) under UV illumination.

Table 2. ADMET Polymerization of 1,4-Di(2-ethylhexyloxy)-2,5-divinylbenzene **2**^a

T (°C)	M_n (10^3)	M_w/M_n	P_n
55	1.4	1.2	4
65	1.7	2.5	5
75	3.9	2.6	11

^a Conditions: 1 mol % of catalyst, initial monomer concentration 0.2 M, reaction time 3 d, solvent 1,2,4-trichlorobenzene, catalyst **2**.

Table 3. ADMET Polymerization of 9,9-Di(2-ethylhexyl)-2,7-divinylfluorene **3**^a

initial monomer concentration (M)	T (°C)	M_n (10^3)	M_w/M_n	P_n
0.20	45	17.4	1.9	42
0.10	45	25.8	2.3	62
0.05	45	34.5	2.7	84
0.05	55	73.5	2.7	178

^a Conditions: 1 mol % of catalyst, reaction time 3 d, solvent 1,2,4-trichlorobenzene, catalyst **2**.

ADMET Polymerization of 9,9-Di(2-ethylhexyl)fluorenyl-2,7-vinylene. The synthesis of poly[9,9-di(2-ethylhexyl)fluorenyl-2,7-vinylene] **3** was carried out according to the optimized procedure for poly[2,5-di(2-ethylhexyl)-*p*-phenylenevinylene]. The polymerization of **3** at 0.2 M initial concentration led to the precipitation of a yellow-green powder after a single day. The amount of insoluble material further increased during the next 48 h. Filtration of the polymer and analysis by GPC analysis showed this to be of relatively low molecular weight (Table 3). Obviously, solubility problems of the growing polymer chain led to the formation of short chains. Consequently, the experiments were repeated using lower initial monomer concentrations of 0.1 and 0.05 M, respectively, which resulted in much longer polymer chains.

The reason for the limited solubility of the fluorene-based polymer could be that in contrast to **poly-1** the solubilizing groups are attached on one side of the molecule only, facilitating the association of the flat aromatic fluorene backbone. In contrast, in **poly-1** the growing chain is encapsulated by the two alkyl chains on both sides of the monomer. This interpretation is supported by the appearance of the **poly-3** which forms a brittle solid, quite unlike the flexible **poly-1**.

Optical Properties of the Polymers. **Poly-1**, **-2**, and **-3** display different colors, which are due to $\pi \rightarrow \pi^*$ transitions in the conjugated π -electron system. The absorption and emission spectra of the respective polymers in solution (10^{-5} M in THF) were determined (Figures 3 and 4). The spectroscopic data of the respective polymers are as follows: (λ_{\max} absorption (nm),

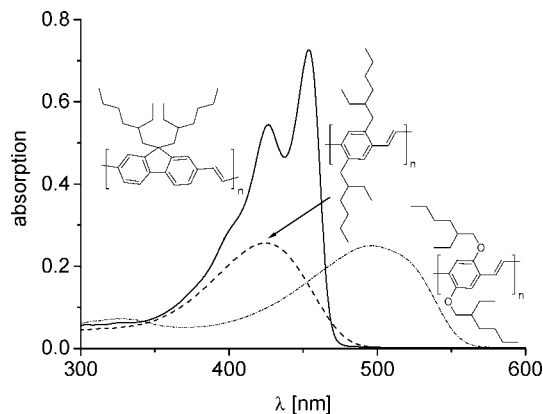


Figure 3. UV/vis spectra of **poly-1**, **-2**, and **-3** (10^{-5} M in THF).

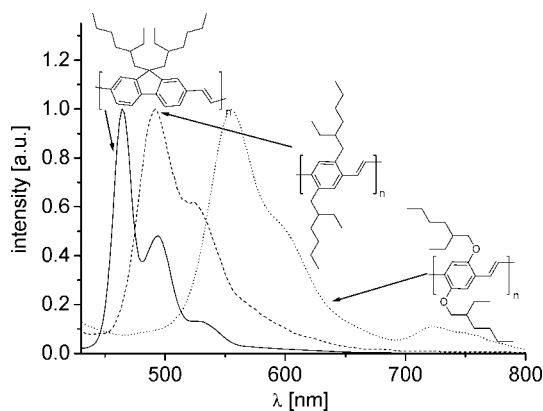


Figure 4. Emission spectra of **poly-1**, **-2**, and **-3** (excitation wavelength 250 nm (**poly-1**, **-3**), 330 nm (**poly-2**); 10^{-5} M, in THF).

ϵ ($L \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), and λ_{\max} emission (nm)) **poly-1** (423, 25300, 492), **poly-2** (496, 24500, 554), and **poly-3** (454, 71600, 464).

The good solvation of poly[2,5-di(2-ethylhexyl)-*p*-phenylenevinylene] and its orientational freedom in solution leads to broad and unstructured absorption spectra.⁴² On comparing the spectrum of **poly-1** with that of poly[2,5-di(2-ethylhexyl)-*p*-phenylenevinylene] reported by Nomura et al., the absorption maximum in the latter polymer lies at 412 nm.²³ The bathochromic shift of 11 nm in **poly-1** should be related to the different chain length and provides evidence for extended conjugation chain lengths.

The broad absorption spectrum of poly[2,5-di(2-ethylhexyloxy)-*p*-phenylenevinylene] has different absorption maxima due to the electron-donating character of the alkoxy groups. In the spectrum of poly[2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene] ($\lambda_{\max} = 501$ nm),⁴³ the absorption maximum is shifted by 5 nm to longer wavelength with respect to **poly-2**. This is caused by the much lower average number of repeating units ($P_n = 11$ in **poly-2**), indicating that the maximum of effective conjugation chain length has not been reached.⁴⁴ The spectrum of poly[9,9-di(2-ethylhexyl)fluorenyl-2,7-vinylene] **poly-3** is more structured, displaying two relatively narrow

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bands at 427 and 454 nm. This is indicative of a more aggregated structure of **poly-3**,⁴² likely caused by π -stacking of the fluorene units and separation of the 2-ethylhexyl groups.

The emission spectra of poly[2,5-di(2-ethylhexyl)-*p*-phenylenevinylene] ($\lambda_{\text{max}} = 492, 524 \text{ nm}$) exhibit two bands, and since those are not the mirror image of the absorption spectrum it follows that the emission comes from individual segments of the polymer.⁴⁵

The emission spectrum of poly[2,5-di(2-ethylhexyloxy)-*p*-phenylenevinylene] ($\lambda_{\text{max}} = 554 \text{ nm}$) experiences a bathochromic shift but is otherwise similar to that of **poly-1**. A comparison with the emission spectrum of poly[2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene] ($\lambda_{\text{max}} = 582 \text{ nm}$) again reveals that the convergence of the conjugation length has not been reached.

The emission of poly[9,9-di(2-ethylhexyl)fluorenyl-2,7-vinylene] ($\lambda_{\text{max}} = 464, 494 \text{ nm}$) is much better resolved than those of the other polymers reported here, and the same arguments regarding the polymer microstructure apply.

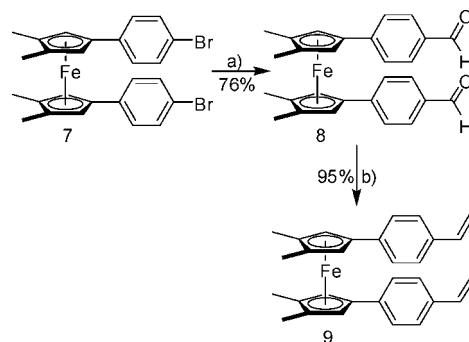
Attempted Synthesis of a Ferrocene-Vinylene Polymer. In an attempt to produce PPV-related ferrocene polymers, we synthesized a ferrocene with two terminal olefins. The five methyl groups were intended to serve as solubilizing units; related ROMP generated ferrocene polymers were reported to be soluble only in the presence of such moieties.^{46–48} The 1,3-substituted pattern was chosen, since it allows a more efficient transfer of electronic information along the chain than 1,1'-substituted ferrocenes.^{49–51} 3-(1-Methylethenyl)-6,6-dimethylfulvene **4** was synthesized using a modified synthesis based on Fenton's work,⁵² and a different procedure was recently published by Erker.⁵³ The reaction of the 1,3-(diisopropenyl)cyclopentadienide with $\text{Cp}^*\text{Fe}(\text{tmeda})\text{Cl}$ ⁵⁴ gave the 1,3-(diisopropenyl)ferrocene **6** in 78% yield.

The optimized ADMET procedure with catalysts 1 and 2 was tried for the synthesis of the respective polymer. Unfortunately, we were not able to obtain the desired ferrocene polymer, even when 5 mol % of catalyst and elevated temperatures (75 °C) were used. Only starting material was isolated following chromatographic workup of the reaction mixture.

ADMET Copolymerization of Fluorene and Ferrocene Divinyls. In order to obtain ferrocene-containing polymers, a different organometallic building block was required (Scheme 5). 1-(4-Bromophenyl)-3,4-dimethylcyclopentadienide was reacted with $\text{FeCl}_2 \cdot (\text{THF})_{1.5}$ to yield 1,1'-di(4-bromophenyl)-3,3',4,4'-tetramethylferrocene **7** in 46% yield; the four methyl groups are required as solubilizing groups. The dilithiation of ferrocene **7** and the reaction with *N*-formylpiperazine gave the dialdehyde **8** in 76% yield, which upon reaction with the Wittig reagent resulted in the formation of the divinyl **9** in 95%. The four methyl substituents are useful as solubilizing groups.

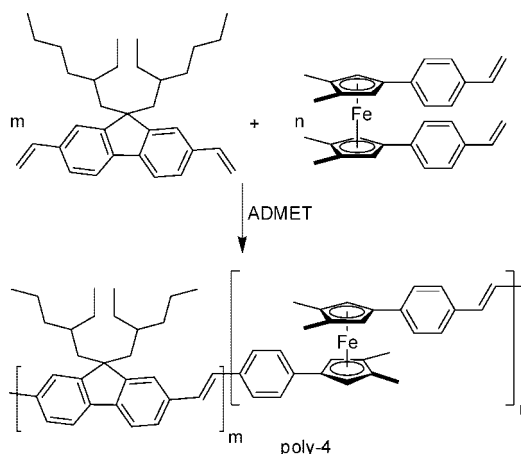
The copolymerization of 4 equiv of divinylfluorene **3** and 1 equiv of divinylferrocene **9** was successful using our optimized

Scheme 5. Synthesis of a Divinyl-Substituted Ferrocene^a



^a Reagent and conditions: (a) *n*BuLi, TMEDA, *N*-formylpiperidine; (b) $(\text{Ph}_3\text{PCH}_3)^+\text{T}^-$, *n*BuLi, THF, rt.

Scheme 6. ADMET Copolymerization (3 d, 55 °C, Catalyst 2 (1 mol %), Initial Monomer Concentration 0.5 M)



ADMET protocol (Scheme 6); the resulting polymer has $M_n = 25100$, $M_w/M_n = 1.6$, and $P_n = 60$. The ratio of the two monomers in the resulting polymer closely resembles the monomer composition, indicative of similar polymerization efficiency.

The mixed fluorene-ferrocene **poly-4** has a significantly better solubility than the polyfluorene **poly-3**. While the poor solubility of **poly-3** was attributed to the efficient packing of the fluorene units, the incorporation of a significant amount of flexible ferrocene units into the polymer seems to disfavor the close association of the arenes.

It is interesting to note that the incorporation of ferrocene into the polymer chain leads to a drastic decrease of the fluorescence intensity of **poly-4** compared to **poly-3** (Figure 5). Several explanations are feasible: (a) ferrocene is known to act as an efficient quencher, (b) the absorption maximum of ferrocene lies at 440 nm, which is close to the emission maximum of **poly-4**, and (c) the effective conjugation length in **poly-4** can be expected to be much shorter due to the less efficient conjugation across the 1,1'-substituted ferrocene unit.

Summary and Conclusions

We have developed a reaction protocol which allows the efficient ADMET polymerization of 1,4-bis(2-ethylhexyl)-2,5-divinylbenzene **1** and 9,9-di(2-ethylhexyl)fluorenyl-2,7-vinylene **3** in high boiling solvents with continuous removal of ethene under 20 mbar dynamic vacuum using equally efficient Grubbs II and Grubbs–Hoveyda–Grela-type catalysts. The highly fluorescent, all-trans-

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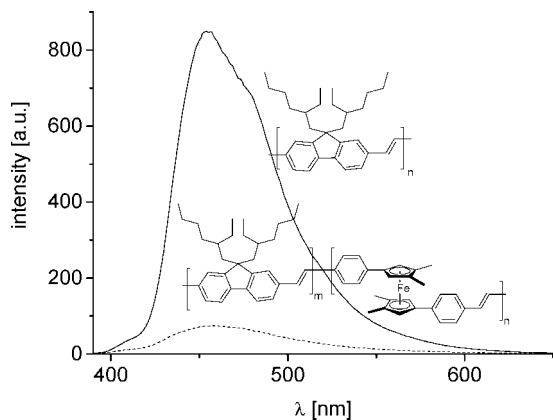


Figure 5. Emission spectra of **poly-3** and **-4** (excitation wavelength 250 nm, 10^{-5} M, in THF).

configured, defect-free PPV-type **poly-1** with $P_n = 330$ and $M_n > 100$ kDa obtained in this manner forms a free-standing film upon evaporation of a toluene solution. The UV/vis spectra are indicative of extended conjugation chain length. The ADMET polymerization of monomer **3** suffers from the diminished solubility of the resulting polymer, nonetheless $P_n = 177$ with $M_n = 75$ kDa is possible, when working in dilute solutions. We were not at all able to ADMET polymerize 1,3-isopropenylferrocene using the optimized ADMET protocol. The incorporation of ferrocene in a polyvinylene-type polymer is possible only when using 1,1'-di(4-vinylphenyl)-3,3', 4,4'-tetramethylferrocene as the monomer. The key to high molecular weights obtained by us is the use of high purity monomers and the slow but continuous removal of solvent and ethene from the reaction mixture.

Experimental Section

NMR spectroscopy: Bruker AM-200 (^1H 200 MHz), Bruker AC-300 (^1H 300 MHz, ^{31}P 121 MHz, ^{13}C 75 MHz), and Bruker Advance 500 (^1H 500 MHz, ^{13}C 125 MHz) and were referenced vs TMS (^1H , ^{13}C) and 85% aq H_3PO_4 (^{31}P). UV/vis spectra: 10 mm quartz glass cuvettes on a Specord S10 (Firma Analytik Jena) using a tungsten-halogen and a D_2 source. Photoluminescence: 10 mm quartz glass cuvettes, Cary eclipse fluorescence photometer (Varian), pulsed Xe-lamp. GPC measurements: in THF with toluene internal standard at 303 K, 1.0 mL/min flow, Waters 486 UV detection (254 nm), Waters RI 410 refractometer; columns, PSS (SDV 1000000, SDV 100000 and SDV 1000) (PSS = polystyrene standard calibration). Starting materials were commercially available or synthesized according to literature procedures: 3,4-dimethylcyclopentadiene⁵⁵ and 1-(4-bromophenyl)-3,4-dimethylcyclopentadiene.⁵⁶

2,5-Di(2-ethylhexyl)benzene-1,4-dicarbaldehyde. A solution of the 2,5-di(2-ethylhexyl)benzene-1,4-dibromide (4.60 g, 10.0 mmol) in diethyl ether (125 mL) was cooled to -78°C and *t*-BuLi (15.0 mL, 22.0 mmol, 1.5 M) added dropwise. The reaction mixture was stirred (1 h) at this temperature and then DMF (1.93 mL, 1.83 g, 25.0 mmol) added, followed after 30 min by more *t*-BuLi (30.00 mL, 44.0 mmol, 1.5 M) and 1 h later by the next batch of DMF (3.86 mL, 3.60 g, 50.0 mmol). The reaction mixture was allowed to room temperature during 12 h and then poured into ice-cooled 2 N HCl (150 mL). The organic layer was separated and the aqueous phase extracted with diethylether (3×50 mL). The combined ethereal solutions were dried over MgSO_4 and filtered, and the volatiles were evaporated. The residue was purified by chromatography (silica, cyclohexane/ethyl acetate = 40:1). Yield: 1.97 g, 5.5 mmol, 55%. ^1H NMR (CDCl_3): δ 10.38 (s, 2 H, aryl-

CHO), 7.71 (s, 2 H, aryl-*H*), 2.98 (d, 4 H, aryl- CH_2 -), 1.57–1.21 (m, 18 H, alkyl-*H*), 0.95–0.88 (m, 12 H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3): δ 191.6, 142.5, 136.9, 133.5, 42.1, 35.9, 32.2, 28.7, 25.5, 22.9, 13.0, 10.7.

1,4-Di(2-ethylhexyl)-2,5-divinylbenzene (1). To a suspension of $(\text{Ph}_3\text{PCH}_3)^+\text{I}^-$ (8.60 g, 21.25 mmol) in THF (250 mL) at 0°C was added *n*-BuLi (8.5 mL, 21.25 mmol, 2.5 M), followed after 10 min by a solution of the 2,5-di(2-ethylhexyl)benzene-1,4-dicarbaldehyde (2.54 g, 7.10 mmol) in THF (70 mL). The reaction mixture was allowed to room temperature and stirring continued for 1 d. The reaction mixture was added to water (250 mL) and stirred for 10 min and then the product extracted with diethyl ether (3×100 mL). The combined organic solutions were dried over MgSO_4 and filtered and the volatiles evaporated. The residue was purified by chromatography (silica, *n*-pentane). Yield: 1.73 g, 4.89 mmol, 69%. ^1H NMR (CDCl_3): δ 7.21 (s, 2 H, aryl-*H*), 6.95 (dd, 2 H, vinyl-*H*), 5.60 (dd, 2 H, vinyl-*H*), 5.22 (dd, 2 H, vinyl-*H*), 2.55 (d, 4 H, aryl- CH_2), 1.56–1.23 (m, 18 H, alkyl-*H*), 0.96–0.84 (m, 12 H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3): δ 136.8, 135.7, 134.8, 127.7, 114.4, 40.3, 37.3, 32.4, 28.7, 25.6, 23.1, 14.1, 10.8.

9,9-Di(2-ethylhexyl)fluorenyl-2,7-dicarbaldehyde. A solution of 9,9-di(2-ethylhexyl)fluorenyl-2,7-dibromide (16.62 g, 30.3 mmol) was cooled to -78°C and *n*-BuLi (28 mL, 70.0 mmol, 2.5 M) added. The solution was warmed to room temperature and stirring continued for another 2 h. After cooling again to -78°C , a solution of DMF (5.6 mL, 5.26 g, 72 mmol) in diethyl ether (15 mL) was added dropwise. The reaction mixture was allowed to room temperature and stirring continued for 18 h. The reaction mixture was dumped on ice-cooled 2 N HCl (100 mL), the organic layer separated, and the aqueous phase extracted with diethyl ether (3×150 mL). The combined ethereal solutions were dried over MgSO_4 , filtered, and evaporated. The residue was purified by chromatography (silica, cyclohexane/ethyl acetate = 10:1). Yield: (6.58 g, 14.7 mmol, 49%). ^1H NMR (CDCl_3): δ 10.10 (s, 2 H, aryl-*CHO*), 7.94 (m, 6 H, aryl-*H*), 2.09 (d, 4 H, aryl- CH_2), 0.85–0.41 (m, 30 H, alkyl-*H*). ^{13}C NMR (CDCl_3): δ 191.9, 152.6, 145.7, 135.9, 129.9, 124.8, 121.3, 55.3, 44.3, 34.7, 33.6, 27.9, 26.9, 22.6, 13.9, 10.2.

1,4-Di(2-ethylhexyloxy)-2,5-divinylbenzene (2). To a suspension of $(\text{Ph}_3\text{PCH}_3)^+\text{I}^-$ (7.15 g, 17.7 mmol) in THF (100 mL) at 0°C was added *n*-BuLi (7.1 mL, 17.7 mmol, 2.5 M), followed after 10 min by a solution of the dialdehyde (2.28 g, 5.9 mmol) in THF (60 mL). The reaction mixture was allowed to room temperature and stirring continued for 1 d. The reaction mixture was added to water (300 mL) and stirred for 10 min and then the product extracted with diethyl ether (3×100 mL). The combined organic solutions were dried over MgSO_4 and filtered and the volatiles evaporated. The residue was purified by chromatography (silica, *n*-pentane). Yield: 1.59 g, 4.1 mmol, 70%. ^1H NMR (CDCl_3): δ 7.05 (dd, 2 H, vinyl-*H*), 6.99 (s, 2 H, aryl-*H*), 5.72 (dd, 2 H, vinyl-*H*), 5.24 (dd, 2 H, vinyl-*H*), 3.85 (d, 4 H, O- CH_2), 1.76–1.31 (m, 18 H, alkyl-*H*), 0.96–0.88 (m, 12 H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3): δ 150.7, 131.6, 127.1, 113.8, 110.1, 71.5, 39.7, 30.7, 29.2, 24.1, 23.1, 14.1, 11.2.

9,9-Di(2-ethylhexyl)-2,7-divinylfluorene (3). To a suspension of $(\text{Ph}_3\text{PCH}_3)^+\text{I}^-$ (17.83 g, 44.2 mmol) in THF (250 mL) at 0°C was added *n*-BuLi (17.68 mL, 44.2 mmol, 2.5 M), followed after 10 min by a solution of the 9,9-di(2-ethylhexyl)fluorenyl-2,7-dicarbaldehyde (6.58 g, 14.7 mmol) in THF (120 mL). The reaction mixture was allowed to warm to room temperature and stirring continued for 1 d. The reaction mixture was added to water (300 mL) and stirred for 10 min and then the product extracted with diethyl ether (3×150 mL). The combined organic solutions were dried over MgSO_4 and filtered and the volatiles evaporated. The residue was purified by chromatography (silica, *n*-pentane). Yield: 5.60 g, 12.6 mmol, 86%. ^1H NMR (CDCl_3): δ 7.51 (d, 2 H, aryl-*H*), 7.29 (m, 4 H, aryl-*H*), 6.70 (dd, 2 H, vinyl-*H*), 5.68 (dd, 2 H, vinyl-*H*), 5.13 (dd, 2 H, vinyl-*H*), 1.90 (d, 4 H, aryl- CH_2), 0.83–0.40 (m, 30 H, alkyl-*H*). ^{13}C NMR (CDCl_3): δ

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151.1, 140.9, 137.5, 135.9, 125.4, 121.6, 119.6, 112.8, 54.7, 44.4, 34.6, 33.7, 28.1, 27.1, 22.7, 14.0, 10.3.

2-Isopropenyl-6,6-dimethylfulvene (4). Na (3.45 g, 150 mmol) was dissolved in cold (0 °C) methanol (100 mL). To the alcoholate solution was added cyclopentadiene (12.4 mL, 9.91 g, 150 mmol) dropwise at this temperature and stirring continued for 1 h. Next, acetone (11.0 mL, 8.71 g, 150 mmol) was added and the reaction mixture allowed to warm to room temperature overnight. Finally, the solution was heated under reflux for 1 h. A second batch of NaOMe (2.97 g, 55 mmol) in methanol (50 mL) was added, followed by acetone (4.04 mL, 3.19 g, 55 mmol). The sequential addition of NaOMe and acetone was repeated three times and the reaction mixture then refluxed overnight. After cooling to room temperature, the reaction mixture was poured on ice/water (300 mL) and the cold mixture extracted with diethyl ether (4 × 100 mL). The combined organic solutions were dried over MgSO₄ and filtered and the volatiles evaporated at 0 °C. The remaining liquid was purified by vacuum distillation; the crude product (bp 50 °C/1 mbar) was then purified by chromatography (silica, *n*-pentane/NEt₃ = 50:1). Yield: 11.09 g, 76 mmol, 51%. ¹H NMR (C₆D₆): δ 6.95 (d, 1 H, Cp-H), 6.67 (d, 1 H, Cp-H), 6.55 (s, 1 H, Cp-H), 6.52 (s, 1 H, isopropenyl-CH₂), 5.12 (s, 1 H, isopropenyl-CH₂), 2.13 (s, 3 H, isopropenyl-CH₃), 1.89 (s, 6 H, isopropylidene-CH₃). ¹³C NMR (C₆D₆): δ 146.9, 146.0, 143.9, 139.8, 129.7, 122.8, 116.5, 112.5, 22.8, 21.2.

1,3-Diisopropenyl-1',2',3',4',5'-pentamethylferrocene (6). Cp*-Fe(TMEDA)Cl (950 mg, 2.77 mmol) was suspended in THF (20 mL) and cooled to -78 °C, and a solution of freshly prepared K⁺(1,3-diisopropenylcyclopentadienide) (580 mg, 3.00 mmol, in situ prepared from 1.1 equiv of KO-*t*-Bu and 1.0 equiv of **4** in THF at 0 °C) in THF (30 mL) was added. The suspension was slowly (overnight) allowed to warm to room temperature. Next, the volatiles were removed in vacuo, and the remaining solid was extracted with *n*-pentane (3 × 30 mL). The pentane extracts were filtered, the solvent was evaporated, and the crude product was purified by chromatography (silica, *n*-pentane/NEt₃ = 50:1). Yield: 725 mg, 2.16 mmol, 78%. ¹H NMR (CDCl₃): δ 4.94 (d, 2 H, isopropenyl-CH₂), 3.87 (s, 1 H, Cp-H), 3.84 (s, 2 H, Cp-H), 1.85 (s, 6 H, isopropenyl-CH₃), 1.63 (s, 15 H, Cp-CH₃). ¹³C NMR (CDCl₃): δ 139.9, 108.0, 87.1, 79.8, 70.1, 65.6, 21.5, 9.6.

1,1'-Di(4-bromophenyl)-3,3',4,4'-tetramethylferrocene (7). 1-Bromophenyl-3,4-dimethylcyclopentadiene (4.98 g, 20.0 mmol) was dissolved in diethyl ether and then cooled to -20 °C followed by LDA (40 mL, 22.0 mmol, 0.55 M/THF) addition. After being stirred for 1 h at this temperature, the solution was slowly added to a suspension of FeCl₂·(THF)₁₅ (2.23 g, 9.5 mmol) in THF (50 mL). The reaction mixture was allowed to warm to room temperature overnight. The volatiles were removed in vacuo, and the residue was extracted with toluene (5 × 200 mL). The toluene solution was filtered, the solvent evaporated, and the crude product purified by sublimation (190 °C, 0.05 mbar). Yield: (5.10 g, 9.2 mmol, 46%). ¹H NMR (CDCl₃): δ 7.26 (d, 4 H, aryl-H), 7.02 (d, 4 H, aryl-H), 4.08 (s, 4 H, Cp-H), 1.71 (s, 12 H, Cp-CH₃). ¹³C NMR (CDCl₃): δ 137.1, 131.3, 126.6, 118.7, 84.7, 81.4, 68.8, 11.5.

1,1'-Di(4-formylphenyl)-3,3',4,4'-tetramethylferrocene (8). To a solution of the ferrocene **7** (1.00 g, 1.81 mmol) in diethyl ether (50 mL) at 0 °C was first added TMEDA (0.54 mL, 0.42 g, 3.62 mmol) followed by *n*-BuLi (1.45 mL, 3.62 mmol, 2.5 M). The reaction mixture was allowed to room temperature and stirred at this temperature for 1 d. Next, *N*-formylpiperidine (0.42 mL, 0.43 g, 3.80 mmol) was added and stirring continued for another 12 h. Finally, the reaction mixture was added dropwise into ice-cooled 2 N HCl (50 mL) and the layers separated. The aqueous phase was extracted with CH₂Cl₂ (3 × 100 mL), the combined organic solutions were dried over MgSO₄ and filtered, and the volatiles were evaporated. The residue was purified by chromatography (silica, cyclohexane/ethylacetate = 2:1). Yield: 0.62 g, 1.38 mmol, 76%. ¹H NMR (CDCl₃): δ 9.85 (s, 2 H, aryl-

CHO), 7.58 (d, 4 H, aryl-H), 7.18 (d, 4 H, aryl-H), 4.18 (s, 4 H, Cp-H), 1.63 (s, 12 H, Cp-CH₃). ¹³C NMR (CDCl₃): δ 191.6, 145.8, 133.5, 129.9, 125.2, 86.2, 80.7, 69.7, 11.4.

1,1'-Di(4-vinylphenyl)-3,3',4,4'-tetramethylferrocene (9). To a suspension of (Ph₃PCH₃)⁺I (650 mg, 1.62 mmol) in THF (15 mL) at 0 °C was added *n*-BuLi (0.65 mL, 1.62 mmol, 2.5 M), followed after 10 min by a solution of the ferrocenedialdehyde **8** (243 mg, 0.54 mmol) in THF (15 mL). The reaction mixture was allowed to room temperature and stirring continued for 1 d. Finally, the volatiles were removed on vacuo, and the residue was purified by chromatography (silica, cyclohexane/THF = 10:1). Yield: (227 mg, 0.51 mmol, 95%). ¹H NMR (CDCl₃): δ 7.25 (d, 4 H, aryl-H), 7.15 (d, 4 H, aryl-H), 6.67 (dd, 2 H, vinyl-H), 5.71 (dd, 2 H, vinyl-H), 5.20 (dd, 2 H, vinyl-H), 4.16 (s, 4 H, Cp-H), 1.64 (s, 12 H, Cp-CH₃). ¹³C NMR (CDCl₃): δ 137.9, 136.9, 134.4, 126.1, 125.2, 112.3, 86.1, 80.2, 69.3, 11.5.

General ADMET Polymerization Procedure. Polymerization of 1,4-Di(2-ethylhexyl)2,5-divinylbenzene. To the divinyl monomer (106 mg, 0.300 mmol) in a Schlenk tube under Ar atmosphere was added olefin metathesis catalyst stock solution (1.5 mL, 1 mol %, 2 mg, 0.003 mmol in 1,2-dichlorobenzene). The mixture was stirred; vacuum (20 mbar) was applied and the mixture heated to the respective reaction temperature for 3 d. After the mixture was cooled to room temperature, toluene (5 mL) was added to dissolve the polymer, followed by ethyl vinyl ether (0.2 mL) to quench the catalyst. The mixture was stirred for 1 h and filtered over a short silica plug into acetone (150 mL). The precipitated polymer was filtered and thoroughly washed with acetone (50 mL). Yield: >90%. All other polymers were synthesized according to this procedure.

Poly[2,5-di(2-ethylhexyl)-*p*-phenylenevinylene] (poly-1). ¹H NMR (CDCl₃): δ 7.41 (br, 2 H, aryl-H), 7.27 (br, 2 H, vinyl-H), 2.70 (br, 4 H, aryl-CH₂), 1.61 (br, 2 H, -CH-alkyl), 1.30 (br, 16 H, alkyl-H), 0.90 (br, 12 H, -CH₃). ¹³C NMR (CDCl₃): δ 137.4, 135.4, 127.9, 126.8, 40.3, 37.9, 32.6, 28.9, 25.7, 23.1, 14.1, 11.0.

Poly[2,5-di(2-ethylhexyloxy)-*p*-phenylenevinylene] (poly-2). ¹H NMR (CDCl₃): δ 7.46 (br, 2 H, vinyl-H), 7.14 (br, 2 H, aryl-H), 3.89 (br, 4 H, aryl-CH₂), 1.76 (br, 2 H, -CH-alkyl), 1.61–1.20 (m, 16 H, alkyl-H), 0.90 (m, 12 H, -CH₃). ¹³C NMR (CDCl₃): δ 150.1, 130.5, 121.5, 109.4, 70.7, 38.8, 29.7, 28.2, 23.3, 22.1, 13.1, 10.4.

Poly[9,9-di(2-ethylhexyl)fluorenyl-2,7-vinylene] (poly-3). ¹H NMR (CDCl₃): δ 7.60 (br, 2 H, aryl-H), 7.49 (br, 4 H, aryl-H), 7.18 (br, 2 H, vinyl-H), 2.10 (br, 4 H, aryl-CH₂), 0.84–0.50 (m, 30 H, alkyl-H). ¹³C NMR (CDCl₃): δ 151.3, 140.7, 136.1, 128.5, 125.8, 121.8, 119.8, 54.7, 44.6, 34.7, 33.7, 28.1, 27.1, 22.7, 14.0, 10.3.

Ferrocenyl-fluorenyl-vinylene Copolymer (poly-4). Four equivalents of the fluorene monomer (177.0 mg, 0.400 mmol) and 1 equiv of the ferrocene monomer (44.5 mg, 0.100 mmol) were polymerized according to the standard procedure. Yield: polymer (190.0 mg, 0.457 mmol, 92%). ¹H NMR (CDCl₃): δ 7.67 (br, 4 H, aryl-H), 7.52 (br, 8 H, aryl-H), 7.42 (br, 4 H, aryl-H), 7.19 (br, 4 H, vinyl-H), 4.18 (br, 2 H, Cp-H), 2.16 (br, 8 H, aryl-CH₂), 1.51 (br, 6 H, Cp-CH₃), 0.86–0.50 (m, 60 H, alkyl-H). ¹³C NMR (CDCl₃): δ 151.3, 140.7, 136.0, 128.5, 126.4, 125.7, 125.5, 121.8, 119.8, 84.8, 69.2, 54.7, 44.7, 34.7, 33.7, 28.1, 27.1, 22.7, 14.1, 11.6, 10.3.

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Supporting Information Available: ¹H and ¹³C NMR spectra of the new compounds described in the manuscript. This material is available free of charge via the Internet at <http://pubs.acs.org>. OM701277P