Exclusive End Functionalization of *all-trans*-Poly(fluorene vinylene)s Prepared by Acyclic Diene Metathesis Polymerization: Facile Efficient Synthesis of Amphiphilic Triblock Copolymers by Grafting Poly(ethylene glycol)

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ABSTRACT: Facile, exclusive end functionalization of poly(9,9-di-*n*-octylfluorene-2,7-vinylene) (PFV), prepared by acyclic diene metathesis polymerization using $Ru(CHPh)(Cl)_2(IMesH_2)(PCy_3)$ [$IMesH_2$ = 1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene], has been achieved by treating the vinyl groups in PFV chain ends with $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Me_2C_6H_3)[OCMe(CF_3)_2]_2$ followed by Wittig-type cleavage with $4\text{-}Me_3SiOC_6H_4CHO$; precise synthesis of ABA type amphiphilic triblock copolymers has been accomplished by grafting PEG into both the PFV chain ends.

Introduction

Organic electronics is one of the most exciting and important emerging technologies, and conjugated polymers such as poly(*p*-arylene vinylene)s, poly(thiophene)s, etc., are promising materials as novel class of organic semiconductors.[1] Since the properties for their device efficiency are generally governed by their structural regularity, chemical purity, and supramolecular order,[1−4] synthesis of structurally regular, chemically pure polymers has thus been desired by development of new synthetic methods.[5] Precise design of end-functionalized conjugated polymers also attracts considerable attention from both academic and practical aspects,[3a] and fluorene-based EL polymers should have advantages in terms of facile introduction of substitutents into the C_9 position, high PL and EL efficiencies, thermal and chemical stabilities.[6,7]

We previously reported synthesis of high molecular weight, *all-trans*, "defect-free" poly(2,5-dialkyl-1,4-phenylene vinylene)s (PPVs)[8−10] and poly(9,9-di-*n*-octylfluorene-2,7-vinylene) (PFV)[6] by acyclic diene metathesis (ADMET) polymerization of divinylarenes using $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Me_2C_6H_3)[OCMe_3(CF_3)_2]_2$ [Mo(**1**)][6,9] or $Ru(CHPh)(Cl)_2(IMesH_2)(PCy_3)$ [Ru(**1**), $IMesH_2$ = 1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene, for PPVs],[9,10] and the resultant PPVs prepared by Ru(**1**) catalyst possessed well-defined polymer chain ends (as vinyl group).[9] Therefore, we herein present our preliminary achievements for precise synthesis of amphiphilic triblock copolymers containing high molecular weight defect-free PFVs, prepared by ADMET polymerization using Ru(**1**), by grafting PEG [poly(ethylene glycol)] via exclusive functionalization of both PFV chain ends.[11−13]

Results and Discussion

In order to obtain PFVs containing vinyl group as the both chain ends, ADMET polymerization of 2,7-divinyl-9,9-di-*n*-octylfluorene[6] has been chosen in the presence of Ru(**1**) under a reduced pressure (Scheme 1). The results are summarized in Table 1. The resultant PFVs prepared under the optimized conditions possessed rather high molecular weights with unimodal molecular weight distributions (runs 2, 5−13); the M_n value increased at the initial stage and reached to a constant value after 5 h (runs 5−7). As demonstrated previously,[6,9,10] optimization of the reaction conditions was required, especially because removal of ethylene from the reaction mixture is prerequisite for obtainment of the high molecular weight PFVs in the present condensation polymerization.

The resultant PFVs possessed exclusive *trans* regularity confirmed by ^1H NMR spectra[14] because, as described previously,[6,8,9] the ADMET condensation proceeds via metallacycle intermediate. The M_n values in the PFVs prepared by Ru(**1**) were somewhat lower than that prepared by Mo(**1**) reported previously,[6] and the attempted polymerization by $RuCl_2(CHPh)(PCy_3)$, Ru(**2**), was not successful. The polymerizations by Ru(**1**) in CH_2Cl_2 also afforded high molecular weight PFVs in high yields (runs 11−13). The resultant PFVs possessed vinyl groups at the both polymer chain ends,[14] as demonstrated in the synthesis of *all-trans*-PPVs by the ADMET polymerization using Ru(**1**),[9] and good agreement in the M_n values was observed between the estimated values based on the integration ratios in the ^1H NMR spectrum and those calculated based on GPC data [$M_{n(calc)} = M_{n(GPC)}/1.6$].[15]

Treatment of the vinyl groups at the PFV chain ends with Mo(**1**) (to generate Mo−alkylidene moieties) and the subsequent addition of $4\text{-}Me_3SiOC_6H_4CHO$ gave PFVs containing Me_3SiO group at the both polymer chain ends (Scheme 2).[16] No significant changes were seen in the M_n values measured by GPC, and the M_n value estimated by the ^1H NMR spectrum (by integration ratio with $SiMe_3$ group, run 1, $M_{n(NMR)} = 6900$) was close to the exact value [$M_{n(calc)}$] estimated from the M_n value by GPC [$M_{n(GPC)}/1.6$, $M_{n(calc)} = 6700$]. The fact thus strongly suggests that precise exclusive synthesis of end-functionalized PFVs (PFV−OTMS) has been achieved by adopting the present approach. Rather excess amount of Mo(**1**) (2.5 equiv to the vinyl group) was required to accomplish the reaction; the reaction with 2.0 equiv of Mo(**1**) led to incompletion and the reaction did not complete if $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(O^tBu)_2$ was employed instead of Mo(**1**).[17] The $SiMe_3$ group in the resultrant polymers (PFV−OTMS) was

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Scheme 1

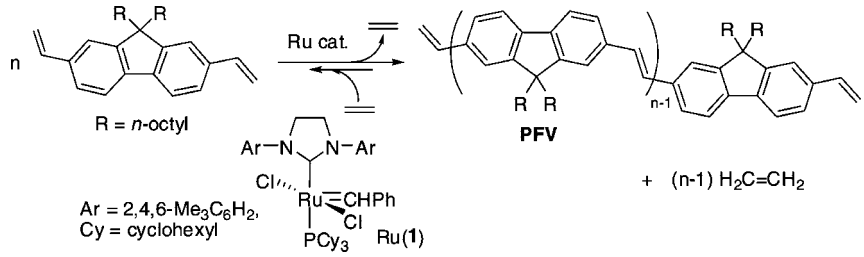
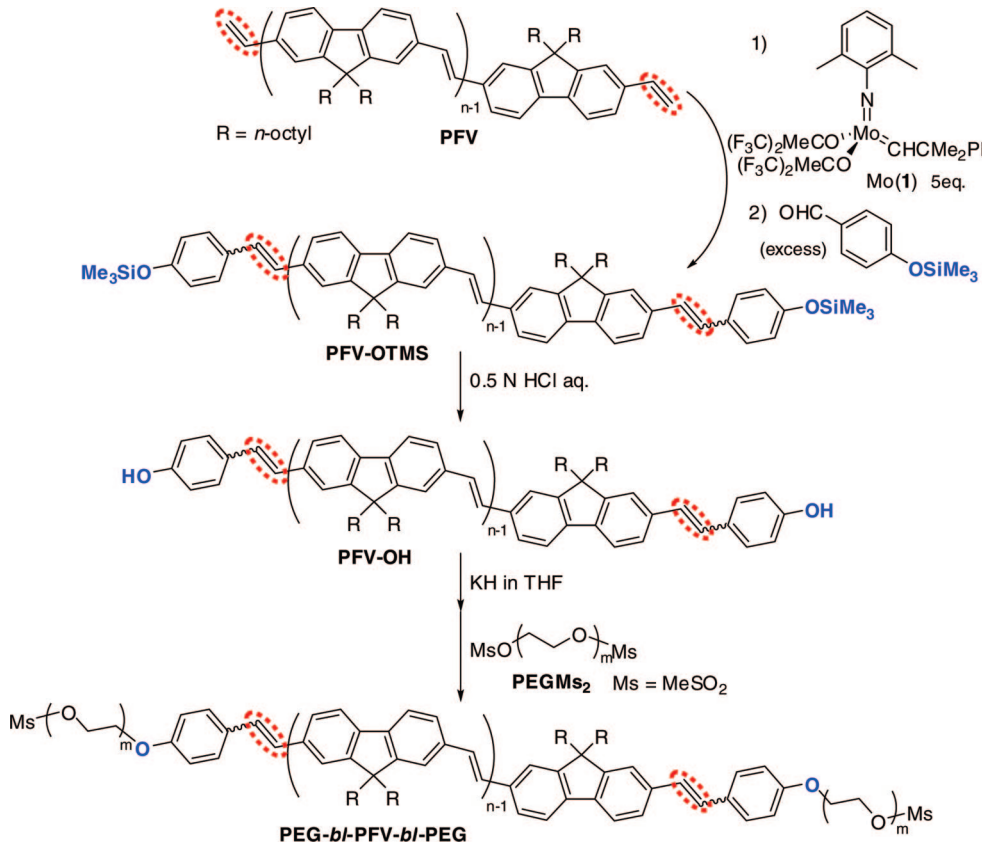


Table 1. ADMET Polymerization of 9,9′-Di-*n*-octyl-2,7-divinylfluorene[a]

run	cat. (equiv)[c]	concn[b]	solvent (mL)	temp/°C	time/h	M_n[d] × 10^{-4}	M_w/M_n[d]	yield[e]/%
1	Ru(**1**) (40)	60	toluene (1.0)	50	8	1.05	1.6	85
						0.31[f]	1.0	
2	Ru(**1**) (40)	90	toluene (1.0)	50	7.5	1.84	1.8	75
3	Ru(**2**)[g] (20)	90	toluene (1.0)	50	8			
4	Ru(**1**) (60)	180	toluene (1.0)	50	8	1.05	1.8	64
						0.24[f]	1.0	
						0.17[f]	1.0	
5	Ru(**1**) (40)	180	toluene (1.0)	50	8	2.75	2.0	90
6	Ru(**1**) (40)	180	toluene (1.0)	50	5	2.58	2.0	80
7	Ru(**1**) (40)	180	toluene (1.0)	50	1	1.43	2.2	81
8	Ru(**1**) (30)	300	toluene (1.2)	50	8	2.59	2.0	87
9	Ru(**1**) (30)	360	toluene (1.0)	50	8	2.58	2.0	87
10	Ru(**1**) (40)	424	toluene (1.7)	50	8	2.75	2.0	90
11	Ru(**1**) (40)	150	CH_2Cl_2 (1.2)	40	5	2.58	2.2	89
12	Ru(**1**) (40)	150	CH_2Cl_2 (1.0)	40	6	2.54	2.2	85
13	Ru(**1**) (30)	240	CH_2Cl_2 (3.0)	40	5	2.02	2.0	85
14	Mo(**1**)[h] (20)	78.3	toluene (1.0)	25	20	3.16 (1.71)[i]	1.8	85

[a] Conditions: solvent 1.0−1.7 mL. [b] Initial monomer concentration in μmol/mL. [c] Molar ratio based on monomer/Ru or Mo. [d] GPC data in THF vs polystyrene standards. [e] Isolated yields. [f] Observed as lower molecular weight shoulders in the GPC traces. [g] $RuCl_2(CHPh)(PCy_3)_2$ [Ru(**2**)] was used in place of Ru(**1**). [h] Mo(N-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)[OCMe(CF_3)$_2$]$_2$ was used in place of Ru(**1**).[6] [i] GPC data vs poly(*p*-phenylene) standards.[6]

Scheme 2



easily cleaved by treating with HCl aq. to afford PFV−OH in high yields (78→99%). No significant changes in the M_n values were seen before/after the procedure (from PFV to PFV−OH).[14]

The OH groups in the PFV chain ends were then treated with KH in THF, and the subsequent reaction with mesylated poly(ethylene glycol) ($PEGMs_2$)[16b,d] gave ABA-type am-

Table 2. End Functionalization of *trans*-Poly(9,9-di-*n*-octylfluorene-2,7-vinylene)s (PFVs) and Synthesis of Amphiphilic Triblock Copolymers, Poly[PEG-*bl*-PFV-*bl*-PEG] [PEG: Poly(ethylene glycol)][a]

	PFV			PFV−OTMS			PFV−OH				PFV-*bl*-PEG				
sample no.[b]	M_n[c]× 10^{-4}	M_w/M_n[c]	yield[d]/%	M_n[c]× 10^{-4}	M_w/M_n[c]	yield[d]/%	M_n[c]× 10^{-4}	M_w/M_n[c]	yield[d]/%	PEG M_n	$M_{n(GPC)}$[c]× 10^{-4}	$M_{n(calc)}$[e]× 10^{-4}	$M_{n(NMR)}$[f]× 10^{-4}	$M_w/M_{n(GPC)}$[c]	yield[d]/%
2	1.84	1.8	75	1.54	1.9	80	1.48	1.9	95	1000	1.96	1.35	1.33	1.8	69
8	2.59	2.0	87	2.52	2.2	87	2.46	2.0	95	1000	2.90	1.82	1.85	2.0	90
1	1.04	2.0	85	1.07[g]	1.8	91	1.07	1.9	78	2000	1.34	1.05	1.04	1.9	77
11	2.58	2.2	89	2.36	2.2	90	2.37	2.2	79	2000	3.35	2.01	1.95	2.0	76
10	2.75	2.0	91	2.70	2.0	89	2.70	1.9	>99	2000	3.43	2.12	2.08	1.9	85
10	2.75	2.0	91	2.91	2.0	91	3.03	1.8	93	3000	2.98	2.32	2.32	2.0	76

[a] Detailed conditions are shown in the Supporting Information. [b] Sample no. in Table 1. [c] GPC data in THF vs polystyrene standards. [d] Isolated yield as methanol-insoluble fraction. [e] Calculated value based on $M_{n(GPC)}$/1.6 plus PEG. [f] Estimated value by ^{1}H NMR spectrum (integration with PEG). [g] $M_{n(NMR)}$ = 6900 (estimated based on TMS), $M_{n(calc)}$ = 6700 [estimated based on $M_{n(GPC)}$/1.6].[15]

phiphilic triblock copolymers in rather high yields (69−90%, Scheme 2). The resultant copolymers possessed uniform molecular weight distributions; the copolymers were identified by ^{1}H and ^{13}C NMR spectra[14] and confirmed that no residual PEG was seen in GPC traces for the isolated polymer(s).

Note that the M_n values in the resultant triblock copolymers estimated based on the integration ratios with methylene protons of the PEG segment were very close to those estimated by both GPC [$M_{n(calc)} = M_{n(GPC)}$/1.6] and the value in the starting PEG (1000, 2000, or 3000).[18] The facts clearly indicate that facile, efficient attachments of a pseudo-phenol terminus on the PFV to $PEGMs_2$ [$MsO(CH_2CH_2O)_nMs$, Ms = $MeSO_2$] could be achieved in a precise manner by adopting the present "grafting to" approach. No remarkable differences were seen in their UV−vis, fluorescent spectra (absorption bands, peak maxima) between PFV and the triblock copolymer, [poly(PEG-*bl*-PFV-*bl*-PEG)].[14]

We have shown that facile, efficient synthesis of ABA type amphiphilic triblock copolymers, poly(PEG-*bl*-PFV-*bl*-PEG)s, has been established in a precise manner (as a rare example) by attachment of PEG into the both chain ends of the *all-trans*, defect-free, high molecular weight PFVs (Scheme 2). Formation of regular one-dimensional conjugated structures on the nanoscale should be thus expected by exploiting the specific assembling properties of rod−coil block copolymers,[12,13] and the control of the block lengths via synthesis opens the way to fine-tuning the lateral dimensions of these nanostructures. We thus believe that the present approach should offer unique, important methodology for precise synthesis of end-functionalized conjugated polymers (PPVs, PFVs) for targeted device materials as well as synthesis of various block copolymers containing conjugated polymer fragments.

Experimental Section

General Procedure. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. All chemicals used were of reagent grade and were purified by the standard purification procedures. Anhydrous grade of toluene (Kanto Kagaku Co. Ltd.) was transferred into a bottle containing molecular sieves (mixture of 3A and 4A 1/16, and 13X) in the drybox, was stored over sodium/potassium alloy in the drybox, and was then passed through an alumina short column prior to use. Anhydrous grade diethyl ether, dichloromethane, tetrahydrofuran (THF), and *n*-hexane (Kanto Kagaku Co. Ltd.) were also transferred into a bottle containing molecular sieves (mixture of 3A, 4A 1/16, and 13X) in the drybox. $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Me_2C_6H_3)[OCMe(CF_3)_2]$ [Mo(**1**)][19] was prepared according to the literature, and $Ru(CHPh)Cl)_2(ImesH_2)(PCy_3)$ [Ru(**1**), $ImesH_2$ = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene, Cy = cyclohexyl] (Strem Chemicals, Inc.) and $Ru(CHPh)(Cl)_2(PCy_3)_2$ [Ru(**2**)] (Fluka) were used in the drybox as received without further purification. Polymerization grade of 2,7-divinyl-9,9-di-*n*-octylfluorene was prepared according to the previous report.[6] 4-$Me_3Si-C_6H_4CHO$ was also prepared according to the previous report.[16a]

All ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ^{1}H; 100.40 MHz, ^{13}C), and all chemical shifts are given in ppm and are referenced to $SiMe_4$. Obvious multiplicities and routine coupling constants are usually not listed, and all spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. Molecular weights and the molecular weight distributions of the resultant polymers were measured by gel permeation chromatography (GPC). HPLC grade THF was used for GPC and was degassed prior to use. GPC were performed at 40 °C on a Shimazu SCL-10A using a RID-10A detector (Shimazu Co. Ltd.) in THF (containing 0.03 wt % of 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 mL/min). GPC columns (ShimPAC GPC-806, 804 and 802, 30 cm × 8.0 mm diameter, spherical porous gel made of styrene/divinylbenzene copolymer, ranging from $<10^2$ to 2×10^7 MW) were calibrated versus polystyrene standard samples. UV−vis spectra for the resultant polymers, PFV and poly(PEG-*bl*-PFV-*bl*-PEG), were measured by using a Jasco V-550 UV/vis spectrophotometer (1.0×10^{-5} M in THF at 25 °C), and the fluorescence spectra were measured by a Hitachi F-4500 fluorescence spectrophotometer (1.0×10^{-6} M in THF at 25 °C) with excitation wavelength at 426 nm.

Polymerization Procedure: Synthesis of Poly(9,9-di-*n*-octylfluorene-2,7-viynlene) (PFV) by $Ru(CHPh)(Cl)_2(ImesH_2)(PCy_3)$. The polymerization procedure employed (run 5, Table 1) was analogous to those reported previously.[6,9] Toluene (1.0 mL), 2,7-divinyl-9,9-di-*n*-octylfluorene (80 mg, 180.7 μmol), and $Ru(CHPh)(Cl)_2(ImesH_2)(PCy_3)$ [Ru(**1**), 4.6 μmol] were charged into a sealed Schlenk-type tube equipped with Kontes high-vacuum valves in the drybox. The tube was then placed into a liquid nitrogen bath and was then connected to the vacuum line for a while.[6,9] The tube was then placed into an oil bath preheated at the prescribed temperature under a reduced pressure, and the mixture was stirred for prescribed time. During the reaction, the mixture was placed into a liquid nitrogen bath with a certain period [every 10 min at the initial 1 h, then every 30 min for 1 h, and then every 1 h] to remove ethylene from the reaction medium by opening the valve connected to the vacuum line and then placed into the oil bath to continue the reaction. The polymerization was quenched by adding ethyl vinyl ether in excess amount. The reaction mixture was then stirred for 1 h for completion. The resultant solution was poured into cold methanol (~50 mL), affording yellow precipitates. The polymer was collected by filtration and was then dried in vacuo. Yield 90%. Most probable reasons for the relatively low yields in certain runs were due to the difficulty to isolate small amount of polymers from the mixture due to the small polymerization scale. Since the resultant polymer was slightly soluble in methanol, the methanol-soluble fraction also contaminated the desired polymer if the polymerization was reached to completion. (The reaction was generally conducted until no further increase in the molecular weight for the resultant polymer was observed.) The ^{1}H NMR spectrum in the resultant polymer was analogous to that reported previously,[6] except the polymer chain end (vinyl group).

^{1}H NMR ($C_2D_2Cl_4$, tetrachloroethane-d_4, at 25 °C): δ 7.67 (br, 2H), 7.51 (br s, 4H), 7.26 (br s, 2H, *trans*-CH=CH−), 2.00 (br),

1.8 (br), 1.23 (br s), 1.09 (br s), 0.85 (br s). In addition, resonances at δ 6.82 (dd), 5.82 (d), and 5.27 (d) ppm were observed. If the sample solution was diluted, the following resonances are observed: δ 7.66 (d, 2H), 7.50 (br, 4H), 7.26 (br s, 2H), 1.99 (br), 1.62 (br s), 1.14 (m), 1.06 (br s), 0.77 (t, 6H, $J = 6.6$ Hz, CH_3), and 0.64 ppm. ^{1}H NMR ($CDCl_3$ at 25 °C): δ 7.67 (d, 2H, $J = 7.2$ Hz), 7.72 (br, 4H), 7.27 (br, 2H, *trans*-CH=CH−), 6.82 (dd), 5.82 (d), 5.27 (d), 2.03 (br, 4H), 1.18−1.07 (br, 20H), 0.79 (t, 6H, $J = 6.4$ Hz, CH_3), 0.66 (br, 4H). ^{13}C NMR (CD_2Cl_4 at 25 °C): δ 151.8, 140.8, 136.4, 125.9, 120.9, 120.2, 55.1, 40.5, 32.1, 31.8, 30.3, 29.5, 24.0, 22.9, 14.4. ^{13}C NMR ($CDCl_3$ at 25 °C): δ 14.1, 15.7, 22.6, 23.8, 29.3, 30.1, 31.8, 40.8, 55.1, 120.0, 120.6, 125.8, 128.6, 136.5, 140.6, 151.6.

Synthesis of PFV−OTMS. Part of the synthetic procedure for PFV−OTMS was somewhat analogous to our previous report for preparation of end-functionalized polynorbornene.[16] Typical procedure (run 1, Table 2) is as follows. A toluene solution containing $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Me_2C_6H_3)[OCMe(CF_3)_2]_2$ [Mo(**1**), 20 mg/1.0 mL of toluene] was added in one portion to a rapidly stirred toluene solution (465 mg) containing poly(9,9-di*n*-octyl-fluorene-2,7-vinylene) (PFV, 35 mg) in toluene at room temperature, and the solution was stirred for 2 h. The solution was then added 4-$Me_3SiOC_6H_4CHO$ in excess amount (~10 mg) and was stirred for an additional 1 h for completion. The solution was then poured dropwise into methanol to afford yellow precipitates, and the resultant polymer, PFV−OTMS, was then collected by filtration and dried in vacuo. Yield 32 mg (91%). Sample polymer, PFV, for this reaction was dissolved in toluene in the drybox and was passed through a pad with Celite, and the filtrate was dried in vacuo; the process is required to remove oxygen and water contaminant in the polymer samples (because the molybdenum catalyst is highly sensitive to the impurities). ^{1}H NMR ($CDCl_3$): δ 7.66 (d, 2H), 7.51 (br, 4H), 7.27 (br, 2H, *trans*-CH=CH−), 7.07 (d), 6.82 (d), 2.03 (br, 4H), 1.18−1.07 (m, 20H), 0.79 (t, 6H, $J = 6.4$ Hz, CH_3), 0.66 (br, 4H), 0.27 ($OSiMe_3$). ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 23.8, 29.2, 30.1, 31.8, 40.7, 55.0, 120.0, 120.6, 125.7, 128.6, 136.5, 140.6, 151.6.

Removal of TMS ($SiMe_3$) Protection from PFV−OTMS: Synthesis of PFV−OH. Typical procedure (run 1, Table 1) is as follows. Into a rapidly stirred solution of THF (2 mL) containing PFV−OTMS (19 mg) was added 0.5 M HCl (2 drops), and the mixture was stirred for 1 h at room temperature. The solution was then poured dropwise into methanol to afford yellow precipitates, and the resultant polymer, PFV−OH, was collected by filtration and dried in vacuo. Yield 15 mg (78%). ^{1}H NMR ($CDCl_3$): δ 7.66 (d, 2H), 7.51 (br, 4H), 7.27 (br, 2H, *trans*-CH=CH−), 7.07 (d), 6.82 (d), 2.03 (br, 4H), 1.18−1.07 (m, 20H), 0.79 (t, 6H, $J = 6.4$ Hz, CH_3), 0.66 (br, 4H). ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 23.8, 29.2, 30.1, 31.8, 40.7, 55.0, 120.0, 120.6, 125.7, 128.6, 136.5, 140.6, 151.6.

Synthesis of Amphiphilic Block Copolymer, Poly(PEG-*bl*-PFV-*bl*-PEG), by Grafting PEG [Poly(ethylene glycol)]. Typical procedure (run 1) for attachment of PEG with the PFV−OH was performed as follows.[16b,d] Into a THF solution (485 mg) containing PFV−OH (15 mg, estimated 1.4 μmol based on GPC/1.6) was added KH (2 mg, 50 μmol), and the mixture was stirred for 3 h at room temperature. The solution was then filtered through a bed of Celite/alumina, and the filter cake was washed with additional THF (1 g). The combined THF solution was then added with a THF solution (500 mg) containing $PEGMs_2$ (10 mg, 5 μmol), and the mixture was stirred at room temperature overnight. The reaction solvent was removed in vacuo, and the residual product was then dissolved with minimum amount of THF and was poured into methanol (60 mL). The resultant yellow precipitates, poly(PEG-*bl*-PFV-*bl*-PEG), was collected by filtration and dried in vacuo. Yield 18.9 mg (77%). ^{1}H NMR ($CDCl_3$): δ 7.66 (d, 2H), 7.51 (br, 4H), 7.27 (br, 2H, *trans*-CH=CH−), 7.07 (d), 6.90 (d), 3.62 (br), 2.03 (br, 4H), 1.18−1.07 (m, 20H), 0.79 (t, 6H, $J = 6.4$ Hz, CH_3), 0.66 (br, 4H). ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 23.8, 29.2, 30.1, 31.8, 40.7, 55.0, 70.6, 120.0, 120.6, 125.7, 128.6, 136.5, 140.6, 151.6.

Supporting Information Available: Selected ^{1}H and ^{13}C NMR spectra of polymers; UV−vis and fluorescent spectra for PFV and poly(PEG-*bl*-PFV-*bl*-PEG). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Müllen, K. *Organic Light Emitting Devices*; Scherf, U., Ed.; Wiley-VCH: Weinheim, Germany, 2006. (b) Skotheim, T. A. *Handbook of Conducting Polymers*, 3rd ed.; Reynolds, J., Ed.; CRC Press: Boca Raton, FL, 2007.

(2) Special Issue in Organic Electronics: *Chem. Mater.* **2004**, *16*, 4381−4842.

(3) (a) Grimsdale, A. C.; Müllen, K. In *Macromolecular Engineering*; Matyjaszewski, K., Gnanou, Y., Leibler, L., Eds.; Wiley-VCH: Weinheim, Germany, 2007; Vol. *4*, pp 2225−2262. (b) Bielawski, C. W.; Wilson, C. G. In ref 3a, pp 2263−2293. (c) Laclerc, N.; Heiser, T.; Brochon, C.; Hadziioannou, G. In ref 3a, pp 2369−2408.

(4) For selected reviews, see: (a) Fumitomo, H.; Díaz-García, M. A.; Schwartz, B. J.; Heeger, A. J. *Acc. Chem. Res.* **1997**, *30*, 430–436. (b) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402–428. (c) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. C. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature (London)* **1999**, *397*, 121–128.

(5) (a) Stirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; de Leeuw, D. M. *Nature (London)* **1999**, *401*, 685–688. (b) Hoofman, J. O. M.; de Haas, M. P.; Siebbeles, L. D. A.; Warman, J. M. *Nature (London)* **1998**, *392*, 54–56. (c) Son, S.; Dodabalapur, A.; Lovinger, A. J.; Galvin, M. E. *Science* **1995**, *269*, 376–378.

(6) Nomura, K.; Morimoto, H.; Imanishi, Y.; Ramhani, Z.; Geerts, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2463–2470.

(7) Synthesis of oligo-, poly-(9,9-dialkylfluorene-2,7-vinylene) by other approaches and the property analysis: (a) Jin, S.-H.; Park, H.-J.; Kim, J. Y.; Lee, K.; Lee, S.-P.; Moon, D.-K.; Lee, H.-J.; Gal, Y.-S. *Macromolecules* **2002**, *35*, 7532–7534. (b) Jin, S.-H.; Kang, S.-Y.; Kim, M.-Y.; Chan, Y. U.; Kim, J. Y.; Lee, K.; Gal, Y.-S. *Macromolecules* **2003**, *36*, 3841–3847. (c) Grisorio, R.; Mastrorilli, P.; Nobile, C. F.; Romanazzi, G.; Suranna, G. P. *Tetrahedron Lett.* **2005**, *46*, 2555–2558. (d) Gruber, J.; Li, R. W. C.; Aguiar, L. H. J. M. C.; Garcia, T. L.; de Oliveira, H. P. M.; Atvars, T. D. Z.; Nogueira, A. F. *Synth. Met.* **2006**, *156*, 104–109. (e) Anuragudom, P.; Newaz, S. S.; Phanichphant, S.; Lee, T. R. *Macromolecules* **2006**, *39*, 3494–3499. (f) Mikroyannidis, J. A.; Yu, Y.-J.; Lee, S.-H.; Jin, J.-I. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 4494–4507. (g) Barberis, V. P.; Mikroyannidis, J. A.; Cimrova, V. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5750–5762. (h) Liu, Q.; Liu, W.; Yao, B.; Tian, H.; Xie, Z.; Geng, Y.; Wang, F. *Macromolecules* **2007**, *40*, 1851–1857.

(8) Synthesis of oligomeric poly(phenylene vinylene)s by acyclic diene metathesis (ADMET) condensation: (a) Thorn-Csányi, E.; Kraxner, P. *Macromol. Rapid Commun.* **1995**, *16*, 147–153. (b) Thorn-Csányi, E.; Kraxner, P. *J. Mol. Catal. A* **1997**, *115*, 21–28. (c) Thorn-Csányi, E.; Kraxner, P. *Macromol. Chem. Phys.* **1997**, *198*, 3827–3843. (d) Thorn-Csányi, E.; Kraxner, P. *Macromol. Rapid Commun.* **1998**, *19*, 223–228. (e) Schlick, H.; Stelzer, F.; Tasch, S.; Leising, G. *J. Mol. Catal. A* **2000**, *160*, 71–84. (f) Thorn-Csányi, E.; Herzog, O. *J. Mol. Catal. A* **2004**, *213*, 123–128. (g) Joo, S.-H.; Jin, J.-I. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 1335–1349. (h) Oakley, G. W.; Wagener, K. *Macromol. Chem. Phys.* **2005**, *206*, 15–24. (i) Pecher, J.; Mecking, S. *Macromolecules* **2007**, *40*, 7733–7735.

(9) Synthesis of high molecular weight poly(2,5-dialkyl-1,4-phenylene vinylene)s (PPVs): Nomura, K.; Miyamoto, Y.; Morimoto, H.; Geerts, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6166–6177.

(10) More recently, improvement in a reaction protocol for synthesis of poly(arylene vinylene)s by ADMET polymerization using Ru(**1**) or the other ruthenium catalysts has been introduced: Weychardt, H.; Plenio, H. *Organometallics* **2008**, *27*, 1479–1485.

(11) Parts of these results were introduced at the 10th Pacific Polymer Conference (PPC10), 6P1S1-017a, Kobe, Japan, Dec **2007**.

(12) Synthesis of alternating block copolymers consisting of oligo-, poly(phenylene) and oligo-, poly(ethylene glycol): (a) Wagner, Z. R.; Roenigk, T. K.; Goodson, F. E. *Macromolecules* **2001**, *34*, 5740–5743. (b) Hargadon, M. T.; Davey, E. A.; McIntyre, T. B.; Gnanamgari, D.; Wynne, C. M.; Swift, R. C.; Zimbalist, J. R.; Fredericks, B. L.; Nicastro, A. J.; Goodson, F. E. *Macromolecules* **2008**, *41*, 741–750 Highly regular organization of conjugated polymer chains via block copolymer self-assembly: (c) Leclère, P.; Calderone, A.; Marsitzky, D.; Francke, V.; Geerts, Y.; Müllen, K.; Brédas, J. L.; Lazzaroni, R. *Adv. Mater.* **2000**, *12*, 1042–1046.

(13) Synthesis of poly(phenylene vinylenes) with well-defined poly(ϵ-caprolactone) or polystyrene: Colak, D. G.; Cianga, I.; Yagci, Y.; Cirpan, A.; Karasz, F. E. *Macromolecules* **2007**, *40*, 5301–5310.
(14) Selected ^{1}H and ^{13}C NMR spectra of polymers, and UV−vis and fluorescent spectra for PFV and poly(PEG-*bl*-PFV-*bl*-PEG) are shown in the Supporting Information.
(15) As reported previously,[6] $M_n = 1.71 \times 10^4$ (ca. 41 repeated units) was recorded in GPC vs PPP standards (run 14). The value is lower than that in GPC vs polystyrene standards ($M_n = 3.16 \times 10^4$) because of the nature of rigid conjugated polymers, and the estimation [$M_{n(calcd)} = M_{n(GPC)}/1.6$] was adopted for further study. Estimation of the M_n values based on the integration ratio with the vinyl group seemed difficult due to the high molecular weight, and we thus estimated the M_n values based on $SiMe_3$ group and PEG shown in Table 2.
(16) Synthesis of end-functionalization of ring-opened polynorbornene via the Wittig type cleavage, for example: (a) Nomura, K.; Takahashi, S.; Imainishi, Y. *Macromolecules* **2001**, *34*, 4712–4723. (b) Murphy, J. J.; Kawasaki, T.; Fujiki, M.; Nomura, K. *Macromolecules* **2005**, *38*, 1075–1083. (c) Murphy, J. J.; Nomura, K. *Chem. Commun.* **2005**, 4080–4082. (d) Murphy, J. J.; Furusho, H.; Paton, R. M.; Nomura, K. *Chem.—Eur. J.* **2007**, *13*, 8985–8997.
(17) The exclusive metathesis with vinyl group without accompanying methathesis with internal olefins should be required. In this regard, Mo(**1**) was more suited than Ru(**1**) because ADMET condensation did not proceed if the reaction was conducted under nitrogen atmosphere, as reported in ref 6.
(18) The M_n value by GPC for the triblock copolymer was somewhat close to that before grafting PEG3000 (Table 2, run 10, last line), but the result was reproducible ($M_n = 2.99 \times 10^4$, $M_w/M_n = 1.9$, by GPC with independent analysis run after preparation of a new calibration curve with polystyrene standards). We also confirmed that PEG was not extracted from the block copolymer after separation of PEG with the block copolymer: both ^{1}H and ^{13}C NMR spectra clearly indicate formation of the block copolymer, and the M_n value estimated by the ^{1}H NMR spectrum is close to the estimated value. We believe that this is due to that the M_n value by GPC was based on polystyrene standards, although we do not have the exact reason.
(19) (a) Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Reagan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378–8387. (b) Bazan, G. C.; Oskam, J. H.; Cho, H.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899–6907.

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