[Regular Paper]

One-pot Synthesis of End-functionalized Conjugated Polymers by Combined Acyclic Diene Metathesis (ADMET) Polymerization Using Molybdenum Catalyst with Wittig-type Coupling

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Precise, one-pot synthesis of end-functionalized conjugated polymers, poly(9,9-di-n-octyl-fluorene vinylene)s (PFVs), have been prepared by acyclic diene metathesis (ADMET) polymerization followed by Wittig-type coupling with aldehyde in the presence of molybdenum-alkylidene catalyst, Mo(CHMe2Ph)(N-2,6-Me2C6H3)\[OC(CH3)(CF3)2\]2 (Mo cat.). Further addition of Mo cat. after the ADMET polymerization was necessary for completion of olefin metathesis (with the vinyl chain end) and for exclusive end-functionalization by the subsequent coupling. Various end-functionalities could be introduced without purification or isolation by this one-pot methodology.

Keywords
Olefin metathesis, Conjugated polymer, Molybdenum catalyst, Wittig-type coupling, One-pot synthesis

1. Introduction

Conjugated polymers are promising materials in their applications as organic electronics in optoelectronic and electrochemical devices\(^1\sim6\), and the performances of these devices are affected by their structural regularity, chemical purity, and supramolecular order\(^1\sim3\). Synthesis of structurally regular, chemically pure polymers requires the development of new synthetic methods. End-group modification is as a promising technique, because modification of the end-groups can induce unique optical and/or electronic properties, as known for poly(fluorene)\(^7\sim13\).

We previously demonstrated syntheses of high molecular weight poly(9,9-dialkyl-fluorene-2,7-vinylene)s (PFVs)\(^14\sim15\), and poly(2,5-dialkyl-phenylene-1,4-vinylene)s (PPVs)\(^16\) by acyclic diene metathesis (ADMET) polymerization (Scheme 1)\(^17\sim21\). The ADMET approach can provide stereo-regular (all trans), defect-free materials (no impurities such as halogen, sulfur etc. and/or cross linking), and is more promising than conventional condensation approaches (such as de-halogenation-condensation in vacuo)\(^11\sim3\). Moreover, exclusive end-functionalization can be achieved by olefin metathesis of the vinyl chain ends in PFVs, which were prepared by the metathesis polymerization using ruthenium catalyst\(^5\sim22\sim27\), with Mo(CHCMe2Ph)(N-2,6-Me2C6H3)(OCMe(CF3)2)2 (Mo cat.) followed by Wittig-type cleavage with aldehyde (Scheme 1)\(^22\sim27\).

The above method enables precise and exclusive synthesis of the various fully conjugated end-functionalized (block, star) polymers (EF-PFVs)\(^22\sim27\), but rather excess Mo cat. (as reagent) is required for completion of the end-functionalization (olefin metathesis with the vinyl chain ends)\(^28\sim29\). Therefore, another methodology is needed for “catalytic one-pot” synthesis of EF-PFVs directly from the monomer (2,7-divinyl-9,9-di-n-octyl-fluorene, DVF).

More recently, we demonstrated direct synthesis of EF-PFVs by one-pot synthesis through combined ADMET polymerization of DVF with end-functionalization/chain transfer using 1,2-disubstituted (bi-functional) olefins (DOs) in the presence of ruthenium catalyst, RuCl2(PCy3)(IMesH2)(CHPh) (Scheme 2)\(^30\sim31\).

Efficient one-pot synthesis of a series of high molecular weight EF-PFVs could be achieved using DOs added after a certain period of the ADMET polymerization. However, this approach has a limited scope in the internal olefins; the metathesis reaction in the presence of DOs with electron withdrawing substituents (such as C6F5, C6H5 etc., Scheme 2) did not reach completion\(^30\).

We previously reported synthesis of PFVs and PPVs by ADMET polymerization using Mo cat., and the resultant polymers possessed similar properties to those
prepared by the ruthenium catalyst. The present study explored the one-pot synthesis of EF-PFVs by combined ADMET polymerization of DVF in the presence of molybdenum catalyst with subsequent Wittig-type coupling.  

2. Experimental  

2.1. General Procedure  

All experiments were carried out under a nitrogen atmosphere in a vacuum atmosphere drybox unless otherwise noted. All chemicals used were of reagent grades and were purified by standard purification procedures. Anhydrous grade toluene (Kanto Chemical Co., Inc.) was transferred into a bottle containing molecular sieves (mixture of 3A 1/16, 4A 1/8 and 13X 1/16) in the drybox, stored over sodium/potassium alloy, and used after passing through an alumina short column under nitrogen flow prior to use. Polymerization grade of 2,7-divinyl-9,9-di-octyl-fluorene was prepared by the ruthenium catalyst. The present study explored the one-pot synthesis of EF-PFVs by combined ADMET polymerization of DVF in the presence of molybdenum catalyst with subsequent Wittig-type coupling.  

Scheme 1 Synthesis of Defect-free, All-trans Conjugated Polymers by Acyclic Diene Metathesis (ADMET) Polymerization: Precise synthesis of end-functionalized polymers by combined olefin metathesis with Wittig-type coupling.
THF was used for GPC and was degassed prior to use. GPC was performed at 40°C using a RID-10A detector (Shimadzu Corp.) in THF (containing 0.03 wt% of 2,6-dichlorobenzyltrimethylsilane). 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 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 was performed at 40°C on a Shimadzu SCL-10A using a RID-10A detector (Shimadzu Corp.) in THF (containing 0.03 wt% of 2,6-dichlorobenzyltrimethylsilane). UV-vis spectra of the resultant polymers were measured using a Hitachi F-7000 fluorescence spectrophotometer (under absorbance 1.0 × 10⁻⁵ M in THF at 25°C), and fluorescence spectra were measured using a Hitachi F-7000 fluorescence spectrophotometer (under absorbance 1.0 × 10⁻⁵ M in THF at 25°C) with excitation wavelength at 460 nm.

2.2. Synthesis of PFV-Fc2: One-pot synthesis of ferrocene terminated poly(di-n-octyl-fluorene vinylene)

In the dry box, a toluene solution (320 mg) containing Mo(CHCMe2Ph)(N-2,6-Me2C6H3)[OCMe(CF3)2]2 (Mo cat., 3.2 mg, 4.52 μmol), 2,7-divinyl-9,9-di-n-octyl-fluorene (40 mg, 90.5 μmol), and toluene (0.83 mL) were charged into a sealed Schlenk-type tube equipped with Kontes high-vacuum valves in the drybox. The tube was then placed into a cold toluene bath precooled at -30°C in the drybox (as shown previously) and was then connected to the vacuum line for a while. The tube was then placed on a magnetic stirrer under a reduced pressure, and the mixture was stirred for 5 h. During the reaction, the mixture was placed into a cold toluene bath (-30°C) at certain intervals (every 10 min during the initial 1 h, then every 30 min for 1 h, and then every 1 h) to remove ethylene by-product from the reaction medium by opening the valve connected to the vacuum line. After the polymerization, the reaction mixture, and the solution was stirred for 2 h. The reaction was then quenched by adding ferrocene carboxaldehyde (FcCHO) in excess amount. The reaction mixture was then stirred for 1 h for completion, and the resultant solution was poured into cold methanol (ca. 50 mL) and precipitated for 10 min at 5000 rpm using a centrifuge. The yellow polymer was collected with 0.45 μm membrane filter and then dried in vacuo. Samples in runs 1, 2 were prepared similarly, except that certain aldehyde was added without further addition of molybdenum catalyst after the (initial) ADMET polymerization.

PFV-Fc2
Yield: 99%.
1H NMR (CDCl3 at 25°C): δ 7.69 (d, 2H, J = 8.1 Hz), 7.55 (br. 4H), 7.29 (br., 2H), 4.53 (s), 4.33 (s), 4.20 (s) ferrocene, 2.05 (br., 4H), 1.26-1.08 (br., 20H), 0.81 (t, 6H, J = 7.0 Hz), 0.69 (br., 4H).

PFV-Ph2
Yield: 95%.
1H NMR (CDCl3 at 25°C): δ [8.00-7.00 benzene], 7.69 (d, 2H, J = 7.6 Hz), 7.54 (br., 4H), 7.29 (br., 2H), 2.05 (br., 4H), 1.25-1.08 (br., 20H), 0.80 (t, 6H, J = 7.0 Hz), 0.68 (br., 4H).

PFV-(Pyrene)2
Yield: 95%.
1H NMR (CDCl3 at 25°C): δ [8.00-7.00 pyrene], 7.70 (d, 2H, J = 7.6 Hz), 7.53 (br., 4H), 7.29 (br., 2H), 2.05 (br., 4H), 1.25-1.08 (br., 20H), 0.81 (t, 6H, J = 7.0 Hz), 0.68 (br., 4H).

3. Results and Discussion

3.1. Synthesis of End-functionalized Poly(9,9-di-n-octyl-fluorene-2,7-vinylene)s (EF-PFVs) by ADMET Polymerization and Subsequent Wittig-type Coupling

Acyclic diene metathesis (ADMET) polymerization of (2,7-divinyl-9,9-di-n-octyl-fluorone, DVF) using Mo(CHCMe2Ph)(N-2,6-Me2C6H3)[OCMe(CF3)2]2 (Mo cat.) afforded high molecular weight polymers (PFVs) with uniform molecular weight distributions, whereas attempted polymerization using the isopropyl analogue, Mo(CHCMe2Ph)(N-2,6-Pr2C6H3)[OCMe(CF3)2]2, afforded low molecular weight oligomers in addition to recovery of DVF. 1H NMR spectroscopy of the polymers terminated by CH2=CH2CHO showed that the resultant PFVs possess high stereo-regularity (all trans) and certain percentages of the resonances could be ascribed to protons in the vinyl chain ends, as also confirmed below (run 1, Table 1). Therefore, we explored the possibility of one-pot synthesis of end-functionalized PFVs according to an approach shown in Scheme 3.

ADMET polymerization of DVF using Mo cat. was conducted in toluene for 5 h (initial molar ratio of DVF/Mo = 20) in vacuo, and the prescribed amount of the Mo cat. was further added for completion of olefin metathesis of vinyl chain ends (Scheme 3). After 2 h, aldehyde (described below) was added in excess (>5-10 equiv.) for the subsequent Wittig-type coupling. The results with various aldehydes are summarized in Table 1.

As reported previously, the resultant polymers (PFVs)
possessed high molecular weights with unimodal molecular weight distributions (runs 1, 2), when the ADMET polymerizations were terminated with propionaldehyde, Me₃SiOC₆H₄CHO without addition of Mo cat. before termination. The Mn values in the resultant polymers did not change even with the addition of Mo cat. after 5 h of ADMET polymerization (runs 3-6), strongly suggesting that further propagation of polymer chain (olefin metathesis reactions with the terminal olefins for propagation or metathesis with internal olefins leading to decrease in the Mn values) did not proceed under these conditions. As described below, the resultant PFVs (PFV-Ar₂) possessed high molecular weights with unimodal molecular weight distributions.

Table 1  One-pot Synthesis of End-functionalized Poly(9,9-di-n-octyl-fluorene-2,7-vinylene)s (EF-PFVs) by Combined Acyclic Diene Metathesis (ADMET) Polymerization Using Mo(CHCMe₂Ph)(N-2,6-Me₂C₆H₃)[OCMe(CF₃)₂]₂ with Wittig-type Coupling with Aldehyde

| Run | Mo (additional) [μmol] | Aldehyde | Conv [%] | Mn [× 10⁴] | Mw/Mn | Yield [%] |
|-----|----------------------|----------|---------|-----------|-------|-----------|
| 1   | -                    | CH₃CH₂CHO | -       | 2.13      | 2.40  | 99        |
| 2   | -                    | 4-Me₃SiOC₆H₄CHO | -       | 1.81      | 2.49  | 90        |
| 3   | 9.59                 | ferrocene-carboxaldehyde (FcCHO) | > 99     | 1.72      | 2.48  | 99        |
| 4   | 8.04                 | ferrocene-carboxaldehyde (FcCHO) | > 99     | 1.96      | 2.25  | 93        |
| 5   | 9.59                 | PhCHO     | > 99     | 2.20      | 2.75  | 95        |
| 6   | 9.59                 | 1-pyrene-carboxaldehyde (PyrCHO) | > 99     | 2.09      | 2.85  | 95        |

a) Conditions: (ADMET polymerization) DFV 40 mg (90.4 μmol), Mo(CHCME₂Ph)(N-2,6-Me₂C₆H₃)[OCMe(CF₃)₂]₂ (Mo cat.) 4.52 μmol, toluene, 25 °C, 5 h, details are shown in the Experimental Section.
b) Additional Mo cat. added after the (initial) ADMET polymerization.
c) Estimated by ¹H NMR (conversion of vinyl chain ends).
d) GPC data in THF vs. polystyrene standards at 40 °C.
e) Isolated yield.

**Figure 1** shows a typical ¹H NMR spectrum (in CDCl₃ at 25 °C) of the resultant PFV terminated with ferrocene-carboxaldehyde (PFV-Fc₂, Table 1, run 3). The resonances ascribed to the vinyl chain ends (in particular, 5.81 ppm and 5.26 ppm) clearly disappeared and resonances ascribed to the ferrocene moiety were observed²⁰. Moreover, the estimated Mn values [Mₙ(NMR)] on the basis of the integration ratios [protons on Fc (marked as x, y, z) versus aromatic protons (marked as a, b, c)] showed good agreements with the values estimated on the basis of GPC [Mₙ(calcd) = Mₙ(GPC)/1.6]³³, strongly suggesting that the resultant polymers are PFVs containing the ferrocene moiety as the both end groups [run 3, Mₙ(NMR) = 10700 vs. Mₙ(calcd) = 11300; run 4: Mₙ(NMR) = 12300 vs. Mₙ(calcd) = 11700], as demonstrated.
previously by other methodologies as shown in Schemes 1 and 2\textsuperscript{22,28).} It also turned out that the resultant PFVs possesses highly trans internal olefinic double bonds (7.29 ppm, marked as d in Fig. 1), as reported previously\textsuperscript{14,16,22,28,30,32,33} because the reaction proceeded via the metallacycle intermediate (steric bulk of fluorenyl group adjacent to the aromatic vinyl group), as demonstrated previously\textsuperscript{14,15,21}. These results clearly indicate that the method achieves efficient and exclusive synthesis of defect-free, stereo-regular (all trans), end-functionalized PFVs (EF-PFVs).

3.2. UV-vis and Fluorescent Spectra of End-functionalized Poly(9,9-di-n-octyl-fluorene-2,7-vinylene)s (EF-PFVs)

Figure 2 shows the UV-vis and fluorescent spectra for the resultant EF-PFVs [in THF at 25 °C, samples shown in Table 1, PFV-Fc\textsubscript{2}: M_m/GPC = 17200, M_w/M_m = 2.48, run 3]. The PFV prepared using the ruthenium catalyst [M_m/GPC = 16400, M_w/M_m = 1.49, possessing vinyl chain ends] according to the reported method\textsuperscript{15,26,27} was also investigated for comparison.

The PFV spectra displays two absorption bands at 455, 427 (and 400) nm, as reported previously\textsuperscript{14,15,22–28,34,35}, that can be ascribed to π-π* transitions (0-0, 0-1, and 0-2 transitions, respectively) of the conjugated backbone\textsuperscript{15,34,35}. No significant differences in the spectra (including λ_{max} values) were observed with different end functional groups as well as even with the PFV before modification\textsuperscript{14,15}. Moreover, the corresponding emission peaks of two/three absorption bands in the UV-vis spectra [at 455, 427 (and 400) nm, ascribed to π-π* transitions (0-0, 0-1, and 0-2 transitions, respectively)], as reported previously\textsuperscript{14,15,22–28,34,35}, were observed at 466, 497, and 530 nm in the fluorescence spectra, irrespective of the type of end groups in these PFVs.

The fluorescent spectra (especially in intensity) of PFV-Ar\textsubscript{2} were affected by the end groups\textsuperscript{22,28).} A placement of the ferrocene (Fc) moiety to the PFV chain end, PFV-Fc\textsubscript{2}, caused a dramatic quenching of photoluminescence (Fig. 2 bottom), as reported previously\textsuperscript{26,27}, probably due to an exciton transfer to the Fc units\textsuperscript{36–38}. The spectrum is highly analogous to those prepared previously (by combined olefin metathesis with Wittig-type cleavage from PFV prepared by Ru catalyst)\textsuperscript{26,27}. Since no clear differences (λ_{max} values etc.) were observed in both UV-vis and fluorescence spectra of the resultant EF-PFVs, it is thus clear that an efficient one-pot synthesis of EF-PFVs is possible by adopting the methodology shown in Scheme 3.
4. Conclusion

We have shown that one-pot synthesis of end-functionalized conjugated polymers, poly(9,9-di-octyl-fluorene vinylene) (EF-PFVs), has been achieved by combined acyclic diene metathesis (ADMET) polymerization using Mo(CHCMe2Ph)(N-2,6-Me(2)C6H4)[OCMe(2)C(2)] (Mo cat.) with subsequent Wittig-coupling (shown in Scheme 3). Further addition of Mo cat. after the ADMET polymerization was necessary for exclusive end-functionalization, and for completion of olefin metathesis with the vinyl chain ends to allow the subsequent Wittig-type coupling with aldehyde. The present method also enables reduction of molybdenum catalyst (Mo cat.), required rather excess for end-functionalization of polymers prepared by ADMET polymerization using ruthenium catalyst). Various aldehydes can be used for the introduction of end-functionality as demonstrated in Scheme 1 [12]–[28], and the method can be applied for synthesis of the other poly(arylene vinylene) derivatives [13]–[16]. Therefore, the present method can be applied to the synthesis of various end-functionalized conjugated polymers that possess unique optical properties modified by the end groups [17]–[19],[22]–[27].

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References

1) Grimsdale, A. C., Müllen, K., “Macromolecular Engineering,” eds. by Matyjaszewski, K., Gnanou, Y., Leibler, L., Wiley-VCH, Weinheim (2007), Part 4, Chap. 6, pp. 2225-2262.
2) Bieleski, C. W., Wilson, C. G., “Macromolecular Engineering,” eds by Matyjaszewski, K., Gnanou, Y., Leibler, L., Wiley-VCH, Weinheim (2007), Part 4, Chap. 7, pp. 2263-2293.
3) Laclerc, N., Heiser, T., Brochon, C., Hadzioannou, G., “Macromolecular Engineering,” eds. by Matyjaszewski, K., Gnanou, Y., Leibler, L., Wiley-VCH, Weinheim (2007), Part 4, Chap. 10, pp. 2369-2408.
4) Grimsdale, A. C., Chan, K. L., Martin, R. E., Jokisz, P. G., Holmes, A. B., Chem. Rev., 109, 897 (2009).
5) Li, C., Liu, M., Pecher, N. G., Baumgarten, M., Müllen, K., Chem. Rev., 110, 6817 (2010).
6) Zade, S. S., Zamoshchik, N., Bendikov, M., Acc. Chem. Res., 44, 14 (2011).
7) J. Pol. Sci., Part A, Polym. Chem.
8) , 6166 (2005).
9) Li, B., Yang, J., Acc. Chem. Res., 38, 500 (2015).
10) Li, Q., Liu, W., Yao, B., Tian, H., Xie, Z., Geng, Y., Wang, F., Macromolecules, 40, 1851 (2007).
11) Beljonne, D., Pourtois, G., Silva, C., Hennebicq, E., Herz, L. M., Friend, R. H., Scholes, G. D., Setayesh, S., Müllen, K., Brédas, J. L., “Macromolecular Engineering,” Proc. Natl. Acad. Sci. U. S. A., 99, 10982 (2002).
12) Asaoka, S., Takeda, N., Iyoda, T., Cook, A. R., Müller, J. R., Am. Chem. Soc., 130, 11912 (2008).
13) El-Khouly, M. E., Chen, Y., Zhuang, X., Fukushima, S., J. Am. Chem. Soc., 131, 6370 (2009).
14) Nomura, K., Morimoto, H., Imanishi, Y., Ramhani, Z., Geerts, Y., J. Polym. Sci., Part A, Polym. Chem., 39, 2463 (2001).
15) Nomura, K., Yamamoto, N., Ito, R., Fujiki, M., Geerts, Y., Macromolecules, 41, 4245 (2008).
16) Nomura, K., Miyamoto, Y., Morimoto, H., Geerts, Y., J. Polym. Sci., Part A, Polym. Chem., 43, 6166 (2005).
17) Lehman Jr., S. E., Wagener, K. B., “Handbook of Metathesis: Catalyst Development,” ed. by Grubbs, R. H., Wiley-VCH, Weinheim (2003), Part 3, Chap. 3, pp. 283-353.
18) Baughman, T. W., Wagener, K. B., “Metathesis Polymerization,” ed. by Buchmeiser, M. R., Springer, Heidelberg (2005), p. 1.
19) Berda, E. B., Wagener, K. B., “Polymer Science, A Comprehensive Reference,” eds. by Matyjaszewski, K., Müllen, M., Elsevier, BV, Amsterdam (2012), Vol. 5, pp. 195-216.
20) Berda, E. B., Wagener, K. B., “Synthesis of Polymers, New Structures and Methods,” eds. by Schlueter, D., Hawker, C., Sakamoto, J., Wiley-VCH, Weinheim, Germany (2012), p. 587.
21) Atallah, P., Wagener, K. B., Schulz, M. D., Macromolecules, 46, 4735 (2013).
22) Yamamoto, N., Ito, R., Geerts, Y., Nomura, K., Macromolecules, 42, 5104 (2009).
23) Kawabara, S., Yamamoto, N., Sharma, P. M. V., Takamizu, K., Fujiki, M., Geerts, Y., Nomura, K., Macromolecules, 44, 3705 (2011).
24) Abbattalif, M. M., Nomura, K., ACS Macro Lett., 1, 423 (2012).
25) Takamizu, K., Inagaki, A., Nomura, K., ACS Macro Lett., 2, 980 (2013).
26) Nomura, K., Haque, T., Onuma, T., Hajjaj, F., Asano, M. S., Inagaki, A., Macromolecules, 46, 9563 (2013).
27) Nomura, K., Haque, T., Miwata, T., Inagaki, A., Takamizu, K., Polym. Chem., 6, 380 (2015).
28) Haque, T., Nomura, K., Catalysis, 5, 500 (2015).
29) Perspectives (related reviewing article including end-function-alization of ROMP polymer by adopting the similar approach, olefin metathesis with Wittig-type coupling), Nomura, K., Abbattalif, M. M., Polymer, 51, 1861 (2010).
30) Miyashita, T., Nomura, K., Macromolecules, 49, 518 (2016).
31) Miyashita, T., Inagaki, A., Nomura, K., The results were partly introduced at 45th Petroleum-Petrochemicals Symposium of Japan Petroleum Institute, November, Nagoya, Japan (2015), 1Fi5.
32) Oskam, H. J., Fox, H. Y., Yap, B. K., McConville, H. D., O’Dell, R., Lichtenstein, J. B., Schroek, R. R., J. Organomet. Chem., 459, 185 (1993).
33) As reported previously, 14-16 the calibration with polystyrene standards often overestimates the molecular weight averages of rigid conjugated polymers. Therefore, GPC curves versus structurally similar soluble PPP [poly(p-phenylene)] standards were recorded, and the Mn values of rodlike polymers measured versus polymer standards are overestimated by a factor of 1.6. For a related article on measuring Mn and Mw/Mn values by PPP standards, Marszitzy, D., Brand, T., Geerts, Y., Klapper, M., Müllen, K., Macromol. Rapid Commun., 19, 385 (1998).
34) Anuragudom, P., Newaz, S. S., Phanichphant, S., Lee, T. R., Macromolecules, 39, 3494 (2006).
35) Liu, Q., Liu, W., Yao, B., Tian, H., Xie, Z., Geng, Y., Wang, F., Macromolecules, 40, 1851 (2007).
要  旨
モリブデン錯体触媒を用いる非環式ジエンメタセシス重合と Wittig 型カップリング反応による
末端官能基化 π 共役ポリマーの one-pot 精密合成

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Mo(CHCMePh)(N-2,6-Me₂C₆H₃)[OCMe(CF₃)₂]₂触媒による
2,7-divinyl-9,9-di-n-octyl-fluorene の非環式ジエンメタセシス
(ADMET) 重合後, 反応系内にモリブデン触媒を追加添加し,さらに所定のアルデヒドとの Wittig 型反応にて, 高収率で両末端
官能基化した共役ポリマー, poly(9,9-di-n-octyl-fluorene vinyl-
enes) (EF-PFVs), を合成した。重合時に残存したポリマーの末端
ビニル基と追加添加したモリブデン触媒とのオレフィンメタ
セシス反応により, ポリマー末端をすべてアルキリデン (カルペン) 種と変換することで, 続く Wittig 型のカップリング反応
による末端官能基化が定量的な収率で進行した。本手法によ
り, 欠陥や不純物の混入のない, 高立体規則性 (all trans) の
各種末端官能基化共役ポリマーが one-pot で精密合成可能となっ
た。