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ARTICLE

Synthesis of All-Trans High Molecular Weight Poly(*N*-alkylcarbazole-2,7-vinylene)s and Poly(9,9-dialkylfluorene-2,7-vinylene)s by Acyclic Diene Metathesis (ADMET) Polymerization Using Ruthenium−Carbene Complex Catalysts

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ABSTRACT: Syntheses of poly(9,9-dialkylfluorene-2,7-vinylene)s (PFVs, alkyl = *n*-hexyl, *n*-octyl, 2′-ethylhexyl) and poly(*N*-alkylcarbazole-2,7-vinylene)s (PCVs, alkyl = *n*-octyl, 9′-heptadecanyl) by acyclic diene metathesis (ADMET) polymerization using Ru−carbene complexes have been explored. The polymerizations in the presence of $Ru(CHPh)(Cl)_2(IMesH_2)(PCy_3)$ and $Ru(CH\text{-}2\text{-}O^iPr\text{-}C_6H_4)(Cl)_2(IMesH_2)$ [Cy = cyclohexyl, $IMesH_2$ = 1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene] afforded relatively high molecular weight PFVs, PCV (alkyl = 9′-heptadecanyl) with unimodal molecular weight distributions, and the olefinic double bonds in the resultant polymers possessed highly trans regularity in all cases. The resultant defect-free PFVs possessed higher absolute quantum yields ($\Phi = 92-99\%$) than those reported previously, whereas no significant differences in the UV−vis and the fluorescent spectra (absorption bands, peak maxima) in the resultant PFVs were observed as an effect of alkyl side chain in the 9-position. The UV−vis and the fluorescence spectra in the PCV were similar to those in the PFVs, indicating that the replacement (from fluorene to carbazole) does not affect the observed spectra; the resultant PCV also possessed remarkable absolute quantum yield ($\Phi = 86\%$).

Introduction

Organic electronics are 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.[1,2] Since the properties for their device efficiency are generally influenced by their structural regularity, chemical purity, and supramolecular order,[1−4] considerable attention has thus been paid to a study concerning synthesis of structurally regular, chemically pure polymers by development of new synthetic methods.[5−7] It has also been reported that fluorene-based EL polymers should have advantages in terms of a facile introduction of substituents into the C_9 position, high PL and EL efficiencies, and thermal and chemical stabilities.[8,9]

We previously reported that synthesis of high molecular weight, *all-trans*-poly(9,9-di-*n*-octylfluorene-2,7-vinylene) [PFV, poly(**1**)] could be achieved by acyclic diene metathesis (ADMET) polymerization of 2,7-divinyl-9,9-di-*n*-octylfluorene using $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Me_2C_6H_3)[OCMe(CF_3)_2]_2$ (**Mo**).[8] We reported later that $Ru(CHPh)(Cl)_2(IMesH_2)(PCy_3)$ [Ru(**A**), Cy = cyclohexyl, $IMesH_2$=1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene] was also effective for syntheses of both high molecular weight poly(2,5-dialkylphenylene-1,4-vinylene)s (PPVs)[10] and poly(**1**)[11] by ADMET polymerization under optimized conditions.[12] The fact introduced interesting contrast because the initial attempts for synthesis of PPVs by this approach afforded oligomer mixtures.[13] It turned out that an optimization of the reaction conditions (catalyst, monomer/catalyst molar ratios, initial monomer concentration, etc.), especially removal of ethylene by-produced from the reaction medium, should be a prerequisite for obtainment of the high molecular weight polymers in this condensation polymerization.[8,10] Although the perfect control of the repeating units cannot be attained in the present condensation polymerization (M_w/M_n = ca. 2), the promising characteristics by adopting this approach can be summarized as follows: (1) the resultant polymers are defect-free without termination of the conjugated units and do not contain any negative impurities (halogen, sulfur, etc.); (2) the resultant polymers (oligomers) possessed highly trans olefinic double bonds (because, as initially proposed by Thorn-Csányi et al.,[8,10,11,13a−13d] the reaction proceeds via metallacycle intermediate).[14] Moreover, the resultant polymers prepared by Ru(**A**) possessed well-defined polymer chain ends (as vinyl group),[10,11] and we thus demonstrated more recently that a facile, exclusive end-functionalization can be achieved by treating the vinyl groups in poly(**1**) with **Mo** followed by Wittig-type cleavage with $4\text{-}Me_3SiOC_6H_4CHO$; precise synthesis of ABA-type amphiphilic triblock copolymers had thus been accomplished by grafting PEG into both the PFV chain ends.[11]

On the basis of the above results, in this paper, we thus conducted the ADMET polymerizations of three 2,7-divinyl-9,9-dialkylfluorenes (alkyl=*n*-hexyl, *n*-octyl, 2′-ethylhexyl) using $Ru(CHAr)(Cl)_2(IMesH_2)(PCy_3)$ [Ru(**A**): Ar = Ph; Ru(**B**): Ar = $2\text{-}O^iPr\text{-}C_6H_4$], $Ru(CHPh)(Cl)_2(IMesH_2)(3\text{-}BrC_5H_4N)_2$ [Ru(**C**)] (Scheme 1). Through this study, we explored the effect of ruthenium complex catalysts in the ADMET polymerization and the effect of alkyl side chain (C_9 position) in the resultant conjugated polymers through measurement in the UV−vis and the fluorescence spectra.

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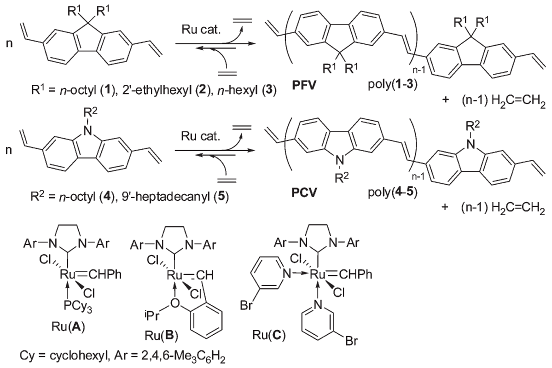
Table 1. Acyclic Diene Metathesis (ADMET) Polymerization of 2,7-Divinyl-9,9-dialkylfluorene Using Various Ru−Carbene Complex Catalysts[a]

run	alkyl in C_9 R	concn[b]	Ru cat. (equiv)[c]	solvent (mL)	temp/°C	time/h	M_n[d] × 10^{-4}	M_w/M_n[d]	yield[e]/%
1	n-C_8H_{17} (**1**)[f]	180	**A** (40)	toluene (1.0)	50	8	2.75	2.0	90
2	n-C_8H_{17} (**1**)[f]	360	**A** (30)	toluene (1.0)	50	8	2.58	2.0	87
3	n-C_8H_{17} (**1**)[f]	150	**A** (40)	CH_2Cl_2 (1.2)	40	5	2.58	2.2	89
4	n-C_8H_{17} (**1**)[f]	240	**A** (30)	CH_2Cl_2 (3.0)	40	5	2.02	2.0	85
5	n-C_8H_{17} (**1**)	180	**C** (40)	CH_2Cl_2 (1.0)	40	3	0.36	1.3	> 99
6	n-C_8H_{17} (**1**)	180	**C** (80)	CH_2Cl_2 (1.0)	40	5	0.45	1.6	> 99
7	n-C_8H_{17} (**1**)	180	**C** (40)	C_6H_5Br (1.0)	90	3.5	0.33	1.8	75
8	2′-ethylhexyl (**2**)	180	**A** (40)	toluene (1.0)	50	3	2.10	2.1	75
9	2′-ethylhexyl (**2**)	270	**A** (40)	toluene (1.0)	50	3	3.30	2.2	82
10	2′-ethylhexyl (**2**)	180	**A** (40)	toluene (1.0)	50	8	3.00	2.6	79
11	2′-ethylhexyl (**2**)	90	**A** (40)	toluene (2.0)	50	8	3.58	1.8	> 99
12	n-C_6H_{13} (**3**)	200	**A** (40)	toluene (1.0)	50	8	5.10	1.2	95
							1.20	1.2	
13	n-C_6H_{13} (**3**)	200	**B** (40)	toluene (1.0)	50	5	2.10	2.1	82
14	n-C_6H_{13} (**3**)	100	**A** (40)	toluene (1.0)	50	3	2.30	2.5	93
15	n-C_6H_{13} (**3**)	103	**A** (35)	CH_2Cl_2 (2.0)	40	8	3.20	2.0	> 99
16	n-C_6H_{13} (**3**)	103	**A** (44)	CH_2Cl_2 (1.0)	40	4	1.56	2.2	90

[a] Conditions: solvent 1.0−3.0 mL, Ru(CHPh)(Cl)$_2$(IMesH$_2$)(PCy$_3$) [Ru(**A**), IMesH$_2$ = 1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene], Ru(CH-2-O^{i}Pr-C$_6$H$_4$)(Cl)$_2$(IMesH$_2$) [Ru(**B**)], Ru(CHPh)(Cl)$_2$(IMesH$_2$)(3-BrC$_5$H$_4$N)$_2$ [Ru(**C**)]. [b] Initial monomer concentration in μmol/mL. [c] Initial molar ratio based on monomer/Ru. [d] GPC data in THF vs polystyrene standards. [e] Isolated yields. [f] Data cited from ref 11.

Scheme 1



Carbazole-based materials have been investigated due to their promising electrical and optical properties,[15−18] as demonstrated by Leclerc et al.,[15b,15c] and alkyl substituents in the carbazole derivatives would be more stable (thermally, toward oxygen, etc.) than those in the fluorene derivatives. There are thus many reports concerning synthesis of copolymers containing 2,7-carbazolevinylene units,[15b,15c,16,17] but no reports for syntheses of high molecular weight poly(N-alkylcarbazole-2,7-vinylene)s (PCVs) were known.[16b] We thus explored the synthesis of PCVs prepared by adopting the ADMET approach (Scheme 1) and compared the observed properties between the PFV and the PCV through the UV−vis and the fluorescence spectra measurements.

Results and Discussion

1. Acyclic Diene Metathesis (ADMET) Polymerizations of 2,7-Divinyl-9,9-dialkylfluorenes Using Various Ruthenium−Carbene Complex Catalysts. 2,7-Divinyl-9,9-dialkylfluorenes (DVFs, **1**−**3**, in Scheme 1) were prepared by the Stille coupling reaction of 2,7-dibromo-9,9-dialkylfluorenes[19] with tributyl(vinyl)tin (2.4 equiv) in the presence of Pd(PPh$_3$)$_4$, as reported previously (for **1**).[8,11] The resultant compounds were purified by a column chromatography in n-hexane and were identified based on ^{1}H and ^{13}C NMR spectra and mass spectrometry. The ADMET polymerizations of the DVFs were carried out using a sealed Schlenk tube equipped with a high-vacuum valve in toluene (or CH_2Cl_2).[8,11] Continuous removal of ethylene from the mixture is prerequisite for obtainment of the high molecular weight polymers in this condensation polymerization; the solution was thus placed in vacuo for a certain period.[10,11] The results are summarized in Table 1.

As reported previously,[13] the polymerizations of 2,7-divinyl-9,9-di-n-octylfluorene (**1**) using Ru(CHPh)(Cl)$_2$(IMesH$_2$)(PCy$_3$) [Ru(**A**)] in toluene under the optimized conditions afforded rather high molecular weight polymers, poly(**1**), with unimodal molecular weight distributions (runs 1 and 2, Table 1). Dichloromethane was also effective as the solvent, especially in terms of improvement of the solubility in the resultant poly(**1**)s (runs 3 and 4). Similar results were observed in the polymerization of the 2′-ethylhexyl analogue (**2**), and the resultant PFVs, poly(**2**)s, possessed high molecular weights with unimodal distributions.[20] The ADMET polymerization of the n-hexyl analogue (**3**) did not complete under the similar conditions (run 12), but the polymerization under low initial monomer concentration conditions reached completion (run 14) probably due to an improvement of solubility in the resultant poly(**3**) in the mixture; the use of CH_2Cl_2 was also effective for improving solubility of poly(**3**). On the basis of these results, the present ADMET method using Ru(**A**) are thus effective for preparation of high molecular weight conjugated polymers. A facile, fast synthesis of these polymers (completed after 3−5 h) should be promising because the synthesis by the Mo catalysts required long hours (completed after 20 h) for completion.[8]

The Ru−carbene complexes are widely used as efficient catalysts for olefin metathesis, and their reactivities are generally dependent upon nature of the donor ligand.[19] In order to clarify effect of the Ru catalysts in the ADMET polymerization, we thus conducted the polymerization using various Ru complexes, and the results are summarized in Table 1.

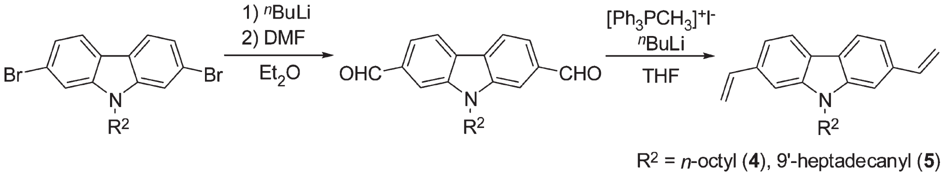
The ADMET polymerization of the n-octyl analogue (**1**) using Ru(CHPh)(Cl)$_2$(PCy$_3$)$_2$ did not proceed,[11] whereas the polymerization by Ru(**A**) afforded high molecular weight polymers under the same conditions.[11] High molecular weight poly(**3**) could be obtained when the polymerization of the n-hexyl analogue (**3**) by Ru(CH-2-O^{i}Pr-C$_6$H$_4$)(Cl)$_2$(IMesH$_2$) [Ru(**B**)] was employed even under rather high initial monomer concentration conditions (run 13), probably due to an improved catalyst efficiency (especially at the initial stage),[10,20] whereas the polymerization by Ru(**A**) did not complete under the same conditions (run 12). However, the polymerization of **1** using Ru(CHPh)(Cl)$_2$(IMesH$_2$)(3-BrC$_5$H$_4$N)$_2$ [Ru(**C**)] afforded low molecular weight oligomers (runs 5 and 6) even if the reaction was conducted at high temperature (90 °C, run 7). This would be

Table 2. Acyclic Diene Metathesis (ADMET) Polymerization of *N*-Alkyl-2,7-divinylcarbazole Using $Ru(CHPh)(Cl)_2(IMesH_2)(PCy_3)$ [Ru(A)][a]

run	alkyl in C_9 R	concn[b]	Ru(A)/ equiv[c]	solvent (mL)	time/h	$M_n{}^d \times 10^{-4}$	$M_w/M_n{}^d$	yield[e]/%
17	n-C_8H_{17}	90	40	toluene (1.0)	1	0.21	1.2	> 99
18	9′-heptadecanyl	180	40	toluene (1.0)	1	1.46	2.1	90
19	9′-heptadecanyl	180	40	toluene (1.0)	3	2.04	2.2	> 99
20	9′-heptadecanyl	180	40	C_6H_5Br (1.0)	5	3.26	2.3	> 99
21	9′-heptadecanyl	325	40	C_6H_5Br (2.5)	3	3.04	2.5	> 99

[a] Conditions: solvent 1.0−3.0 mL, 50 °C, $Ru(CHPh)(Cl)_2(IMesH_2)(PCy_3)$ [Ru(**A**), $IMesH_2$ = 1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]. [b] Initial monomer concentration in μmol/mL. [c] Initial molar ratio based on monomer/Ru. [d] GPC data in THF vs polystyrene standards. [e] Isolated yields.

Scheme 2



probably explained as due to a favored formation of the pyridine-coordinated dormant species. Taking into account of these results, it is clear that Ru(**A**) and Ru(**B**) are suited for the polymerization under these conditions.[21]

As demonstrated previously,[8,11] olefinic double bonds in the resultant PFVs possessed exclusive trans regularity confirmed by ^{1}H NMR spectra[22] because the ADMET condensation proceeds via metallacyclobutane intermediate.[8,10,11,13] As also described previously,[10,11] the resultant PFVs possessed vinyl groups at the both polymer chain ends.[22] These are remarkable contrasts with that prepared by the previous (precursor) method;[22,23] especially two broad resonances ascribed to protons at 4.5−4.8 ppm (that seem to be apparently different from olefinic protons in the chain end as well as protons due to the internal olefins) in addition to rather broad resonances ascribed to aromatic protons were observed in the polymer prepared by the precursor method.[22,23]

2. Synthesis of Poly(*N*-alkylcarbazole-2,7-vinylene)s (PCVs) by the ADMET Polymerization. 2,7-Divinyl-9-*N*-alkylcarbazoles [alkyl=*n*-octyl (**4**), 9′-heptadecanyl (**5**)] have been prepared from the 2,7-dibromo-*N*-alkylcarbazoles (prepared by the reported procedures[24,25]) according to the analogous procedures reported previously[12] (Scheme 2). The resultant compounds were identified by their NMR spectra and mass spectrometry. The polymerizations of **4** and **5** were conducted in toluene in the presence of Ru(**A**), and the results are summarized in Table 2.

The ADMET polymerization of the *n*-octyl analogue (**4**) afforded toluene insoluble low molecular weight oligomer after 1 h, and no significant increases in the M_n values were seen even by further stirring. In contrast, the ADMET polymerization of the 9′-heptadecanyl analogue (**5**) afforded (toluene soluble) high molecular weight polymer with uniform molecular weight distribution (run 20, $M_n = 2.04 \times 10^4$, $M_w/M_n = 2.2$). Use of C_6H_5Br in place of toluene was effective for obtainment of the high molecular weight polymer (run 21), and increase in the initial monomer concentration does not show any positive influences toward the M_n values in the resultant polymers (run 22). As demonstrated previously,[8,10,11,13] olefinic double bonds in the resultant PCVs possessed exclusive trans regularity confirmed by their ^{1}H NMR spectra (Figure 1), and the resultant PCVs possessed vinyl groups at both polymer chain ends; the M_n value estimated by integration was close to that estimated on the basis of that by GPC [run 18, $M_{n(calcd)} = 9.49 \times 10^3$, $M_{n(NMR)} = 9.06 \times 10^3$]. The results clearly indicate that the present ADMET approach should also be effective for synthesis of high molecular weight, all-trans PCVs with uniform molecular weight distributions.

3. UV−vis and Fluorescence Spectra. Figure 2 shows UV−vis spectra (in THF, 1.0×10^{-5} M at 25 °C) for PFVs, poly(**1**−**3**), prepared by the ADMET polymerization using Ru(**A**). The spectrum for the *n*-hexyl analogue prepared by the ordinary (precursor route) method [poly(**3′**), available from Aldrich, $M_n = 2.41 \times 10^4$, $M_w/M_n = 1.70$ and $M_n = 1720$, $M_w/M_n = 1.11$ (bimodal molecular weight distribution), prepared from the sulfonium salt precursor monomer under high-temperature (180−300 °C) and vacuum conditions (10^{-6} mbar)][22] was also measured under the same (concentration, temperature) conditions for comparison (Figure 2a).

As reported previously in poly(**1**),[8] the spectrum for poly(**3**) prepared by the ADMET polymerization displays two absorption bands at 427 and 455 nm (Figure 2a), which can also be attributed to $\pi-\pi^*$ transitions of the conjugated backbone.[9e] On the basis of the spectra with oligo(9,9-di-*n*-octylfluorene-2,7-vinylene)s reported previously,[9h] three absorption peaks at 455, 427, and 400 nm are attributed to 0−0, 0−1, and 0−2 transitions, respectively, with corresponding emission peaks at 465, 496, and 530 nm (described below, Figure 3a). As shown in Figure 2b,c, no significant changes were observed in the spectra for poly(**1**), poly(**2**), and poly(**3**). The spectrum of poly(**1**) seems somewhat similar to that prepared by the Hormer−Emmons route [reaction of 2,7-bis(methylenediethyl phosphate)-9,9-di-*n*-octylfluoene with 9,9-di-*n*-octylfluorene-2,7-dicarbaldehyde in the presence of KO^{t}Bu].[9e] However, it seems that the sample prepared by the ADMET polymerization showed a rather sharp contrast, probably because that the resultant polymer possessed higher stereoregularity (all-trans in the internal olefinic double bond) than that prepared by the Hormer−Emmons route (mixture of cis/trans).

In contrast, as also shown in Figure 2a, the spectrum for poly(**3′**) prepared by the ordinary method (the precursor route) shows a broad absorption band with $\lambda_{max} = 414$ nm; this band can be attributed to $\pi-\pi^*$ transitions of the conjugated backbones with a shoulder at ca. 380 nm.[9a,9b] The bands for the samples prepared by the ADMET polymerization are intensified and red-shifted when compared to that for the sample prepared by the precursor method. The observed difference would be due to presence of defect in the poly(**3′**), leading to an enhanced conjugation length in poly(**3**) as pointed out previously.[9e]

Figure 3 shows fluorescence spectra (in THF, 1.0×10^{-6} M at 25 °C, excitation wavelength at 390 or 426 nm) for PFVs, prepared by the ADMET polymerization using Ru(**A**). The

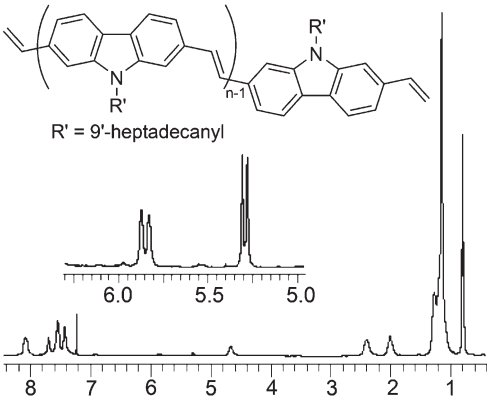


Figure 1. ^{1}H NMR spectrum (in CDCl$_3$ at 25 °C) for poly(*N*-9′-heptadecanyl-carbazole-2,7-vinylene) prepared by ADEMT polymerization using Ru(CHPh)(Cl)$_2$(IMesH$_2$)(PCy$_3$) (**A**) (run 18, Table 2).

spectrum for the *n*-hexyl analogue prepared by the ordinary method [poly(**3′**), excitation at 390 nm] was also measured under the same conditions for comparison (Figure 3a). The spectrum in poly(**3**) with excitation at 390 nm showed a strong emission band at 465 nm with a shoulder at 496 nm along with a slight shoulder at 530 nm (Figure 3a). It is explained that the shoulder arises from coupling between the fluorene and vinylene units to form a new electronic state with a lower energy.[26] No significant differences were seen in the spectrum with excitation at 426 nm (Figure 3b).

Moreover, no significant differences were observed in the spectra for the other alkyl analogues [Figure 3c,d for poly(**1**) and poly(**2**), respectively]. The spectrum in poly(**3′**) prepared by the precursor route also showed a rather strong emission band at 464 nm with a shoulder at 494 nm, but remarkable differences in their intensities between these samples were seen [poly(**3**) vs poly(**3′**), Figure 3a]. Moreover, a shoulder observed at 450 nm in the sample prepared by the Hormer−Emmons route[9e] was not observed in the samples prepared by the ADMET route, and the emission band at 465 nm possessed narrow half-width (17 nm). The observed difference in samples prepared by the ADMET polymerization would be probably due to that the resultant polymer possessed high stereoregularity (all-trans olefinic double bond) without any defects. Note that the absolute quantum yields [Φ in THF by calibration with an excitation at 400 nm][27] in poly(**1**−**3**)s prepared by the ADMET procedures are remarkably high in all cases [Φ: poly(**1**) 99%, poly(**2**) 92%, poly(**3**) 99%, respectively], and the value by poly(**3**) was much higher than that by poly(**3′**) [Φ (in THF by calibration with an excitation at 400 nm): 86%];[27] these values are also much higher than those reported previously [e.g., Φ = 54% {*n*-hexyl-PFV, poly(**3**), prepared by Heck coupling},[9f] 85−86% (PFV oligomers, 8−11 repeating units)[9h]]. Taking into account the above results, it is clear that PFVs prepared by the ADMET polymerization are defect-free polymers with high stereoregularity as well as with better optical property compared with samples prepared by the other methods.

Figure 4a shows UV−vis spectra (in THF, 1.0×10^{-5} M at 25 °C) for poly(**5**). The spectrum displays two absorption bands at 430 and 457 nm in addition to a shoulder observed slightly above 400 nm, and the spectrum is similar to those for PFVs shown in Figure 2. The fluorescence spectrum (in THF, 1.0×10^{-6} M at 25 °C) for poly(**5**) with excitation at 430 nm showed a strong emission band at 470 nm with a shoulder at 501 nm along with a slight shoulder at 528 nm (Figure 4b); the spectrum was also very similar to those in PFVs shown in Figure 3. On the relevance to the spectra in

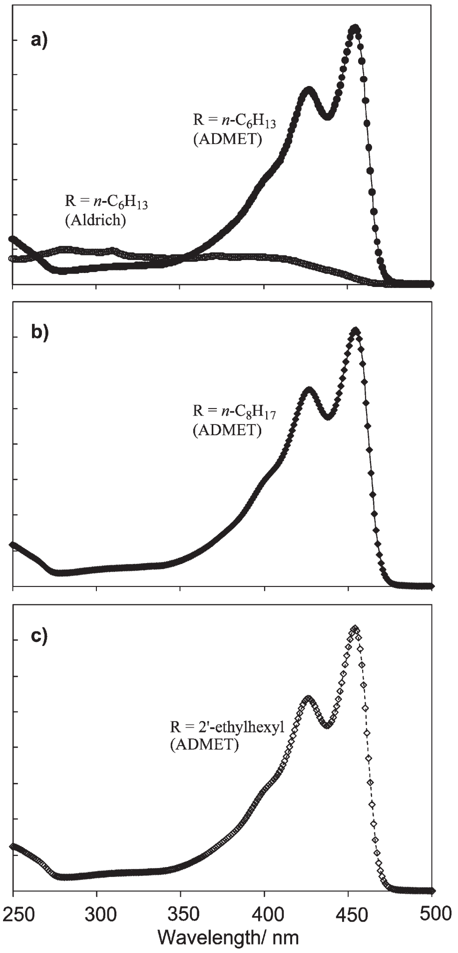


Figure 2. UV−vis spectra for PFVs in THF at 25 °C (concentration 1.0×10^{-5} M). (a) PFV (R = *n*-C$_6$H$_{13}$, ADMET; M_n = 32 000, M_w/M_n = 2.0 by GPC, run 13) and PFV (R = *n*-C$_6$H$_{13}$, Aldrich; $M_n = 2.41\times10^4$, M_w/M_n = 1.70 and M_n = 1720, M_w/M_n = 1.11); (b) PFV (R = *n*-C$_8$H$_{17}$, M_n = 25 800, M_w/M_n = 2.2 by GPC, run 5); (c) PFV (R = 2′-ethylhexyl, M_n = 35 800, M_w/M_n = 1.8 by GPC, run 10).

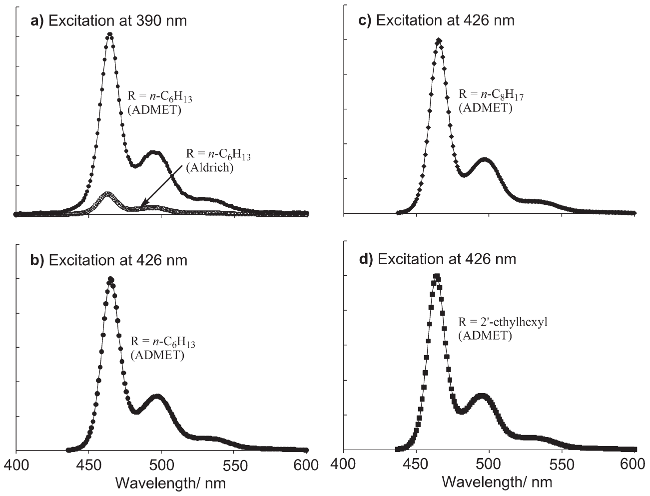


Figure 3. Fluorescent spectra for PFVs in THF at 25 °C (concentration 1.0×10^{-6} M). (a) PFV excitation at 390 nm (R = *n*-C$_6$H$_{13}$, ADMET; M_n = 32 000, M_w/M_n = 2.0 by GPC, run 13) and PFV (R = *n*-C$_6$H$_{13}$, Aldrich; $M_n = 2.41 \times 10^4$, M_w/M_n = 1.70 and M_n = 1720, M_w/M_n = 1.11), (b) PFV excitation at 426 nm (R = *n*-C$_6$H$_{13}$, M_n = 32 000, M_w/M_n = 2.0 by GPC, run 13), (c) PFV excitation at 426 nm (R = *n*-C$_8$H$_{17}$, M_n = 25 800, M_w/M_n = 2.2 by GPC, run 5), (d) PFV excitation at 426 nm (R = 2′-ethylhexyl, M_n = 35 800, M_w/M_n = 1.8 by GPC, run 10).

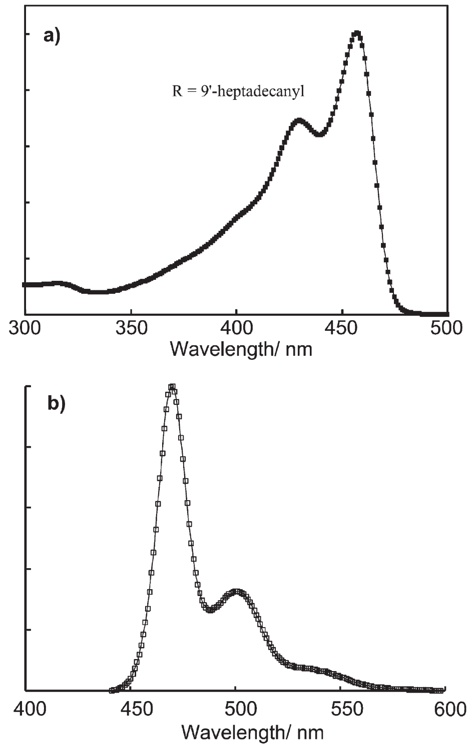


Figure 4. UV−vis spectrum (top, concentration $1.0{\times}10^{-5}$ M in THF at 25 °C) and the fluorescent spectrum (bottom, concentration 1.0×10^{-6} M in THF at 25 °C, excitation at 426 nm) for poly(*N*-9′-heptadecanylcarbazole-2,7-vinylene) (run 19, Table 2).

PFVs, three absorption peaks at 457, 430, and 400 nm are attributed to 0−0, 0−1, and 0−2 transitions, respectively, with corresponding emission peaks at 470, 501, and 528 nm. The results clearly indicate that no significant differences toward these spectra were seen between PFVs (fluorene units) and the PCV (carbazole units). The absolute quantum yield [Φ in THF by calibration with an excitation at 400 nm][27] in poly(**5**) prepared by the ADMET procedure was 86%, and the value was lower than those in PFVs [poly(**1**−**3**)s] but seemed higher than those reported previously with poly(2,7-carbazole) (Φ=59−76%).[28] The facts should be important for designing conjugated polymers (as EL, PL materials) and clearly indicate that PCVs can also be used as promising materials in addition to PFVs and PPVs by adopting this approach.

Summary

We have prepared poly(9,9-dialkylfluorene-2,7-vinylene) (alkyl = *n*-hexyl, *n*-octyl, 2′-ethylhexyl) and poly(*N*-alkylcarbazole-2,7-vinylene) by the acyclic diene metathesis (ADMET) polymerization using a series of ruthenium−carbene complex catalysts. Ru(CHPh)(Cl)$_2$(IMesH$_2$)(PCy$_3$) [Ru(**A**)] was an effective catalyst for this polymerization, affording defect-free high molecular weight polymers with unimodal molecular weight distributions (only after several hours);[21] the olefinic double bonds in the resultant poly(fluorene-2,7-vinylene)s possessed trans regularity. No significant differences in the UV−vis and the fluorescent spectra (absorption bands, peak maxima) were observed as the effect of the alkyl side chain substituent in the C$_9$ position; replacement of fluorene to carbazole did not give any significant influences/differences in the UV−vis and the fluorescence spectra. These results should emphasize an importance of this method (halogen- and salt-free process) to prepare “defect-free” polymers with high regularity. Since both polymer chain ends are vinyl group in this catalysis, as we demonstrated previously,[11] we are now exploring a possibility to expand the utility of this approach for the precise modification as devices for the desired purposes (for precise control of the supramolecular order by grafting).

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 grades and were purified by the standard purification procedures. Anhydrous grade toluene (Kanto Kagaku Co. Ltd.) 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 in the drybox, and then passed through an alumina short column prior to use. Anhydrous grade diethyl ether, dichloromethane, bromobenzene, tetrahydrofuran (THF), and *n*-hexane (Kanto Kagaku Co. Ltd.) were also transferred into a bottle containing molecular sieves (mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox. Ru(CHPh)(Cl)$_2$(IMesH$_2$)(PCy$_3$) [Ru(**A**), Cy = cyclohexyl, IMesH$_2$ = 1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene, Strem Chemicals, Inc.], Ru(CH-2-O^{i}Pr-C$_6$H$_4$)(Cl)$_2$(IMesH$_2$) [Ru(**B**), Aldrich], and Ru(CHPh)(Cl)$_2$(IMesH$_2$)(3-BrC$_5$H$_4$N)$_2$ [Ru(**C**), Aldrich] were used in the drybox as received without further purification. Poly(9,9-di-*n*-hexylfluorene-2,7-viynlene) [poly(**3′**)], 2,7-dibromo-9,9-di-*n*-octylfluorene, 2,7-dibromo-9,9-di-*n*-hexylfluorene, and 2,7-dibromo-9,9-di(2′-ethylhexyl)fluorene were purchased from Aldrich and were used as received [except that poly(**3′**) was used after precipitation in MeOH]. Tributyl(vinyl)tin was purchased from TCI and was used as received.

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). All deuterated NMR solvents were stored over molecular sieves, and all chemical shifts are given in ppm and are referenced to Me$_4$Si. 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 Shimadzu SCL-10A using a RID-10A detector (Shimadzu 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 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 an Hitachi F-4500 fluorescence spectrophotometer (1.0×10^{-6} M in THF at 25 °C) with excitation wavelength at 390 and 426 nm.

2,7-Divinyl-9,9-di-*n*-octylfluorene (1). Synthesis of **1** was conducted according to a procedure in our previous report[8,11] with some improvements. A toluene solution (35 mL) containing 2,7-dibromo-9,9-di-*n*-octylfluorene (2.00 g, 3.65 mmol), tributyl(vinyl)tin (2.80 g, 8.83 mmol), Pd(PPh$_3$)$_4$ (168 mg, 0.146 mmol), and a few crystals of 2,6-di-*tert*-butyl-4-methylphenol as the radical trap was purged with nitrogen and refluxed under dark conditions. After 12 h, the resultant solution was poured into a 1 M NaOH(aq), and the mixture was stirred for 2 h at room temperature. The solution was then filtered through a Celite pad, and the organic phase was extracted with *n*-hexane. The extract was then washed with 1 M NaOH(aq) and was with saturated NaCl(aq) solution. After the solvent was removed in vacuo, the resultant oil was purified by a column chromatography on silica with *n*-hexane. The monomer was further purified by a column chromatography to give the title compound as a white solid (849 mg, 52%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.59 (2H, J=7.72 Hz, d), 7.36 (2H, J=8.08 Hz, d), 7.33 (2H, s), 6.78

(2H, $J = 17.6$ Hz, 11.0 Hz, dd), 5.77 (2H, $J = 17.6$ Hz, d), 5.23 (2H, $J = 11.0$ Hz, d), 1.93 (4H, m), 1.24−1.02 (20H, m), 0.79 (6H, $J = 7.0$ Hz, t), 0.60 (4H, m). ^{13}C NMR (75 MHz, acetone-d_6): δ 151.7, 141.2, 137.2, 125.8, 120.9, 120.2, 137.8, 113.0, 55.3, 40.4, 32.0, 30.1, 24.0, 22.7, 13.8. MS *m/e* (%): $[M]^+$ 442 (100%).

2,7-Divinyl-9,9-di(2′-ethylhexyl)fluorene (2). Compound **2** was prepared according to the procedure used for compound **1**. **2** was obtained as a colorless oil (yield 72.4%). ^{1}H NMR ($CDCl_3$): δ 7.58 (2H, J=8.04 Hz, d), 7.38 (2H, m), 7.33 (2H, m), 6.76 (2H, J=17.6 Hz, 11.0 Hz, dd), 5.74 (2H, J=17.6 Hz, d), 5.20 (2H, $J = 11.0$ Hz, d), 1.96 (4H, m), 0.86−0.63 (22H, m), 0.49 (4H, m).

2,7-Divinyl-9,9-di-*n*-hexylfluorene (3). Compound **3** was prepared according to the procedure used for compound **1**. **3** was obtained as a white solid (yield 72.4%). ^{1}H NMR ($CDCl_3$): δ 7.59 (2H, J=7.68 Hz, d), 7.36 (2H, J=8.04 Hz, d), 7.33 (2H, s), 6.78 (2H, J=17.6 Hz, 10.6 Hz, dd), 5.77 (2H, J=17.6 Hz, d), 5.23 (2H, $J = 10.6$ Hz, d), 1.93 (4H, m), 1.11−1.01 (12H, m), 0.74 (6H, J=7.0 Hz, t), 0.60 (4H, m).

2,7-Divinyl-*N*-*n*-octylcarbazole (4). Compound **4** was prepared from *N*-*n*-octyl-2,7-dibromocarbazole[24] via *N*-*n*-octyl-2,7-bis(formyl)carbazole according to a analogous method[12] reported for synthesis of 2,7-divinyl-9,9-di-*n*-octylfluorene (**1**).

(i) Synthesis of *N*-*n*-octyl-2,7-bis(formyl)carbazole. Into a Schlenk tube containing *N*-octyl-2,7-dibromocarbazole 2.077 g (4.75 mmol) dissolved in Et_2O (60 mL), ^{n}BuLi (1.55 M in *n*-hexane, 10.3 mL, 15.97 mmol) was slowly added at −78 °C. The stirred reaction mixture was warmed slowly to room temperature and was stirred for 1.5 h at room temperature. The mixture was then cooled at −78 °C and was then added anhydrous DMF (1.3 mL in Et_2O 1.2 mL) dropwise; the solution was stirred overnight at room temperature. The resultant mixture was cooled at 0 °C and was added 2 N HCl(aq) (12 mL), and the reaction product was extracted with Et_2O (100 mL × 3). After removal of the volatiles from the extract, the residue was purified by column chromatography (5−10% ethyl acetate/*n*-hexane), affording a yellow solid (1.398 g, yield 87%). ^{1}H NMR ($CDCl_3$): δ 10.20 (s, 2H), 8.29 (d, 2H, J=8.1 Hz), 8.01 (s, 2H), 7.80 (dd, 2H, J=8.1, 1.1 Hz), 4.44 (t, 2H, J=7.3 Hz), 1.96−1.88 (m, 2H), 1.39−1.26 (m, 10H), 0.86 (t, 3H, J=6.8 Hz).

(ii) Synthesis of 2,7-divinyl-*N*-*n*-octylcarbazole (**4**). Into a Schlenk tube containing $(Ph_3PCH_3)^+I^-$ (4.466 g, 12.5 mmol) dissolved in THF (70 mL), ^{n}BuLi (1.55 M in *n*-hexane, 8.1 mL, 12.56 mmol) was added slowly at 0 °C. After the mixture was stirred for 10 min, THF solution (34 mL) containing *N*-*n*-octyl-2,7-bis(formyl)carbazole (1.398 g, 4.17 mmol) was added slowly, and the solution was stirred overnight at room temperature. The reaction mixture was then added water (100 mL), and the organic products were extracted with Et_2O (100 mL × 3). The resultant residue by removal of volatile from the mixture was purified by column chromatography (5% ethyl acetate/*n*-hexane), and the recrystallization of the resultant solid in a mixed solution of methanol/*n*-hexane afforded pure compound **4** as a pale yellow solid (1.046 g, yield 76%). ^{1}H NMR ($CDCl_3$): δ 7.99 (d, 2H, J=8.1 Hz), 7.37 (s, 2H), 7.33 (d, 2H, J=8.1 Hz), 6.91 (dd, 2H, J=17.6, 10.6 Hz), 5.86 (d, 2H, J=17.6 Hz), 5.29 (d, 2H, J=11.0 Hz), 4.29 (t, 2H, J=7.3 Hz), 1.91−1.84 (m, 2H), 1.37−1.31 (m, 10H), 0.86 (t, 3H, J=6.8 Hz). ^{13}C NMR ($CDCl_3$): δ 141.3, 137.8, 135.4, 122.5, 120.3, 117.4, 113.1, 106.6, 42.9, 31.8, 29.3, 29.2, 28.9, 27.2, 22.6, 14.1. MS (EI) (*m*/*z*) 331.230.

2,7-Divinyl-*N*-9′-heptadecanylcarbazole (5). Compound **5** was prepared similarly from *N*-9′-heptadecanyl-2,7-dibromocarbazole.[25]

(i) Synthesis of *N*-9′-heptadecanyl-2,7-bis(formyl)carbazole. The synthesis was similar to that for *N*-*n*-octyl-2,7-bis(formyl) carbazole, except that *N*-9′-heptadecanyl-2,7-dibromocarbazole (1.846 g) was used in place of *N*-*n*-octyl-2,7-dibromocarbazole. Yield 1.089 g (72%). ^{1}H NMR ($CDCl_3$): δ 10.18 (s, 2H), 8.30 (t, 2H, J=9.0 Hz), 8.14 (br, 1H), 8.01 (br, 1H), 7.80 (br, 2H), 4.74−4.67 (m, 1H), 2.32 (m, 2H), 2.02 (m, 2H), 1.26−1.10 (m, 22H), 0.97 (m, 2H), 0.80 (t, 6H, J=7.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 192.4, 143.3, 139.8, 135.2, 134.8, 127.8, 126.4, 121.9, 121.6, 121.1, 113.2, 110.5, 57.4, 33.7, 31.7, 29.2, 29.0, 26.8, 22.5, 14.0. Multiple resonances in the ^{1}H and ^{13}C NMR spectra are due to the phenomenon of atropisomerism.[25,29] MS (EI) (*m*/*z*) 461.329.

(ii) 2,7-Divinyl-*N*-9′-heptadecanylcarbazole (**5**). The synthetic procedure for **5** was similar to that for **4** from *N*-9′-heptadecanyl-2,7-bis(formyl)carbazole, described above, except that *N*-9′-heptadecanyl-2,7-bis(formyl)carbazole (1.084 g, 2.37 mmol) was used in place of *N*-*n*-octyl-2,7-bis(formyl)carbazole. After a column chromatography (0−2% ethyl acetate/*n*-hexane) afforded pale yellow solids of **5** (937 mg, yield 87%). ^{1}H NMR ($CDCl_3$): δ 8.00 (t, 2H, J=9.7 Hz), 7.53 (s, 1H), 7.35 (br, 3H, J= 10.3 Hz), 6.90 (dd, 2H, $J = 17.6$, 11.0 Hz), 5.84 (d, 2H, $J = 17.6$ Hz), 5.29 (d, 2H, $J = 11.0$ Hz), 4.59−4.51 (m, 1H), 2.28 (m, 2H), 1.92 (m, 2H), 1.26−1.08 (m, 22H), 1.06−0.98 (m, 2H), 0.82 (t, 6H, J=7.0 Hz). ^{13}C NMR ($CDCl_3$): δ 142.8, 139.4, 138.0, 135.3, 134.8, 123.6, 122.2, 120.3, 120.0, 117.0, 113.0, 109.8, 106.9, 56.3, 33.7, 31.7, 29.4, 29.3, 29.2, 26.8, 22.6, 14.0. Multiple resonances in the ^{1}H and ^{13}C NMR spectra are due to the phenomenon of atropisomerism.[25,29] MS (EI) (*m*/*z*) 457.371.

General Polymerization Procedure: Synthesis of Poly(9,9-di-*n*-octylfluorene-2,7-vinylene) by $Ru(CHPh)(Cl)_2(IMesH_2)(PCy_3)$. The polymerization procedure employed (run 2, Table 1) was analogous to that reported previously.[8,10,11] 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(**A**), 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.[8,13] 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. The ^{1}H NMR spectrum in the resultant polymer was analogous to that reported previously, 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.[10,11] ^{1}H NMR ($CDCl_3$ at 25 °C): δ 7.72 (d, 2H, J= 7.2 Hz), 7.67 (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.

Poly[9,9-di(2′-ethylhexyl)fluorene-2,7-vinylene], Poly(2). ^{1}H NMR ($CDCl_3$ at 25 °C): δ 7.68 (d, 2H, J = 7.68 Hz), 7.52 (br, 4H), 7.28 (br, 2H, *trans*-CH═CH−), 6.80 (dd), 5.79 (d), 5.25 (d), 2.03 (br, 4H), 1.24−1.07 (br, 20H), 0.81−0.66 (br, 10H). ^{13}C NMR ($CDCl_3$): δ 10.5, 14.3, 23.0, 28.3, 33.8, 34.8, 44.8, 54.9, 119.9, 121.9, 125.9, 128.6, 136.2, 140.9, 151.5.

Poly(9,9-di-*n*-hexylfluorene-2,7-vinylene), Poly(3). ^{1}H NMR ($CDCl_3$ at 25 °C): δ 7.67 (d, 2H, J=8.08 Hz), 7.51 (br, 4H), 7.27 (br, 2H, *trans*-CH═CH−), 6.80 (dd), 5.79 (d), 5.25 (d), 2.03

(br, 4H), 1.23−1.06 (br, 12H), 0.75 (t, 6H, J=6.96 Hz, CH_3), 0.66 (br, 4H). ^{13}C NMR ($CDCl_3$): δ 14.2, 22.8, 24.0, 30.0, 40.8, 55.1, 120.1, 120.8, 125.8, 128.7, 136.6, 140.8, 151.7.

Poly(*N*-9′-heptadecanylcarbazole-2,7-vinylene), Poly(5). ^{1}H NMR ($CDCl_3$ at 25 °C): δ 8.08 (d, 2H, J = 12.4 Hz), 7.56 (m, 6H), 6.92 (dd), 5.86 (d), 5.30 (d), 4.68 (s, 1H), 2.42 (s, 2H), 2.03 (s, 2H), 1.24 (m, 24H), 0.82 (t, 6H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 143.1, 139.7, 135.4, 134.9, 129.4, 123.5, 122.1, 120.5, 120.2, 117.5, 117.3, 110.1, 107.1, 33.9, 31.8, 29.5, 29.4, 29.2, 27.0, 22.6, 14.0.

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Supporting Information Available: ^{1}H NMR spectra (in $CDCl_3$ at 25 °C) for poly(9,9-di-*n*-hexylfluorene-2,7-vinylene)s prepared by ADMET and by the precursor method (purchased from Aldrich) and ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) for poly(*N*-9′-heptadecanylcarbazole-2,7-vinylene). This material is available free of charge via Internet at http://pubs.acs.org.

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1,2,4-trichlorobenzene at 45 or 55 °C, 3 days (72 h)]. The resultant polymers possessed similar molecular weights with unimodal molecular weight distributions [$M_n = 1.74 \times 10^4$, $M_w/M_n = 1.9$ (at 45 °C, initial monomer concentration = 200 μmol/mL), $M_n = 3.45 \times 10^4$, $M_w/M_n = 2.7$ (at 45 °C, initial monomer concentration = 50 μmol/mL), $M_n = 7.35 \times 10^4$, $M_w/M_n = 2.79$ (at 55 °C, initial monomer concentration = 50 μmol/mL)]. The results are interesting contrasts to our results because obtainment of high molecular weight poly(**2**) could be achieved only after 3 h in toluene according to our procedure [for example, run 9, $M_n = 3.30 \times 10^4$, $M_w/M_n = 2.2$ (at 50 °C, initial monomer concentration = 270 μmol/mL), Ru-(**A**) 40 equiv]. The results also indicate that certain optimizations are necessary for obtainment of high molecular weight polymers. The results also clearly suggest that continuous removal of ethylene (and initial monomer concentration, amount of ruthenium catalyst) should be the key for obtainment of high molecular weight polymer, as we previously emphasized,[8,10,11] and the effect of solvent may not be very important for obtainment of the high molecular weight polymers (if the resultant polymers are soluble).

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