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Precise Synthesis of Amphiphilic Multiblock Copolymers by Combination of Acyclic Diene Metathesis (ADMET) Polymerization with Atom Transfer Radical Polymerization (ATRP) and Click Chemistry

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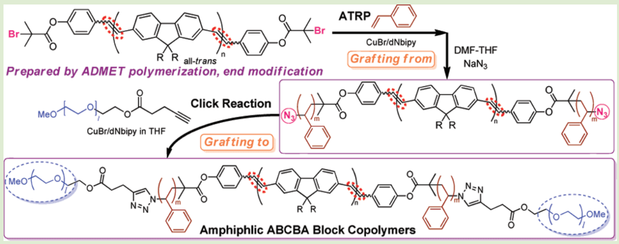
Supporting Information

ABSTRACT: Various block (graft) copolymers have been prepared by combination of acyclic diene metathesis (ADMET) polymerization of 9,9-dialkyl-2,7-divinyl-fluorene with Cu-catalyzed atom transfer radical polymerization (ATRP) of styrene using macroinitiators prepared by introduction of initiating functionalities into poly(9,9-dialkylfluorene-2,7-vinylene)s (PFVs) chain ends: a precise synthesis of the amphiphilic ABCBA-type block copolymers has also been attained by subsequent combination with click reaction after modification of the chain end with NaN_3.



Organic electronics are one of the most important emerging technologies, and conjugated polymers, such as poly(*p*-arylene vinylene)s, poly(thiophene)s, are promising semiconducting materials.[1−4] Synthesis of structurally regular, chemically pure polymers by development of new synthetic methods attracts considerable attention,[1] because their device performances are affected by polymer structural regularity, chemical purity, and supramolecular order.[2,3] Fluorene-based electroluminescent (EL) polymers are known to be promising in terms of a facile introduction of substituents into the C_9 position, high photoluminescence (PL) and EL efficiencies, and thermal and chemical stabilities.[5−7]

We recently demonstrated syntheses of *defect-free*, stereoregular (all-*trans*), high molecular weight poly(9,9-dialkylfluorene-2,7-vinylene)s (PFVs), poly(2,5-dialkylphenylene-1,4-vinylene)s (PPVs) by acyclic diene metathesis (ADMET) polymerization of 9,9-dialkyl-2,7-divinyl-fluorene.[5,8−10] Because the resultant polymers prepared by Ru-carbene catalyst possessed well-defined polymer chain ends (as vinyl group),[5b−d,9] a facile, exclusive end-functionalization can be achieved by treating the vinyl groups with Mo-alkylidene (Mo cat.) followed by Wittig-type cleavage with aldehyde:[5b,d,11,12] we thus demonstrated precise syntheses of ABA type amphiphilic triblock copolymer by grafting PEG [poly(ethylene glycol)] into both the PFV chain ends[5b] and of PFVs containing oligo(thiophene)s in both the chain ends which exhibiting unique emission properties by an energy transfer.[5d] 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,[13,14] and the control of the block lengths via synthesis shall open the way to fine-tuning the lateral dimensions of these nanostructures.

On the basis of the above results, in this paper, we wish to present that various block (graft) copolymers have been prepared by combination of ADMET technique with Cu catalyzed atom transfer radical polymerization (ATRP) technique by using macroinitiators prepared by introductions of initiating functionalities into PFV chain ends (*grafting from* approach).[15,16] Moreover, we succeeded in preparation of amphiphilic ABCBA type block copolymers containing PEG fragment by additional combination with click chemistry (*grafting to* approach).[17]

Acyclic diene metathesis (ADMET) polymerization of 2,7-divinyl-9,9-di-*n*-octylfluorene was conducted in the presence of Ru catalyst according to our established conditions under a reduced pressure (reaction time, 3 h; Scheme 1).[5b−d] The resultant poly(9,9-di-*n*-octylfluorene-2,7-vinylene) (PFV) possessed high molecular weight with unimodal molecular weight distribution (by GPC analysis: $M_n = 1.96 \times 10^4$, $M_w/M_n = 1.94$).[18] As demonstrated previously,[5] the resultant PFVs possessed exclusive *trans* regularity as well as vinyl groups at the both polymer chain ends as confirmed by ^1H NMR spectra.[5b−d,18] According to our reported procedure shown in Scheme 1,[5b−d] the vinyl groups at the PFV chain ends were treated with Mo cat. (2.5 equiv to the vinyl group to generate Mo-alkylidene moieties) and the subsequent addition of excess amount (ca. 2 equiv to Mo) of various aldehydes (ArCHO)

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Scheme 1. Syntheses of Macroinitiators [PFV($C_6H_4CH_2Br$)$_2$, PFV($C_6H_4OCOCMe_2Br$)$_2$] and Block Copolymers [PFV-(PS-Br)$_2$] by Combination of Acyclic Diene Metathesis (ADMET) Polymerization with Cu-Catalyzed Atom Transfer Radical Polymerization (ATRP)

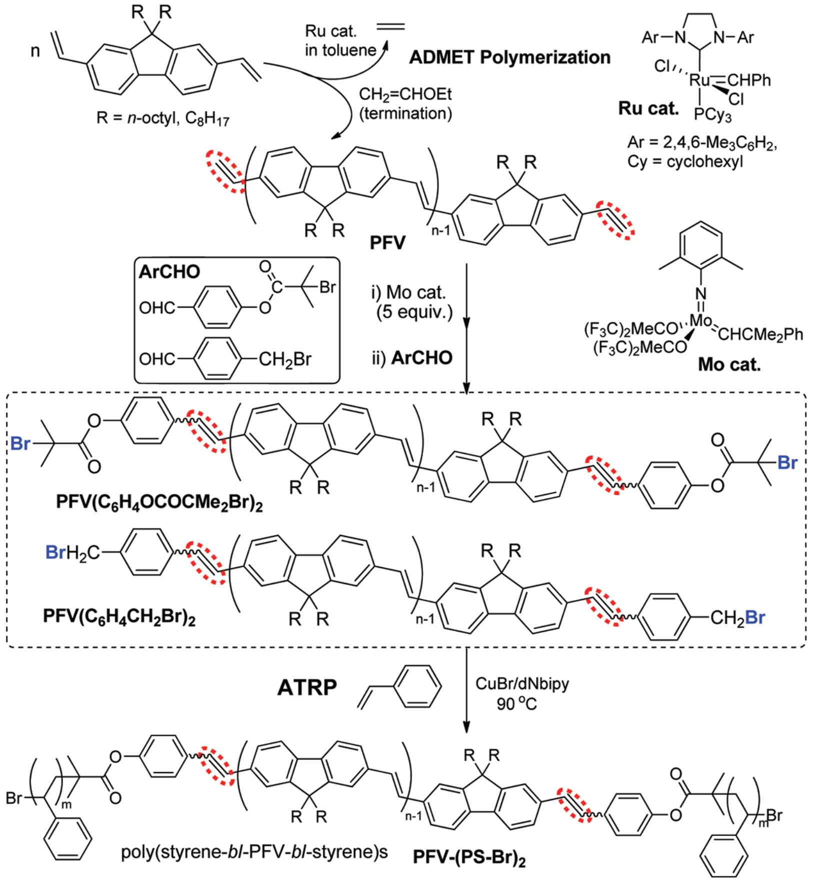


Table 1. Synthesis of Block Copolymers, Poly(styrene-*bl*-PFV-*bl*-styrene)s [PFV-(PS-Br)$_2$], by Cu-Catalyzed Atom Transfer Radical Polymerization (ATRP) of Styrene Initiated from Macroinitiators Containing PFV [PFV($C_6H_4CH_2Br$)$_2$ or PFV($C_6H_4OCOCMe_2Br$)$_2$][a]

			PFV-(PS-Br)$_2$			
run	initiator[b]	time/h	$M_{n(GPC)}$[c] × 10^{-4}	$M_{n(NMR)}$[d] × 10^{-4}	M_w/M_n[c]	conv[e]/%
1	PFV($C_6H_4CH_2Br$)$_2$	24	2.99	1.55	1.49	4.3
2	PFV($C_6H_4CH_2Br$)$_2$	35	3.51	1.77	1.49	5.5
3	PFV($C_6H_4CH_2Br$)$_2$	48	6.10	3.60	1.48	7.5
4	PFV($C_6H_4OCOCMe_2Br$)$_2$	12	2.86	1.40	1.70	5.0
5	PFV($C_6H_4OCOCMe_2Br$)$_2$	24	3.40	1.60	1.50	6.0
6	PFV($C_6H_4OCOCMe_2Br$)$_2$	36	4.10	2.00	1.58	7.0

[a] Conditions: PFV($C_6H_4CH_2Br$)$_2$ or PFV($C_6H_4OCOCMe_2Br$)$_2$/CuBr/DNbipy = 1/8.5/17 (molar ratio), the polymerization of styrene was conducted in bulk at 90 °C (details are shown in the Supporting Information),[18] dNbipy: 4,4-dinonyl-2,2′-dipyridyl. [b] Estimated molecular weight: $M_{n(NMR)}$ = 1.22 × 10^4 [PFV($C_6H_4CH_2Br$)$_2$], 1.24 × 10^4 [PFV($C_6H_4OCOCMe_2Br$)$_2$]. [c] GPC data in THF vs polystyrene standards. [d] Estimated by ^{1}H NMR spectra (integration ratios of protons between styrene and PFV). [e] Styrene conversion in %.

gave PFVs containing functionalities at the both polymer chain ends. Protons corresponding to the chain ends could be observed in the ^{1}H NMR spectra,[18] and the M_n values in the resultant macroinitoators, PFV($C_6H_4CH_2Br$)$_2$ and PFV-($C_6H_4OCOCMe_2Br$)$_2$, estimated by ^{1}H NMR spectra, were relatively close to those estimated based on the exact M_n value of PFV (corrected from GPC data as demonstrated previously),[19] strongly suggesting that both polymer chain ends could be exclusively modified by adopting the present approach.[19] The resultant macroinitiators, PFV($C_6H_4CH_2Br$)$_2$ and PFV($C_6H_4OCOCMe_2Br$)$_2$, were added in styrene in the presence of CuBr, dNbipy (4,4-dinonyl-2,2′-dipyridyl) at 90 °C for conducting subsequent atom transfer radical polymerization (ATRP), and the results are summarized in Table 1.

The NMR spectra in the resultant polymers indicate that styrene repeat units were incorporated and the styrene contents increased over time (upon increasing the yields, conversion). As shown in Figure 1, relatively linear relationships between M_n values estimated by their ^{1}H NMR spectra (based on integration ratios of protons between styrene and PFV)[18] and the conversion or polymerization time were observed, and relatively close relationships were observed when the M_n values

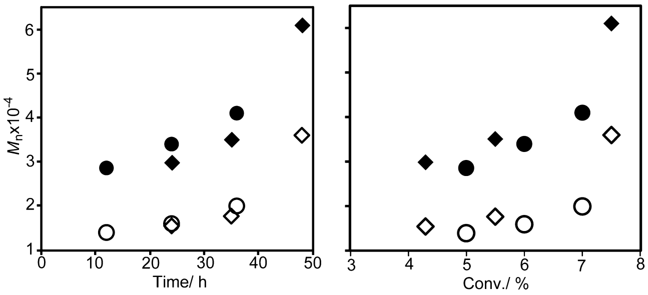


Figure 1. Plots of M_n values (by GPC, NMR) vs time (left), conversion (right) in ATRP of styrene. M_n values of PFV-(PS-Br)$_2$ from PFV(C$_6$H$_4$CH$_2$Br)$_2$ by ◆ (GPC), ◇ (NMR); from PFV-(C$_6$H$_4$OCOCMe$_2$Br)$_2$ by ● (GPC), ○ (NMR). The detailed results are shown in Table 1.

Table 2. Synthesis of ABCBA Block Copolymers, PFV-(PS-*bl*-PEG)$_2$[a]

copolymer	$M_{n\,(GPC)}$[b] × 10^{-4}	$M_{n(NMR)}$[c] × 10^{-4}	$M_{n(calcd)}$[d] × 10^{-4}	M_w/M_n[b]	yield[f]/%
PFV-(PS-Br)$_2$[g]	2.86	1.40		1.70	
PFV-(PS-N$_3$)$_2$	2.50			1.60	95.0
PFV-(PS-*bl*-PEG)$_2$	2.50	1.29	1.32	1.44	91.6
PFV-(PS-*bl*-PEG)$_2$	2.46	1.30	1.32	1.44	90.0

[a]Conditions: PFV-(PS-N$_3$)$_2$/4-pentanoate terminated poly(ethylene glycol) methyl ether/CuBr/dNbipy = 1/3.5/5/10 (molar ratio) in 2.0 mL of THF at 35 °C for 5 days. [b]GPC data in THF versus polystyrene standards. [c]Estimated value by ^{1}H NMR spectra (integration ratios of protons between styrene and PFV, or on the basis of PEG). [d]Calculated value based on the exact M_n value of PFV (corrected from GPC data, 1.22 × 10^4)[19] and integration ratio of PFV and styrene in the ^{1}H NMR spectra. [f]Isolated yield. [g]Sample in run 4, Table 1.

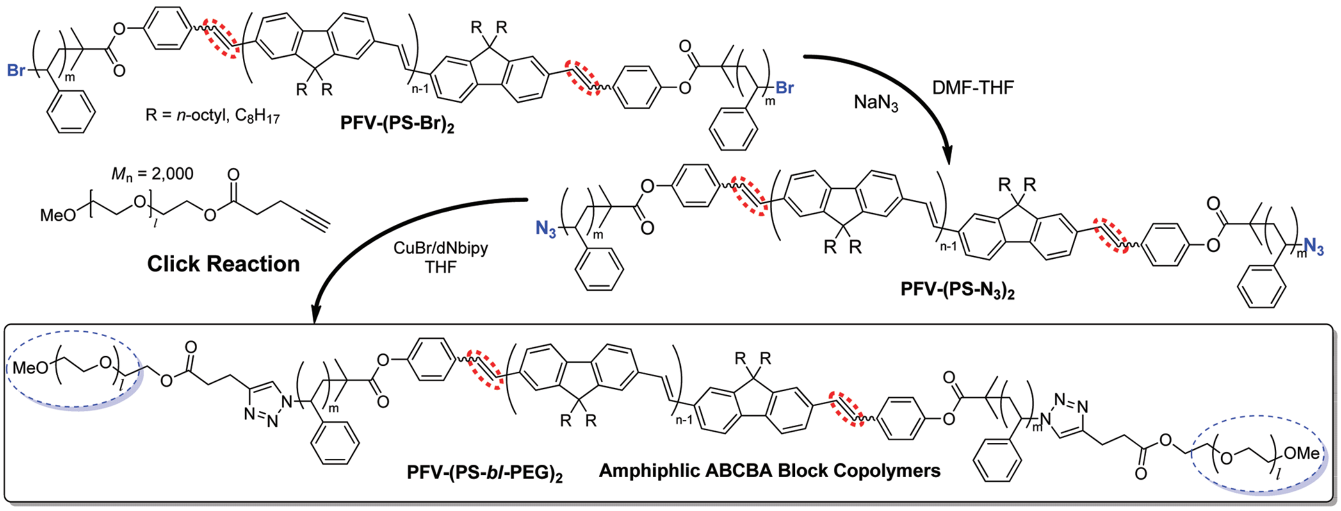
by GPC were employed for the plots. These would suggest that these polymerizations proceeded in a living manner.

However, the initiation efficiencies in the macromoinitiator were uncertain through these experiments, and we, therefore, converted the bromide in the chain end (the sample in run 4, Table 1) by treating NaN$_3$ and the resultant polymer, PFV-(PS-N$_3$)$_2$, was reacted with 4-pentanoate terminated poly(ethylene glycol) methyl ether (M_n = 2000, Aldrich) in the presence of CuBr and dNbipy in THF (at 35 °C for 5 days). The results are shown in Table 2.

^{1}H NMR spectra for the resultant polymers possessed protons ascribed to PEG units, suggesting incorporation of PEG segment. Note that the M_n values estimated by ^{1}H NMR spectra (on the basis of methylene protons in the PEG segment) were very close to those calculated (based on M_n value of PFV and integration ratio of PFV and styrene). The results are reproducible, as demonstrated in Table 2. These results strongly demonstrate that precise, exclusive synthesis of amphiphilic ABCBA-type block copolymers have been attained by adopting this approach (Scheme 2). Moreover, importantly, the results strongly demonstrate that the end-functionalization of PFV chain ends [preparation of macroinitiators], ATRP of styrene, and subsequent treatment with NaN$_3$ took place with exclusive yields in all cases.

Taking into account the above facts, we have shown that various block (graft) copolymers have been prepared by adopting a combination of ADMET polymerization of 9,9-dialkyl-2,7-divinyl-fluorene with ATRP of styrene from macro-initiators prepared by introductions of initiating functionalities into the PFV chain ends (*grafting from* approach). Moreover, the precise synthesis of amphiphilic ABCBA-type block copolymers has been attained by subsequent combination with click reaction. As described above, 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,[13,14] and the precise control of the amphiphilic nature as well as of the block lengths via synthesis shall open the way to fine-tuning the lateral dimensions of these nanostructures. Because the methodology presented here should also have many applications (with various monomers for ATRP, and click reactions), the results presented here should be highly promising for designing precise conjugated materials for the desired purposes.

Scheme 2. Synthesis of Amphiphilic ABCBA Block Copolymers, PFV-(PS-*bl*-PEG)$_2$, by Combination of ATRP with Click Coupling



■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures for synthesis of various block copolymers, their NMR spectra, and selected GPC traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(18) Experimental procedures for synthesis of various block copolymers and their NMR spectra, selected GPC traces are shown in the Supporting Information.

(19) The M_n values for PFV($C_6H_4CH_2Br$)$_2$, PFV($C_6H_4OCOCMe_2Br$)$_2$ estimated by ^{1}H NMR spectra (on the basis of aromatic protons in PFV vs initiating fragment)[18] were 1.22×10^4 and 1.24×10^4, respectively. These values are relatively close to the estimated values ($M_n = 1.25 \times 10^4$ and 1.27×10^4) on the basis of the exact value of PFV estimated by GPC [$M_{n(\text{corrected})} = 1.22 \times 10^4$ and $M_{n(\text{GPC})} = 1.96 \times 10^4$] and the initiating fragment. As reported previously,[5a] the M_n value in GPC versus polystyrene standards is higher than that in GPC versus PPP standards because of the nature of rigid conjugated polymers, and the estimation [$M_{n(\text{calcd})} = M_{n(\text{GPC})}/1.6$] was adopted for further study.[5]