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Synthesis of Polyethylene and Polystyrene Miktoarm Star Copolymers Using an "In-Out" Strategy

Pingwei Liu,[1,2] Zhibin Ye,[2,3,*] Wen-Jun Wang,[1,4,*], Bo-Geng Li[1]

[1] State Key Lab of Chemical Engineering, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou, 310027, China

[2] Bharti School of Engineering, Laurentian University, Sudbury, Ontario P3E 2C6, Canada

[3] Department of Chemistry and Biochemistry, Laurentian University, Sudbury, Ontario P3E 2C6, Canada

[4] Key Lab of Biomass Chemical Engineering of Ministry of Education, Zhejiang University, Hangzhou, Zhejiang 310027, China

[*] Corresponding authors' addresses: wenjunwang@zju.edu.cn (WJW); zye@laurentian.ca (ZY).

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ABSTRACT

Miktoarm star copolymers (MSPs) having multiple polyethylene (PE) and polystyrene (PS) arms joined at a crosslinked polydivinylbenzene (PDVB) core were synthesized using an "in-out" synthesis approach. The "in" step involved the atom transfer radical polymerization (ATRP) of divinylbenzene initiated by a narrowly distributed PE macroinitiator (MI), generated via Pd-catalyzed living polymerization, to produce star homoarm PEs containing core -Br functionality. The star PEs were then employed as MIs to initiate an ATRP of styrene in the "out" step to produce $(PE)_m-PDVB-(PS)_n$ MSPs. A variety of $(PE)_m-PDVB-(PS)_n$ MSPs were synthesized possessing PE arm lengths and numbers of 7.3–13.7 kg/mol and 11.6−33.4, respectively, and PS arm lengths and numbers of 6.7−32.5 kg/mol and 3.7–9.0, respectively. Star-star couplings were observed when the shielding protection of the PE arms on the PS propagating radicals vanished, leading to a rapid increase of molecular weights for the MSPs. Characterizations of dilute MSP solutions indicate that the generated copolymers possess highly compact spherical chain conformations.

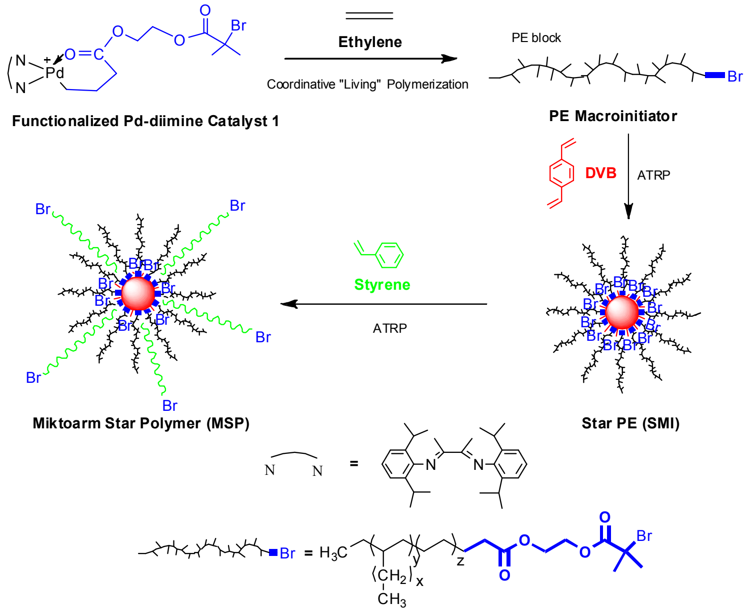
INTRODUCTION

Polyolefins are used in a wide variety of commodity applications and are considered one of the most important commercial thermoplastic products in the world.[1] However, because they lack polar functional groups, polyolefin plastics demonstrate poor adhesion and compatibility with most other materials, limiting their application scope. Thus, the functionalization of these polymers is of great interest and is being pursued by both academic and industrial researchers.[2] Structures that appear to hold great promise are polyolefin block copolymers.[3] The incompatibility of their polymer blocks provides these species with a wide variety of microstructures and morphologies in bulk and solution and may extend their applications to broader range of industries.[2c-2j]

Miktoarm star polymers (MSPs) are block copolymers containing multiple polymer arms joined at a core.[4] Their three-dimensional globular structures with tunable inner and peripheral functionalities offer high solubility, low melt or solution viscosity, and high functionality.[5] In addition, the unique nonlinear block structures of the MSPs can form intriguing morphologies after assembling in bulk or solution, which are not achievable with linear block copolymers[6] but are highly desirable for drug delivery and biomedical applications.[5g,5h] Synthesis of the MSPs is facilitated using individual or combined "living" or controlled polymerization techniques,[4,5] including anionic[7] and cationic polymerization,[8] ring-opening polymerization,[9] ring-opening metathesis polymerization,[10] and controlled/living radical polymerization (CLRP).[11-13] In particular, the CLRP techniques such as atom-transfer radical polymerization (ATRP) offer a great deal of flexibility in the choice of monomer stocks utilized.[5e-5g] Four CLRP strategies including "arm-first", "coupling", "core-first", and "in-out" have been developed. The "arm-first" strategy requires synthesis of different polymer macroinitiators (MIs) or macromonomers first via the ATRP followed by a crosslinking reaction.[14] The "coupling" reaction between polymer chains having complementary reactive groups results in MSPs. The use of multifunctional cores and "click" reactions is common with this technique.[5h,15] In the "core-first" strategy, a multifunctional initiator containing orthogonal initiating sites is used for the ATRP to lead the formation of arms. The protection and/or de-protection of functional groups in the core is generally required.[16] In most cases, the "coupling" and "core-first" strategies are used together.[5g-h,15e] For the "in-out" strategy, the MI initiates or participates in the ATRP of a crosslinkable monomer to form a homoarm star polymer. The initiating functional groups preserved in the core of the homoarm star polymer can further initiate the ATRP of second monomer to form the MSP. The "in-out" approach is relatively convenient for synthesizing MSPs.[17]

Although a significant advance has been achieved in the "living" olefin coordination polymerization during the past decade or so,[2j,18,19] less attention has been paid to polyolefin MSPs. So far there is only one report on the synthesis and self-assembly of a (polyethylene)$_2$-(polystyrene)$_2$ (PE$_2$-PS$_2$) MSP having two linear crystalline PE arms with low number-average molecular weight (M_n) of 1.1 kg/mol and two PS arms. A complicated "core-first" approach combined with chain shuttling ethylene polymerization, "click" reaction and ATRP was used for synthesizing the PE$_2$-PS$_2$. The core was a special multifunctional molecule prepared via multiple modification steps.[20]

Here, we report on a versatile "in-out" strategy for synthesizing a functionalized polyolefinic material with well-defined miktoarm star structure (Scheme 1). Narrowly-distributed PE MIs were first synthesized via an ethylene "living" coordination polymerization,[3b] and participated in the consecutive ATRP of divinylbenzene (DVB) to produce PE homoarm star copolymers with a crosslinked PDVB core and controllable arms.[21] The homoarm star PEs further initiated the ATRP of styrene to render well-defined miktoarm stars, PE$_n$-PDVB-PS$_m$. The kinetics of styrene ATRP initiated by the star PEs were investigated. The structures and compositions of the PE$_n$-PDVB-PS$_m$ samples as well as their dilute solution properties were also studied.



Scheme 1. “In-out” strategy for the synthesis of miktoarm star polymer with multiple PE and PS arms joined at a crosslinked PDVB core.

EXPERIMENTAL SECTION

Materials

All experimental operations involving air and/or moisture sensitive materials were conducted in a N_2-filled glove box or using the Schlenk technique. The functionalized Pd-diimine catalyst **1**, $[(ArN{=}C(Me)\text{-}(Me)\text{-}C{=}NAr)Pd(CH_2)_3C(O)O(CH_2)_2OC(O)C(CH_3)_2Br]^+SbF_6^-$ (Ar = 2,6-(iPr)$_2$C$_6$H$_3$), was synthesized as described in a previous study.[3b] HPLC grade chlorobenzene (>99%, Aldrich) and toluene (>99%, Fisher Scientific) were deoxygenated and purified using an Innovative Technologies, Inc. solvent purification system prior to use. CuBr (>99%, Aldrich) was purified by washing with glacial acetic acid and methanol and drying under vacuum. Styrene (>99%, Aldrich) and divinylbenzene (DVB, 80%, mixture of isomers, Aldrich) were distilled under vacuum to remove inhibitors prior to use. Other chemicals including 1-phenylethyl bromide (1-PEBr) (>97%, Alfa Aesar), $CuBr_2$ (>99%, Aldrich), N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA, >99%, Aldrich), anhydrous diethyl ether (ACS, >99%), anhydrous dichloromethane (>99%, Aldrich), tetrahydrofuran (THF, ACS reagent grade, Fisher Scientific), and methanol (ACS reagent, Fisher Scientific) were used as received.

Synthesis of Miktoarm Star Polymer $(PE)_n{-}PDVB{-}(PS)_m$s

The preparation of PE macroinitiators (MIs) by ethylene polymerization with **1** and the synthesis of homoarm star polymer (PE)n−PDVBs are described in the Supporting Information. The $(PE)_n{-}PDVB{-}(PS)_m$s were prepared with the $(PE)_n$-PDVB star copolymers serving as the macroinitiator (SMI). The -Br functionalities were assumed to be fully preserved in the $(PE)_n{-}PDVB$. Take Run 3 as an example for synthesizing $(PE)_n{-}PDVB{-}(PS)_m$ miktoarm star polymer: SMI3 (0.2g, 13.8 μmol Br), styrene (3.2 mL, 27.6 mmol), toluene (3.3 mL), CuBr (24.0 mg, 165.7 μmol), $CuBr_2$ (3.7 mg, 16.6 μmol), and PMDETA (31.9 μL, 182.0 μmol). The polymerization was carried out at 100 °C. The polymer sample was obtained through precipitating and washing (3 times) with methanol and drying overnight at room temperature under vacuum. The styrene conversion was calculated from the ^{1}H NMR spectrum of the $(PE)_n$−PDVB−$(PS)_m$ sample subsequent to purification. In addition, the ATRP of St with 1-phenylethyl bromide (1-PEBr) as initiator was conducted as a control. The same experiment recipe and conditions were used.

Characterizations

The molecular weight, polydispersity index (PDI), weight-average gyration radius ($R_{g,w}$s), and intrinsic viscosity for each polymer sample were determined using a Polymer Laboratories PL-GPC220 gel permeation chromatography (GPC). The GPC is equipped with a differential refractive index detector (DRI) (Polymer Laboratories), a three-angle (45, 90, and 135º) light scattering detector (LS) (687nm, Wyatt Technology), and a four-bridge capillary viscosity detector (Polymer Laboratories). A PL# 1110-1120 guard column and three PLgel 10 μm MIXED-B 300 × 7.5 mm columns were used for the chromatographic separation.[21,22] All measurements were conducted at 33 °C with THF as the mobile phase at a flow rate of 1.0 mL/min. The average refractive index increment of the miktoarm star polymer (dn/dc_{MSP}) was calculated using Eq. 1 based on the feed mass of SMI (W_{SMI}), feed mass of styrene (W_{St}), and styrene conversion (x_{St}).

$$\begin{aligned} dn/dc_{MSP} = dn/dc_{PE} \times \frac{W_{SMI} \times (1 - w_{DVB}) \times Y_s}{W_{SMI} \times Y_s + x_{St} W_{St}} + dn/dc_{PDVB} \times \frac{W_{SMI} \times w_{DVB} \times Y_s}{W_{SMI} \times Y_s + x_{St} W_{St}} \\ + dn/dc_{PS} \times \frac{x_{St} W_{St}}{W_{SMI} \times Y_s + x_{St} W_{St}} \end{aligned} \qquad (1)$$

where dn/dc_{PE} = 0.078 mL/g, dn/dc_{PDVB} = dn/dc_{PS} = 0.185 mL/g, Y_s is the star yield based on the SMI, and w_{DVB} is the mass fraction of DVB in the SMI. The EasiVial PS-H (narrow polystyrene standards, molecular weights = 0.58-6,000 kg/mol) from Polymer Laboratories were used for the universal calibration.

The ^{1}H NMR measurements were performed on a 200 MHz Varian Gemini 2000 spectrometer using CD_2Cl_2 or $CDCl_3$ as solvent.[21] The differential scanning calorimetry (DSC) thermograms were acquired on a TA Instrument Q100 DSC under N_2 gas at a flow rate of 50 mL/min. The procedure involved heating the sample from room temperature to 160 °C at 10 °C/min, then cooling it down to 90 °C at 10 °C/min, and heating again from 90 to 160 °C at 10 °C/min. The data was acquired during the second heating cycle.[21] Dynamic light scattering measurements of the star samples in n-heptane at a concentration of 5 mg/mL were performed at room temperature using a Malvern ZS 90 equipped with an argon ion laser of 633 nm at a detection angle of 90°.

RESULTS AND DISCUSSION

Synthesis of $(PE)_n$−PDVB SMIs

In a previous study, we reported on the synthesis of a range of star polymer $(PE)_n$-PDVBs with narrowly distributed arm lengths of 7.3 to 13.7 kg/mol and average arm numbers of 5 to 43. High star yields were achieved at low PE MI concentrations and high DVB to MI molar ratios.[21] Five SMIs with star yields from 79% to 87% were produced accordingly as shown in Table 1. The SMI1, SMI2, and SMI3 samples possessed the same PE arm length ($M_{n,LS}$ = 7.3 kg/mol) but varied PE arm numbers (N_{PE}) of 11.6, 20.0, and 33.4, respectively, while the SMI4 and SMI5 had different arm lengths of 10.3 and 13.7 kg/mol with an approximately same N_{PE} (~20) as SMI2. All SMI samples comprised a large PDVB core with 35−51 wt % of DVB in the copolymers.

Table 1. Five star $(PE)_n$−PDVB macroinitiators (SMIs) synthesized via the ATRP of DVB [a]

SMI	**PE arm [b]**		**$[DVB]_0/[MI]_0$**	**t [c] (h)**	**w_{DVB} [d] (wt%)**	**Y_s [e] (wt%)**	**N_{PE} [f]**
	$M_{n,LS}$ (kg/mol)	**PDI**					
1	7.3	1.08	120:1	3	35	79	11.6
2	7.3	1.08	180:1	3	46	83	20.0
3	7.3	1.08	180:1	5	51	87	33.4
4	10.3	1.11	180:1	3	39	84	20.4
5	13.7	1.14	180:1	3	30	83	24.2

[a] Polymerization conditions: the initial concentration of PE macroinitiator (MI) $[MI]_0$ = 3.8 mM; $[MI]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0$ = 1:12:1.2:13.2; solvent, toluene; temperature, 100 °C; [b] Absolute number-average molecular weights ($M_{n,LS}$) determined by the GPC with the laser light scattering (LS) detector, polydispersity indexes (PDI) calculated from the universal calibration against PS standards; [c] Polymerization time; [d] The weight percentage of DVB in the copolymers; [e] The star yield refers to the percentage of MIs forming the star $(PE)_n$−PDVBs;[21] [f] The number-average number of PE arms in the SMI.[21]

Synthesis of $(PE)_n$-PDVB-$(PS)_m$ Miktoarm Star Polymers (MSPs)

The $(PE)_n$-PDVB-$(PS)_m$ MSPs were synthesized via the ATRP of styrene using the SMIs as initiator. In order to minimize radical coupling reactions and enhance the initiation efficiency of the macroinitiators, a low SMI concentration of 2.1 mM, a high $[Cu^+]_0$ to $[MI]_0$ ratio of 12, and an addition of Cu^{2+} (10% of Cu^+) as a deactivator were used during the ATRPs.[3b,21]

Effect of SMI arm number on MSP synthesis

The influence of the star polymer $(PE)_n$-PDVBs containing various PE arm numbers (SMI1-3) on the formation of $(PE)_n$-PDVB-$(PS)_m$ miktoarm stars was studied. The polymerization conditions and characterization results are summarized in Table 2. Figure 1 shows semi-logarithmic plots of styrene conversions versus polymerization times for all three runs. It can be seen that all runs followed first-order kinetics, suggesting the “livingness” characteristics during the ATRP courses. In general, initiator groups located in the core cannot all be initiated and participated in the formation of secondary arms during the synthesis of miktoarm star copolymers using the “in-out” strategy owing to a highly cross-linked core. This led to the embedment of functional groups and large steric hindrance. The initiation efficiency (IE) of the SMIs is defined as the percentage of initiated –Br groups, which was determined by a kinetic method proposed by the Matyjaszewski group provided in the Supporting Information.[17d] The kinetic results for the control run of St ATRP with 1-PEBr as initiator are also provided (Figure S1) in the Supporting Information and used for the IE estimation.

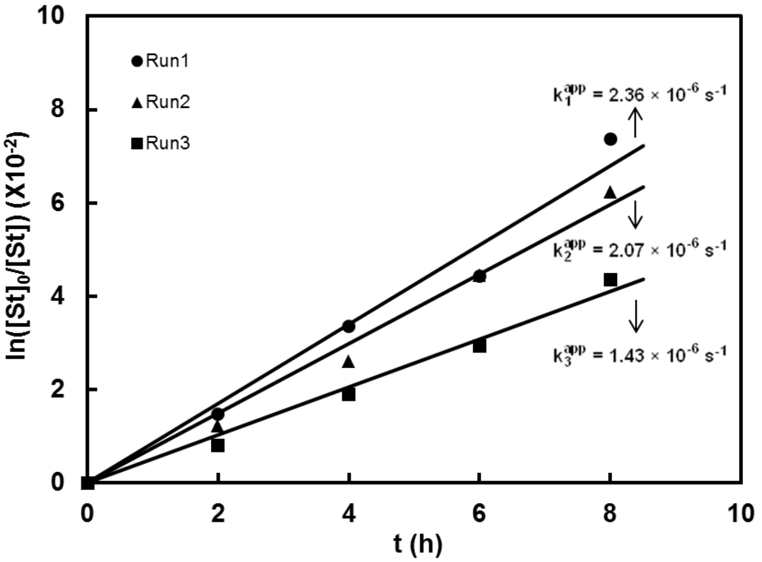


Figure 1. Semi logarithmic kinetic plot of styrene conversion versus polymerization time for Run 1 (SMI1 as macroinitiator), Run 2 (SMI2), and Run 3 (SMI3). $[SMI]_0$ = 2.1 mM; $[SMI]_0:[St]_0:[CuBr]_0:[CuBr_2]_0$: $[PMDETA]_0$ = 1:2000:12:1.2:13.2, temperature = 100 °C, and toluene as solvent.

The IE values for the SMIs were 19.0-31.3%. The increased average PE arm number from SMI1 (N_{PE} = 11.6) in Run 1 to SMI3 (33.4) in Run 3 and DVB mass content from SMI1 (35 wt %) to SMI3 (51 wt%) decreased the IE from 31.3% of Run 1 to 19.0% of Run 3, further confirming the adverse effect of the compact star structures on the initiation efficiency of the –Br groups in the core. Basing on the IE and N_{PE} values, the average number of PS arms (N_{PS}) can be estimated from Eq 2.

$$N_{PS} = N_{PE} \times IE \qquad (2)$$

As shown in Table 2, an increase in the N_{PS} was observed for Runs 1-3 from 3.7 (Run 1) to 6.4 (Run 3).

Table 2. Miktoarm star copolymers synthesized with SMIs having different arm numbers but the same arm length [a]

Run	IE [b] (%)	N_{PS} [c]	t (h)	x_{St} [d] (%)	E: DVB: St [e]	Y_{MSP} [f] (%)	dn/dc [g] (mL/g)	GPC results of MSPs [h]					L_{PS} [j] (kg/mol)
								$M_{n,LS}$ (kg/mol)	PDI_{LS}	$[\eta]_w$ (mL/g)	$R_{g,w}$ (nm)	α [i]	
1	31.3	3.6	0	0	90:10:0	79	0.116	131.5	1.34	15.2		0.069	0.0
			2	1.5	80:10:10	80	0.134	163.3	1.40	16.6		0.059	8.7
			4	3.3	72:9:19	87	0.147	217.6	1.54	21.9		0.182	23.7
			6	4.3	68:8:24	92	0.152	335.5	1.68	30.6	15.4	0.304	56.1
			8	7.1	59:7:34	94	0.160	734.0	1.73	42.2	23.9	0.363	165.8
2	27.5	5.5	0	0	84:16:0	83	0.128	272.4	1.40	15.4		0.135	0.0
			2	1.2	78:15:7	83	0.138	313.9	1.39	15.4		0.135	7.6
			4	2.6	72:13:15	87	0.146	412.9	1.44	19.5	13.0	0.197	25.6
			6	4.3	65:12:23	91	0.154	611.3	1.47	25.7	18.2	0.285	61.7
			8	6.0	60:11:29	93	0.158	917.8	1.48	34.0	26.8	0.356	117.4
3	19.0	6.3	0	0	82:18:0	87	0.133	497.2	1.33	15.0	10.9	0.145	0.0
			2	0.8	77:18:5	87	0.139	539.5	1.36	15.7	11.4	0.114	6.7
			4	1.9	73:16:11	87	0.145	611.7	1.32	16.9	12.9	0.171	18.1
			6	2.9	68:16:16	88	0.150	703.8	1.35	19.9	15.8	0.209	32.6
			8	4.3	63:15:22	88	0.154	878.0	1.35	25.1	20.5	0.271	60.1

[a] Polymerization condition: SMI1-3 were used for Runs 1-3, respectively; $[SMI]_0$ = 2.1 mM; $[SMI]_0$:$[St]_0$:$[CuBr]_0$: $[CuBr_2]_0$:$[PMDETA]_0$ = 1:2000:12:1.2:13.2; solvent, toluene; temperature, 100 ºC.

[b] Initiation efficiency of the –Br groups in the SMIs.

[c] Number-average number of polystyrene arms.

[d] Styrene conversion calculated from the ^{1}H NMR spectrum.

[e] Mole percentages of ethylene, DVB, and styrene in the SMIs and MSPs.

[f] Star yield calculated from area percentage of the MSP to overall polymer sample determined by the GPC.

[g] Average refractive index increment of the MSP.

[h] $M_{n,LS}$, PDI_{LS}, weight-average gyration radius ($R_{g,w}$) data (over 10 nm listed due to the measurement limit of the LS technique), and Weight-average intrinsic viscosity ($[\eta]_w$) of the MSPs were determined with the triple-detection GPC. Two low molecular weight peaks for linear polymers were excluded from the overall GPC traces in the calculations.

[i] α is the Mark-Houwink exponent of the MSPs.

[j] Length of PS arm estimated from eq (3).

Figure 2 shows the GPC elution traces for Runs 1-3. A continuous decrease of elution volume in the GPC curves with the polymerization time can be seen, indicating the propagation of the PS arms. There is no evidence of the peak change at elution volume > 23 mL, which refers to the two linear polymer components without terminal functionality.[21] In order to quantitatively determine the MSP molecular weights and yields, a deconvolution method (see Figure S2 in the Supporting Information for details) was undertaken through peak fitting for MSP and two linear components in the GPC curves by assuming the three peaks follow Gaussian distributions.[21]

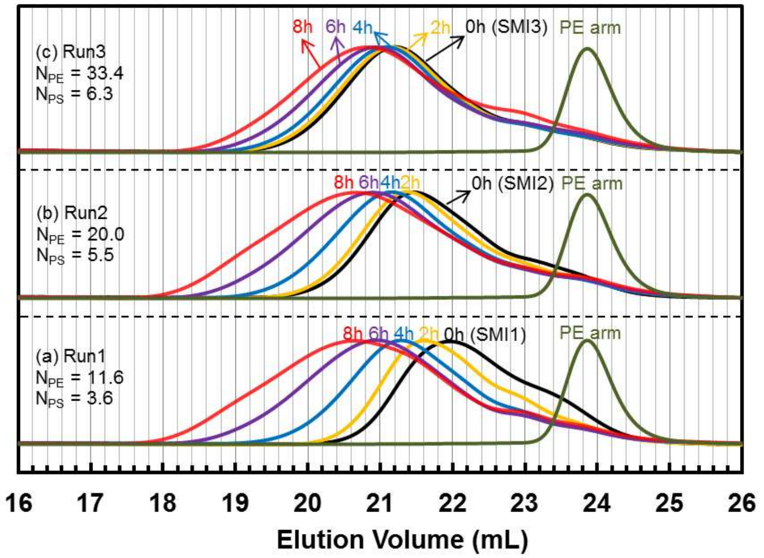
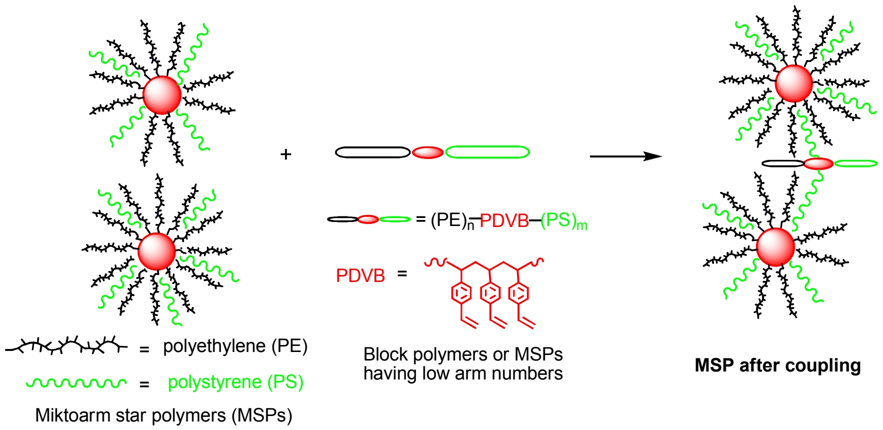


Figure 2. GPC traces from DRI detector for the MSP samples (a) Run 1 (SMI1 as macroinitiator), (b) Run 2 (SMI2), and (c) Run 3 (SMI3).

The star yields increased with the progress of St polymerization and the MSP formation efficiency increased slightly with the SMIs having lower PE arm number (N_{PE}) MSP formation. The number- and weight-average molecular weights (M_n and M_W) and polydispersity indexes (PDI) of the MSPs were determined after truncating the linear polymer components in the GPC traces. The deconvolution of the DPC traces is given in Figure S2 of the Supporting Information. Figure 3 plots the M_n and PDI versus the styrene conversion (x_{St}). The M_n increased but the increment rate enlarged with the x_{St} suggesting star-star coupling occurred with the "in-out" synthesis strategy. This was further indicated by the molecular weight increment of the MSP from the SMI by 1.55 times for Run 1 compared to 1.24 for Run 2 and 0.77 for Run 3 after 4.3% of added styrene was converted and broadening of the molecular weight distributions with an order of Run 1 > Run 2 > Run 3. The star-star coupling was also observed by Chen et al.[17] when using the "in-out" strategy to synthesize [poly(ethylene oxide)]$_m$–PDVB–(PS)$_n$ MSPs with poly(ethylene oxide) (PEO) star polymers as MIs. The authors attributed the coupling to the interaction between the radicals of the stars when the PS arms became longer than the PEO arms and the PEO arms lost the protection on the propagating PS radicals.[17a] In this study, the radical concentrations in Runs 1-3 were approximately one order of magnitude lower than those in the (PEO)$_m$–PDVB–(PS)$_n$ system[17a] in addition to low initiation efficiency of the –Br groups in the SMIs (19.0-31.3%). We speculate that the inter reaction between the radicals of the stars might not be the main reason for the coupling. Since the DVB concentrations used here were approximately one order of magnitude higher than those used in the (PEO)$_m$–PDVB–(PS)$_n$ system,[17a] there existed a high content of PDVB with a large number of pendent double bonds in the SMIs.[21] Scheme 2 shows the coupling through the interaction between the radicals of the stars and the pendent double bonds in the linear block copolymers or MSPs having low arm numbers. This is further indicated by more coupling reactions in synthesizing the MSPs with the SMIs having lower N_{PE}.



Scheme 2. A schematic description of the star-star coupling

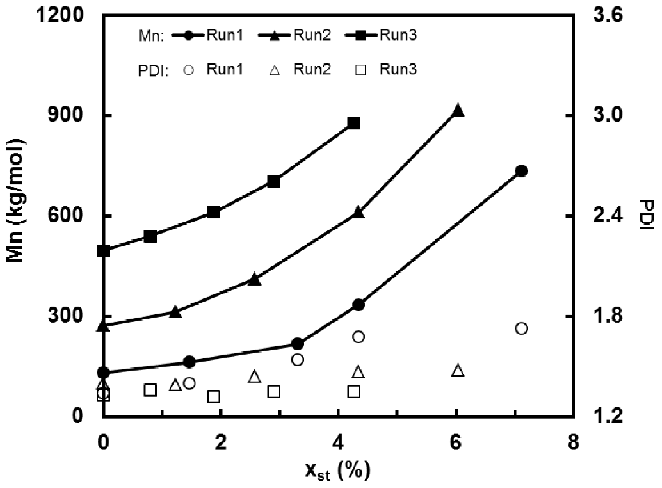


Figure 3. (a) number-average molecular weight (M_n) and (b) polydispersity (PDI) of the miktoarm star polymers with linear polymers excluded versus styrene conversion (x_{St}) in Run 1 (SMI1 as macroinitiator), Run 2 (SMI2), and Run 3 (SMI3).

The propagation of the PS arms in the MSPs was also studied. The PS arm lengths (L_{PS}) were estimated from Eq. 3. The propagation of the PS arms was assumed to follow the "living" polymerization characteristics and the star-star coupling was negligible during the calculation

$$L_{PS} = (M_{n,MSP} - M_{n,SMI}) / N_{PS} \qquad (3)$$

where, $M_{n,MSP}$ and $M_{n,SMI}$ are the number-average molecular weights of the MSPs and the corresponding SMIs, respectively, and N_{PS} is the average number of the PS arms in the MSPs. The L_{PS} results are plotted against the polymerization times in Figure 4. A control run of the St ATRP was also plotted (Figure S1) to represent the theoretical growth of the PS arm with time. It can be seen the L_{PS} values for Runs 1 and 2 were consistent with the control run in the first 4 h while the L_{PS}s of Run 3 followed the control run till 6 h, suggesting the coupling reactions in these periods were negligible. However, the L_{PS} values increased rapidly and diverged greatly from the control run in Runs 1-2 after 4 h, in contrast with less deviation in Run 3 after 6 h. This indicates participation of coupling reactions in star formation. The PS arms in these turning points had 228 (Run 1), 246 (Run 2) and 313 (Run 3) styrene units. Compared with the 260 ethylene units in the PE arms, it can be seen that the coupling occurred when the PS arms were longer than the PE arms. The shielding protection of the PE arms restrained the coupling reactions during the synthesis of the MSPs.

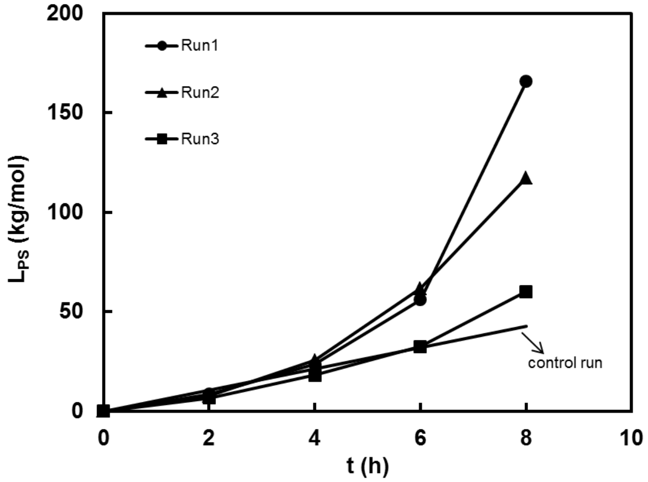


Figure 4. PS arm lengths of the miktoarm star polymers versus polymerization time in Runs 1-3. ATRP of styrene was also plotted as a control run.

Effect of SMI arm length on MSP synthesis

The influence of the star polymer $(PE)_n$-PDVBs with various PE arm lengths (SMI2, 4, and 5) on the formation of $(PE)_n$-PDVB-$(PS)_m$ miktoarm stars was investigated. The characterization results of the MSPs are summarized in Table 3. It was found that Run 5 formed a gel after 8 h. The semi-logarithmic plots of styrene conversions versus polymerization times for all three runs are given in Figure S3 of the Supporting Information. First-order kinetics was also observed to confirm the "living" characteristics of styrene polymerizations in the three runs.

The influence of the PE arm length on the initiation efficiency of the –Br groups in the SMI was also examined. The IE values of Runs 2, 4, and 5 were 28.1, 31.3 and 35.7%, respectively, indicating the increase of the IE with the PE arm length of the SMIs. This might be attributed to the amount of DVB used in the SMIs. The DVB weight percentages in the SMIs were 46% (SMI2), 39% (SMI4), and 30% (SMI5), respectively. Lower DVB usage reduced the embedment of –Br groups in the PDVB core, thus leading to more functional groups participating in the ATRP of St. The average number of PS arms, N_{PS}, thus increased from 5.6 of Run 2, to 6.4 of Run 4, and to 8.7 of Run 5 with the PE arm length.

The GPC elution traces of the three runs are shown in Figure S4 of the Supporting Information. Using the peak deconvolution method, the star yield, molecular weight, and PS arm length results were estimated and summarized in Table 3. Figure 5 gives the changes of $M_{n,LS}$, PDI, and L_{PS} of the MSPs during the polymerization. The molecular weights of the MSPs in all three runs increased smoothly with a good control at the beginning followed by a rapid increment after 4 h, and gelling at 8 h in Run 5. The coupling reactions accelerated the increment of increase in the MSP molecular weights.

Table 3. Miktoarm star copolymers synthesized with SMIs having different arm lengths [a]

Run	IE [b] (%)	N_{PS} [c]	t (h)	x_{St} [d] (%)	E:DVB:St [e]	Y_{MSP} [f] (%)	dn/dc [g] (mL/g)	GPC results of MSPs [h]					L_{PS} [j] (kg/mol)
								$M_{n,LS}$ (kg/mol)	PDI_{LS}	$[\eta]_w$ (mL/g)	$R_{g,w}$ (nm)	α [i]	
2	27.5	5.5	0	0	84:16:0	83	0.128	272.4	1.40	15.4		0.135	0.0
			2	1.2	78:15:7	83	0.138	318.3	1.37	15.6		0.135	7.6
			4	2.6	72:13:15	87	0.146	417.8	1.43	19.7	12.9	0.197	25.6
			6	4.3	64:13:23	91	0.154	630.2	1.47	25.5	18.1	0.285	61.7
			8	6.0	60:11:29	93	0.158	927.8	1.48	34.1	26.7	0.356	117.4
4	31.5	6.4	0	0	88:12:0	84	0.120	343.9	1.39	18.4		0.065	0
			2	1.6	82:11:7	83	0.133	390.6	1.32	18.7		0.076	7.3
			4	3.5	75:10:15	87	0.143	518.8	1.41	24.1	13.5	0.199	27.2
			6	4.9	71:10:19	90	0.147	801.8	1.44	30.7	21.2	0.304	71.3
			8	6.4	67:9:24	92	0.152	1260	1.43	40.5	32.7	0.382	142.7
5	37.4	9.0	0	0	92:8:0	83	0.110	475.6	1.38	22.1	10.8	0.017	0
			2	1.8	86:8:6	83	0.124	567.6	1.31	23.0	11.6	0.042	10.2
			4	3.8	80:8:12	86	0.135	819.3	1.33	28.6	17.3	0.183	37.9
			6	6.1	75:7:18	88	0.143	1470	1.32	40.4	31.6	0.334	109.8
			8	Gelled									

[a] Polymerization conditions: SMI2, SMI4 and SMI5 were used for Runs 2, 4, and 5, respectively; $[SMI]_0$ = 2.1 mM; $[SMI]_0:[St]_0:[CuBr]_0:[CuBr_2]_0:[PMDETA]_0$ = 1:2000:12:1.2:13.2; solvent, toluene; temperature, 100 ºC.

[b] Initiation efficiency of the –Br groups in the SMI.

[c] Number-average number of polystyrene arms.

[d] Styrene conversion calculated from the ^{1}H NMR spectrum.

[e] Mole percentage of ethylene, DVB, and styrene in the SMIs and MSPs.

[f] Star yield calculated from area percentage of the MSP to overall polymer sample determined by the GPC.

[g] Average refractive index increment of the MSP.

[h] $M_{n,LS}$, PDI_{LS}, weight-average gyration radius ($R_{g,w}$) data (over 10 nm listed due to the measurement limit of the LS technique), and weight-average intrinsic viscosity ($[\eta]_w$) of the MSPs were determined with the triple-detection GPC. Two low molecular weight peaks for linear polymers were excluded from the overall GPC traces in the calculations.

[i] α is the Mark-Houwink exponent of the MSPs.

[j] Length of PS arm estimated from eq (3).

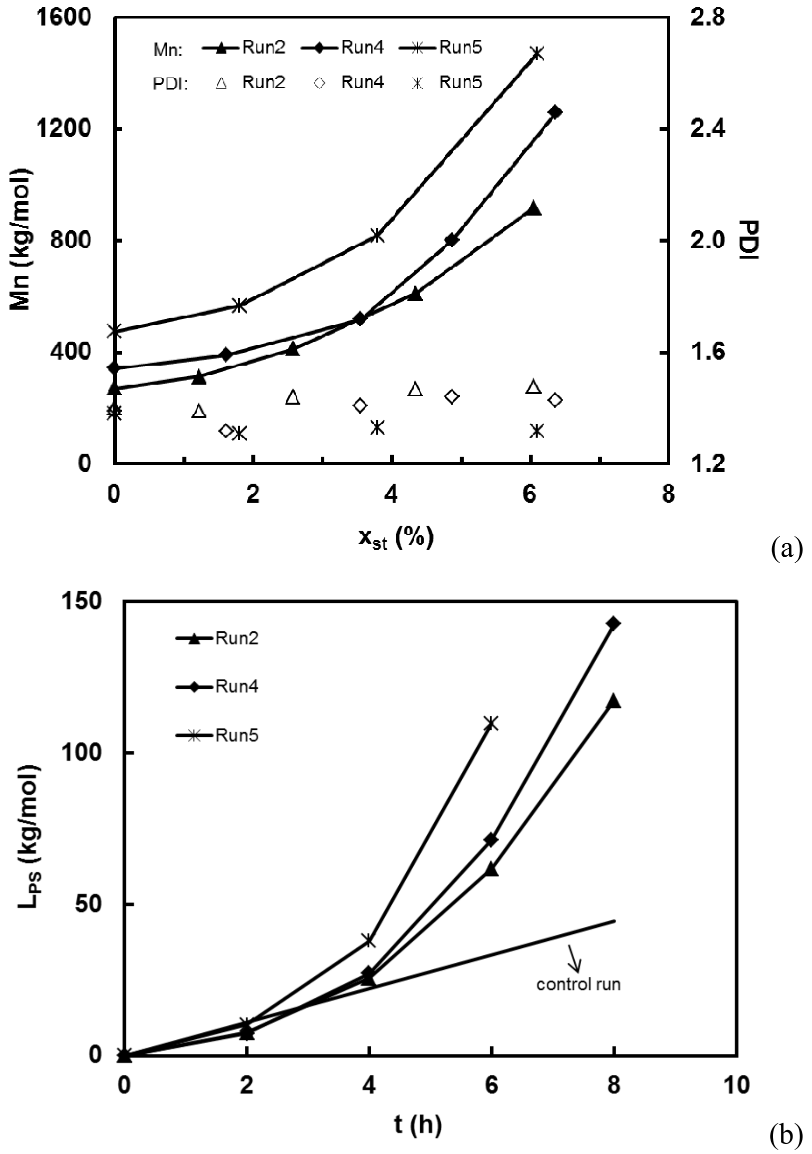


Figure 5. (a) number-average molecular weight (M_n) and polydispersity (PDI) of the miktoarm star polymers (MSPs) with linear polymers excluded versus styrene conversion (x_{St}) and (b) PS arm lengths of the MSPs versus polymerization time in Run 2 (SMI2 as macroinitiator), Run 4 (SMI4), and Run 5 (SMI5). ATRP of styrene was also plotted as a control run.

DLS Study of MSPs in n-Heptane

The DLS measurements were conducted to study the MSPs in n-heptane, which is a good solvent for PE, but a poor solvent for PS. The SMI4, Run 4 after 2 h (Run 4-2h), and Run 4 after 4 h (Run 4-4h) were used as samples. All three samples could be well dispersed in n-heptane (Figure S6 in the Supporting Information). Figure 6 shows the intensity-average sizes increase from 12.1 nm (SMI4 or Run 4-0h) to 90.2 nm (Run 4-2h) to 290.1 nm (Run 4-4h) and the particle size distribution indexes (PD) change slightly from 0.185 (SMI4) to 0.244 (Run 4-2h) to 0.248 (Run 4-4h), suggesting constant growth of PS arms from the SMI to form the MSP and the existence of MSP aggregation in n-heptane. A peak at 106.3 nm in the SMI4 might be also attributed to a small amount of the aggregated SMIs.

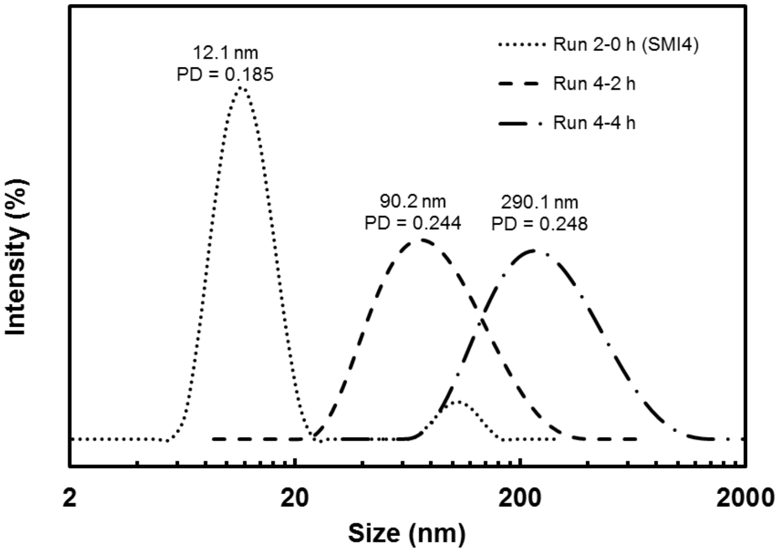


Figure 6. Intensity size distributions of SMI4 (Run 4-0 h), Run 4-2h, and Run 4-4 h in n-heptane at a concentration of 5 mg/mL.

DSC Characterization of MSPs

Figure 7 plots the DSC thermograms for the Run 2 samples collected at different polymerization times. The SMI2 and PE samples were also determined for comparison. It should be pointed out that the change tendency of the DSC thermograms for the MSP samples at different polymerization times was similar for all runs. The glass transition and melting endotherm peaks within –60 ºC to

10 ºC for all MSP samples and SMI2 (N_{PE} =20.0) became very weak in comparison with transitions for the PE arm sample. This indicates poor segmental mobility of the PE arms in the star polymers, attributing to steric crowdedness of the PE arms and their one-end fixation on a crosslinked core.[21] A gradually visible glass transition at approximately 108 ºC attributed to PS can be observed in the Run 2-6 h and Run 2-8 h samples. Apparently, the PS arms in the MSP samples of Run 2-2 h and Run 2-4 h were not long enough and their segmental mobility was still shielded or restrained by the multiple arms. These results further support the findings in the PS arm length constantly increased with polymerization time as shown in Figure 4. In addition, because there were only a few of PS arms (N_{PS} = 5.5) in the miktoarm star, such a small number of PS arms will not sterically hinder each other.

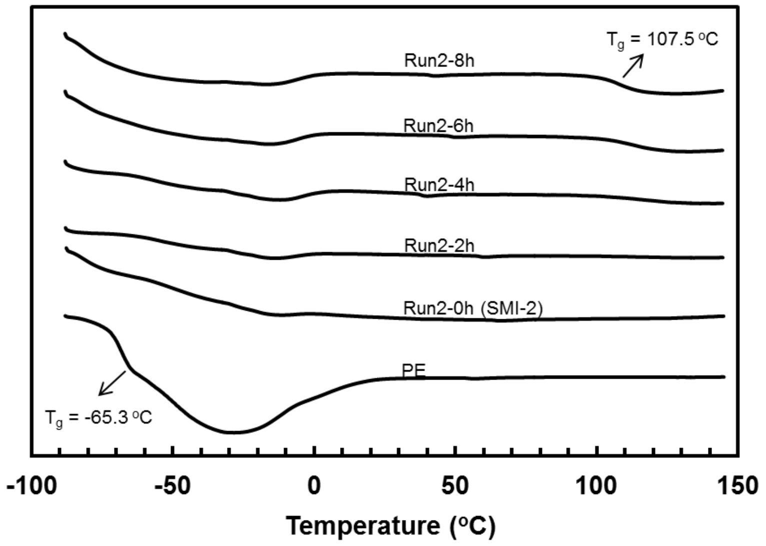


Figure 7. Differential scanning calorimetry (DSC) thermograms of MSP samples at different polymerization times in Run 2 and their PE arm sample.

Dilute Solution Properties and Chain Conformation of MSPs

The weight-average intrinsic viscosity ($[\eta]_w$), weight-average gyration radius ($R_{g,w}$), and Mark-Houwink exponent (α) of the MSPs in their dilute solutions were determined by the triple-detection GPC.[21-23] Note only $R_{g,w}$ values over 10 nm were reported owing to the measurement limitation of the multi-angle LS technique. They were summarized in Tables 2 and 3. Figure 8 gives the Mark-Houwink plots of the MSPs. The intrinsic viscosity curves of linear PEs synthesized with Pd-diimine catalysts **1** at 400 psi and 5 ºC[23] ($[\eta] = 0.0621\ M^{0.61}$ (mL/g)) and linear PSs ($[\eta] = 0.0128\ M^{0.71}$ (mL/g)) were also included for comparison. The $[\eta]_w$ values of corresponding PE and PS arms with theoretical lengths were also plotted in the figure.

Figure 8(a) shows the comparison of the Mark-Houwink plots of all samples in Run 1 (N_{PE} = 11.6 and N_{PS} = 3.7) and Run 3 (N_{PE} = 33.4 and N_{PS} = 6.4) with the same PE arm length. The intrinsic viscosities of all the MSP samples were substantially lower than those of the linear PE or PS arms at the same molecular weights. The $[\eta]_w$ plots of the SMIs (refer to the samples at 0 h) and the samples collected at 2h were overlapped, suggesting that the PS had minor effect on the intrinsic viscosities of the MSPs arms when the incorporation amounts of styrene were low, although the PS possessed a lower $[\eta]_w$ value than the PE. The plots with continuously increasing intrinsic viscosities can be observed in the samples collected after 4 h. The contribution of the PS arms on the intrinsic viscosities became apparent, in particular, for Run 1 samples having lower N_{PE} values and higher N_{PS} to N_{PE} ratios.

The α value is closely related to the polymer chain conformation in the dilute solution. In general, α = 0 for rigid spheres, 0.5 and 0.8 for flexible polymers in Θ solvents and good solvents, respectively.[24] Low α values of 0-0.2 have been reported for multiple-arm star copolymers.[21-22, 25] For example, α = 0.2 for star PEs having 27 arms and arm length of 9.5 kg/mol[22b] and α = 0.17 for star PEs possessing 29.8 arms and arm length of 7.3 kg/mol.[21] The α values less than 0.20 were obtained for the MSP samples of Runs 1-3 collected in 4 h, indicating highly compact spherical chain conformation of these copolymers in the dilution solutions. The α values of the MSP samples collected after 4 h in Run 1-Run 3 increased with the Run 1 samples from 0.182 to 0.363 and Run 3 from 0.171 to 0.271. The MSPs became slightly flexible. This might be attributed to the increment of the PS arm lengths and the star-star coupling reaction. The coupling reactions in Run 1 slightly more intense than Run 3 resulted in a greater increase of the α value.

The Mark-Houwink plots of the MSPs collected at different polymerization times in Run 2 (N_{PS} = 5.6 and $M_{n,PE}$ = 7.3 kg/mol) and Run 5 (N_{PS} = 8.7 and $M_{n,PE}$ = 13.7 kg/mol) with similar N_{PE} but different PE arm length are given in Figure 8(b). The intrinsic viscosities and α values over the polymerization time in these two runs were comparable to those observed in Runs 1 and 3. The Run 5 samples collected before 4 h had higher intrinsic viscosities than the Run 2 samples owing to longer PE arm in Run 5.[21-22] It is interesting to see that the intrinsic viscosity curve of Run 2-8 h overlapped with that of Run 5-6 h although both MSP samples had different PE and PS arm lengths. This might also be attributed to the star-star coupling.

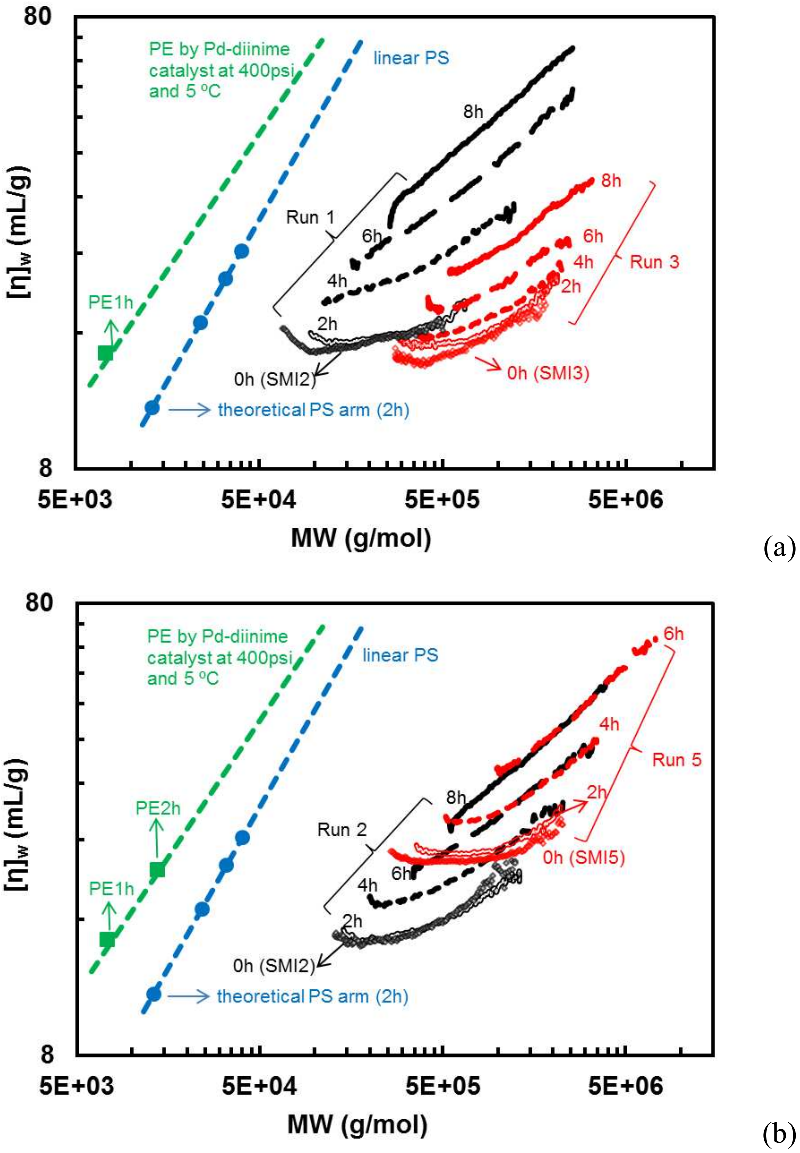


Figure 8. Mark-Houwink plots of MSPs with linear polymers excluded (a) Runs 1 and 3; and (b) Runs 2 and 4. The intrinsic viscosity curves of linear PE ($[\eta] = 0.0621\ M^{0.61}$ (mL/g)) and PS ($[\eta] = 0.0128\ M^{0.71}$ (mL/g)) are included for comparison.

CONCLUSIONS

A range of $(PE)_n$-PDVB-$(PS)_m$ miktoarm star copolymers (MSP) were synthesized with star PEs as a ATRP macroinitiator using the "in-out" strategy. The MSPs had PE arm lengths of 7.3–13.7 kg/mol and arm numbers of 11.6 −33.4, and PS arm lengths of 6.7−32.5 kg/mol and arm numbers of

3.7–9.0. The St propagations in the MSPs using the star PEs as ATRP macroinitiator showed the "livingness" characteristics during the polymerization. The observed initiation efficiencies of –Br groups in the star PEs were 19.0-37.4%. Less PDVB embedment on the –Br groups promoted an increase in the molecular weights of the MSPs when the shielding protection of the PE arms on the PS propagating radicals vanished. Characterization via dynamic light scattering indicated the formation of the MSPs from the SMI during the St polymerization. The DSC measurements suggested segmental mobility of the PS arms in the MSPs was restrained by the presence of multiple arms. The MSPs maintained highly compact chain conformations in their dilute solutions. The star-star couplings resulted in the MSPs having increased $[\eta]_w$ and α values in the dilute solutions.

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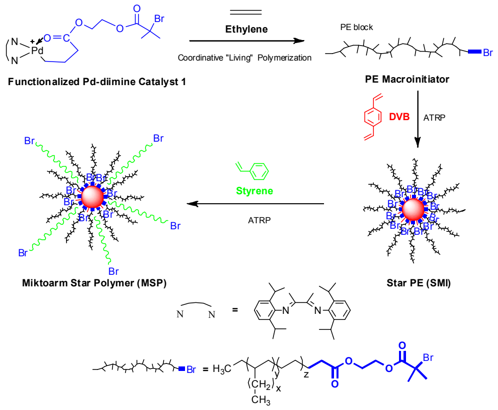
TOC Graphics



TOC Text:

Miktoarm star copolymers having multiple polyethylene and polystyrene arms joined at a crosslinked polydivinylbenzene core were synthesized using an “in-out” strategy with a combined Pd-catalyzed ethylene “living” polymerization and atom transfer radical polymerization.