

SHORT COMMUNICATIONS

“Island-Suspension Bridge” Like Polymer Made from Polymerization of Styrene with Branched Multi-Styryl MacromonomerRen-Hua JIN,[†] Ke FENG, and Chyongjin PAC*Synthetic Chemistry Lab., Kawamura Institute of Chemical Research, 631 Sakado, Sakura-shi, Chiba 285–0078, Japan*

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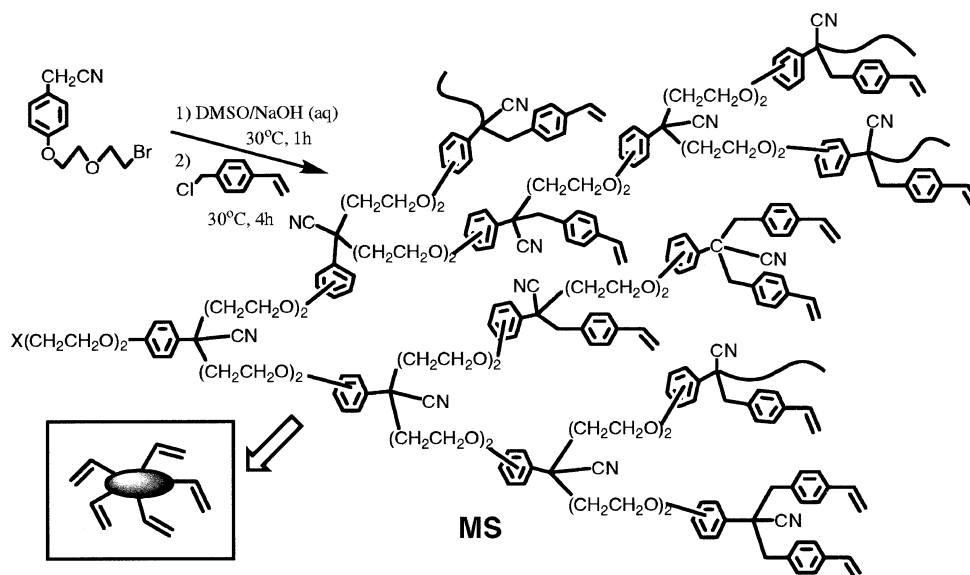
Macromonomers are particularly interesting due to their versatile applicability in architecture of polymeric materials. Comblike polymers,¹ core-shell spheres² as well as block copolymers³ can be conveniently obtained from macromonomers. However, many usual macromonomers are limited in such polymers where only one polymerizable group is attached at one end of linear polymer. Recent progress in synthetic polymers has showed the importance of non-linear polymers such as dendrimers,⁴ hyperbranched polymers,⁵ starlike polymers⁶ and comblike polymers¹ in materials fabrications. Such polymers imply multi-end in their structures. We reported that hyperbranched polymers obtained from the activated methylene AB₂ compounds can be easily turned *in situ* into multi-styryl branched macromonomers by reacting with chloromethylstyrene.⁷ The activated methylene AB₂ monomers can be obtained from derivatives of cyanomethylbenzene having halogenated or tosylated alkyl/alkoxyl on benzene ring.⁸ Along this aspect, we developed a series of AB₂ monomers.⁹ Here, we report application of the multistyryl macromonomer in preparation of soluble branched polystyrene consisted of “island-suspension bridge” like structure.

As shown in Scheme 1, an AB₂ monomer, *p*-(2-bromoethoxy-2-ethoxy)phenylacetonitrile (BEPA), was polymerized in DMSO in the presence of excess alkali (45% NaOH aqueous solution) at room temperature for 90 min. Then, 4 eq of 4-chloromethylstyrene was added and the mixture was stirred furthering at the same temperature for 4 h. After workup and reprecipitation, the multistyryl macromonomer (MS) was obtained by 85% yield. MS was identified by means of ¹H NMR, GPC and Matrix assisted laser desorption ionization–time of flight mass spectrometry (MALDI-TOFMS).^{8b} The content of styrene units determined

from ¹H NMR was 2.46 mmol g⁻¹. MS was soluble in toluene, anisole, chlorobenzene, THF, chloroform, DMF but insoluble in acetone and methanol.

Because of multistyryl character, MS can be reasonably used as a cross-linker for gelation in radical polymerization. A few recent reports described preparation of cross-linked polymeric materials (gels) using multi-styryl dendrimer,¹⁰ multi-methacrylate dendrimer¹¹ and multi-methacrylate inorganic cluster¹² as cross-linkers. However, our purpose here is use of the multi-styryl macromonomer not as cross-linker for gelation but as branching director for architecture of star-bridge-star in radical polymerization. We performed the copolymerization of MS with styrene (St) by atom transfer radical polymerization (ATRP) using 1-bromoethylbenzene (I) and CuBr/bipyridine as initiator and catalyst, respectively. As seen in Table I, firstly, the number-average molecular weights (*M_n*) observed in polymerization of St with very small amount of MS were similar with that in polymerization of styrene only in bulk condition while the weight-average molecular weights (*M_w*) were slightly increased as participation of MS (see Runs 1–3). This is likely the case of the products mixed by homopolymer (polystyrene) and small amount of copolymer (poly(St-co-MS)). We increased the MS amount in copolymerization with styrene for avoiding the formation of homo polystyrene. Under the conditions with the constant feeding ratios of [MS]/([St]+[MS]) = 2.34 mol% (by styryl unit) and of [St]/[I] = 33, it was found that the copolymerization of St with MS were strongly influenced by solvent amount (*i.e.*, weight ratio of toluene to St). When the weight ratio of toluene to St was 0.1, the copolymerization resulted in gelation with partly soluble fractions in short reaction time. As the ratio was 1.5, copolymers without gelation was given with *M_w* = 171 × 10³ and 9.3 polydispersity (Run 5). Fur-

[†]To whom correspondence should be addressed.



Scheme 1.

Table I. Polymerizations of Styrene with and without Multistyryl Macromonomer^a

Run	$\frac{[\text{MS}]}{([\text{MS}]+[\text{St}])}$ mol%	Tol/St w/w	$[\text{St}]/[\text{I}]$	Temp. °C	Time h	Conv ^b %	M_w $\times 10^{-3}$	M_n $\times 10^{-3}$	PD
1	0	0	65	120	17	97	9.7	8.4	1.15
2	0.083	0	65	120	17	96	10.9	8.4	1.30
3	0.248	0	65	120	17	96	15.3	8.98	1.70
4	2.34	0.1	33	100	15	gel			
5	2.34	1.5	33	100	48	98	171	18.4	9.3
6	2.11	1.5	33	100	48	99	98.0	17.0	5.7
7	0	1.5	33	100	48	99	6.2	5.1	1.21
8	2.34	5.0	33	100	66	>95	19.2	8.68	2.22
9	4.03	1.5	33	100	6	54	34.6	7.68	4.5

^a $[\text{I}]/[\text{CuBr}]/[\text{bpy}] = 1:1:3$; I : 0.195 mmol. ^bestimated by ¹H NMR.

ther increase of the amount of toluene (tol/St = 5 in w/w) resulted in decrement of the polydispersities to 2.22 (Run 8). In comparison, the control experiment, where no MS was used in the polymerization of St ($[\text{St}]/[\text{I}] = 33$), yielded polystyrene with $M_w = 6200$ and 1.21 polydispersity (Run 7). Such distinguishable results suggest strongly that the contribution of MS is in enlarging significantly M_w of poly(St-co-MS) even in the lowered ratio of $[\text{St}]/[\text{I}]$. In addition, under constant weight ratio of tol/St at 1.5 and $[\text{St}]/[\text{I}]$ at 33, we increased the ratio of $[\text{MS}]/([\text{St}]+[\text{MS}])$ to 4.03 mol% and found that gelation did not take place until the conversion of styrene was over 50% (Run 9). It is evident that monomer feeding ratio $\{[\text{MS}]/([\text{St}]+[\text{MS}])\}$ and solvents amounts (*i.e.*, MS concentration) strongly influenced whether the polymerization gives soluble polymer or insoluble gel. In the higher feeding ratio in $[\text{MS}]/([\text{St}]+[\text{MS}])$, copolymers with apparently higher molecular weight and wide polydispersity were produced. Also, with adjusting the feeding ratio, we were able to overcome the gelation in the preparation of high

molecular weight polystyrene incorporated with multistyryl macromonomer.

In order to estimate the role of multistyryl macromonomer MS in copolymerization with styrene, we examined the relationship between reaction time, monomer conversion and molecular weight. When St only was polymerized in the ratio of $[\text{St}]/[\text{I}] = 33$ at 120°C for 4 h, 93% of styrene was consumed. The corresponding linear polystyrene showed $M_w = 5000$ and 1.26 polydispersity (see top in Figure 1A). In this homopolymerization, the molecular weight should be defined by ratio of $[\text{St}]/[\text{I}] = 33$ and cannot exceed 10^4 amplitude due to the living character of ATRP. At the same molar ratio of $[\text{St}]/[\text{I}] = 33$, however, the participation of a few amounts of MS (2.34 mol% in styrene residues) offered very different results. Figure 1A showed the GPC traces at different polymerization time. It was obvious that the molecular weight of the propagating polymer formed by 2 h (at which only 25% of styrene was consumed) is largely over the molecular weight of homopolymer obtained by con-

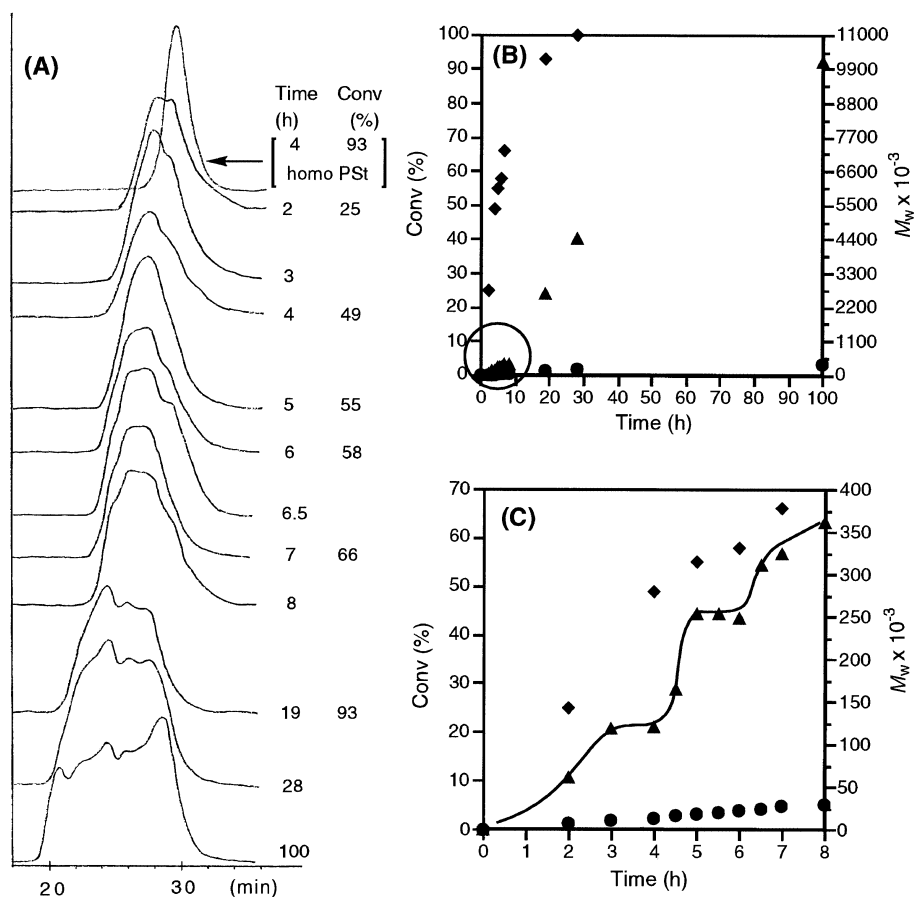


Figure 1. (A) Representation of GPC traces at different reaction time in polymerization of St with MS (exception the upper). Polymerization conditions: $[I]/[CuBr]/[bpy] = 1/1/3$; $[St]/[I] = 33$; I : 0.96 mmol ; MS: 0.30 g; toluene: 6.25 mL; Temp: 100°C. (B) and (C) Relationships of conversions and molecular weights with reaction time. (B) time elongated to 100 h. (C) enlargement of the circled time region from B. \blacklozenge : conversion, \blacktriangle : M_{onset} , \bullet : weight-average molecular weight.

sumption of 93% styrene in the polymerization of St without MS. Then, the GPC trace shifted continuously towards increasing of molecular weight with time elongation. This means that copolymerization of MS with styrene took place in the early state of the reaction to give poly(St-co-MS) and that the species of poly(St-co-MS) propagated continuously to larger copolymer with time. From the plots of conversion and M_w against reaction time (Figure 1C), it can be seen that the M_w increased linearly during 10 h from the start of polymerization. After that, the M_w increased extremely even though St monomer was nearly exhausted (Figure 1B). Especially, we paid attention on the onset of the GPC trace at different reaction time where the propagating polymers will show the greatest molecular weight (M_{onset}). In plot of M_{onset} v.s. the reaction time, it is obvious that M_{onset} increased with stair up fashion (*i.e.*, M_{onset} remained sometimes and then jump up sharply) during 10 h (Figure 1C) and then increased largely with time (Figure 1B). This stair-up phenomenon reflects at least that several propagating polystyrene chains attack on styrene units bound on an MS. Such process is just likely arm-first star formation. This arm-first stars must

induce the living radical ends near on the core and these radical ends will continue its propagating with a way of core-first like star formation due to living radical character of ATRP. Accordingly, it can be said that a few amounts of the multistyryl macromonomer play as a core for formation of stars combining arm-first with core-first in polymerization of styrene.

To prove stars formation *via* arm-first following core-first, we attempted several approaches as shown in Figure 2. The reaction between end-brominated linear polystyrene **1** (which was isolated from polymerization of St with ATRP, Br-content: 12.5 mmol g⁻¹) and MS in the presence of CuBr/bpy yielded the corresponding arm-first type star polymer (**2a**) which showed higher M_w than both reactants of **1** and MS. To the solution of **2a** obtained from reaction of **1** with MS was added 38 eq of St and the mixture was stirred for 72 h at 100°C. The resulting polymer **3** showed M_w higher than **2a**. The molecular weight increments from **1** to **2a** and from **2a** to **3** indicate the procedure of arm-first followed core-first stars formation (see inset GPC trace). In the similar way, to the solution of **2b** was added 38 eq of St and 0.3 eq of MS and the mixture were stirred

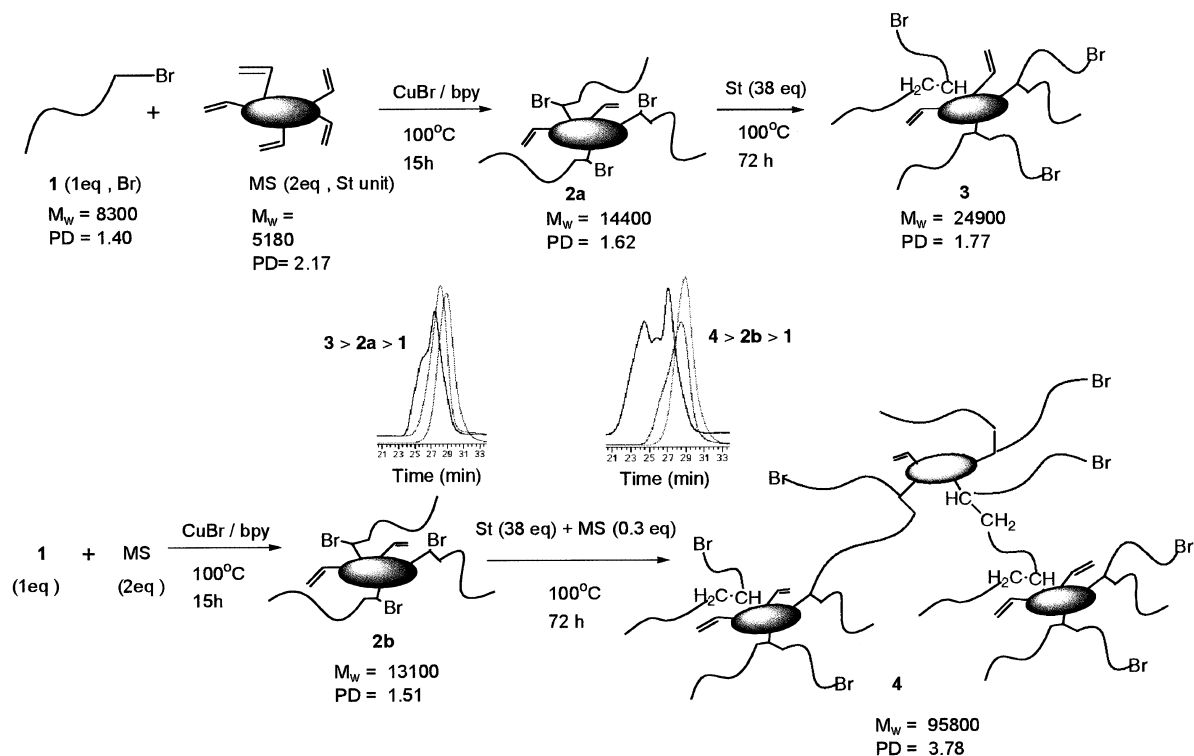
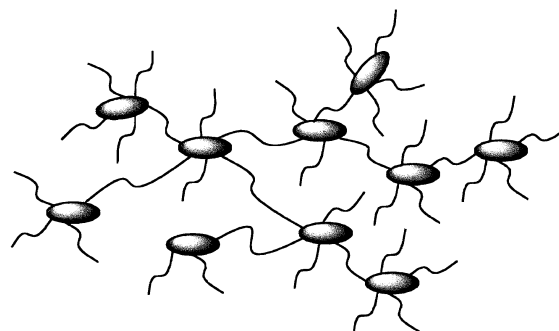


Figure 2. Polymerization with use of end-brominated linear polystyrene **1** as initiator *via* arm-first and then core-first procedures. **1**: 0.10 g; CuBr: 0.03 mmol; bpy: 0.09 mmol. Inset: GPC traces for polymers from **1** to **2a** to **3** and for polymers from **1** to **2b** to **4**.

for 72 h at 100°C. This reaction produced polymer **4** with significantly increased molecular weight and the GPC trace of **4** became multimodal (inset in Figure 2). In this route, evidently, a few amounts of MS, which was added to the core-first polymerization of St, participated the core-first propagating reaction. The fact that molecular weight of **4** is larger than that of **3** suggests that bridges formed between stars. In absence of St, however, it was found that addition of MS (without St) to the solution of **2** did not give any changes of molecular weight. This means at least that MS is not reactive to the star polymer **2**. The reason would be due to steric hindrance, *i.e.*, MS hardly accesses to the active ends of the brominated groups on **2** because the brominated groups are enclosed in core of the star polymer.

Based above results, it can be concluded that arm-first star polymers possessing active-end (Br⁻) on the cores induce core-first procedure to form a new arms with polymerizing styrene monomer. The active ends (Br⁻) of the new arms propagated in the core-first procedure react again to the styryl moieties on MS forming links between the star polymer and MS. The links formation is just likely the second arm-first procedure. Such circulation by arm-first/core-first/arm-first might be a reason to induce jump-up of molecular weight (M_{onset}) in the copolymerization of styrene with MS. Consequently, many of polystyrene bridges would be suspended between MS moieties to form “island-suspension bridge” like structure in the result-



Scheme 2. Image of “Island-Suspension Bridge”.

ing copolymer (Scheme 2). Although we cannot exclude the possibility that a few unreacted styryl units bound on MS remain in “island-suspension bridge” like structure, we consider that the styryl units would be exhausted with elongation of reaction time as likely as the trend appeared in Figure 1.

Our work described here provided an example of application of hyperbranched multistyryl macromonomer in improvement of traditional linear polystyrene. In this application, a few amounts of the multistyryl macromonomer can act as a director of star-like branching but not as a cross-linker for gelation. In our preliminary experimental, we found that the T_g of the star-branched polystyrene obtained by copolymerization of styrene with MS was lower (95°C) than that of traditional linear polystyrene (102°C). Thus, we expect that the method provided here would be very helpful in

the preparation of highly branched polymeric materials with novel performance property.

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