Living Coupling Reaction in Living Cationic Polymerization. 2. Synthesis and Characterization of Amphiphilic A_2B_2 Star−Block Copolymer: Poly[bis(isobutylene)-*star*-bis(methyl vinyl ether)]

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ABSTRACT: Amphiphilic A_2B_2 star−block copolymers (A = polyisobutylene (PIB) and B = poly(methyl vinyl ether) (PMeVE)) have been prepared via the living coupling reaction of living PIB, using 2,2-bis-[4-(1-tolylethenyl)phenyl]propane (BDTEP) as a living coupling agent, followed by the chain ramification reaction of methyl vinyl ether (MeVE) at the junction of the living coupled PIB. Model reactions for the synthesis of A_2B_2 star−block copolymers indicated that the fine-tuning of Lewis acidity to the reactivity of MeVE is a crucial step for the structural integrity of the resulting A_2B_2 star−block copolymers. Side products were negligible using a $[Ti(OEt)_4]/[TiCl_4]$ ratio of 0.7 and the minimum tuning time (∼5 min). Fractionation of the crude A_2B_2 star−block copolymer was carried out on a silica gel column, and on the basis of the weights of fractions, the purity of the crude A_2B_2 star−block copolymer was calculated to be ≥93.5%. Two T_gs (−60 °C for PIB and −20 °C for PMeVE) were observed for the star−block copolymer by DSC indicating the presence of two microphases. An A_2B_2 star−block copolymer with 80 wt % PMeVE composition ($(IB_{45})_2$-*s*-$(MeVE_{170})_2$) exhibited a critical micelle concentration (cmc) of 4.25×10^{-4} M in water, which is an order of magnitude higher than cmcs obtained with linear diblock copolymers with same total M_n and composition (IB_{90}-*b*-$MeVE_{340}$) or with same segmental lengths (IB_{45}-*b*-$MeVE_{170}$). This suggests that block copolymers with star architectures exhibit less tendency to micellization than their corresponding linear diblock copolymers. Average particle sizes in aqueous solution above the cmc were measured to be from 41 to 177 nm, depending on the architecture and/or the molecular weight.

Introduction

There has been growing interest on the design and construction of nonlinear block architectures, such as star polymers, as evidenced by the abundance of review articles and monographs in recent years.[1−7] The term "star polymers" is used to specify macromolecular architectures where at least three or more linear polymeric chains are connected at the same junction irradiating outward. The prototype of these would be A_n-type star polymers where *A* represents the polymeric chain and the subscript, *n*, represents its number. A_3- or A_4-type star polymers have been prepared by the living cationic polymerization using two different methods: (1) via multifunctional initiators and (2) via linking reactions of living polymeric chains. The first has been the most unique and versatile method due to the affluence of tri- or tetrafunctional initiators for a variety of monomers.[2,6] Recently, this method has been extended to the preparation of A_8-type star polyisobutylenes by Kennedy et al.[8]

Synthesis of star polymers by a living anionic process involves mostly the second method, due to the lack of multifunctional initiators.[9] This approach was first introduced by Morton et al.[10] in 1962 for the preparation of A_3- and A_4-type star polystyrenes, using chlorosilane compounds as linking agents. Henceforth, the linking reaction of living anionic polymers with chlorosilane compounds has been the most rigorous method for the preparation of A_n-type star polymers. However, inevitable post-fractionation and a relatively long reaction time have been some of the shortcomings in this approach.[11]

Incorporation of different homopolymer segments into star architectures distinguishes "star−block" copolymers from star polymers. $(AB)_3$- or $(AB)_4$-type star−block copolymers have been prepared by a living cationic process either using multifunctional initiators[12,13] or by linking reactions.[14,15] Recently, Sawamoto et al. introduced cationic linking agents which are effective for living poly(vinyl ethers), and prepared $(AB)_3$-,[14] or $(AB)_4$-type[15] star−block copolymers. Some drawbacks of this coupling method appear to be the inapplicability to block copolymers with high molecular weights and large difference in the reactivities of linking agents depending on the structure of living ends.

Star−block copolymers with compositionally different arms (A_nB_n- or ABC-type) have been prepared exclusively by living anionic polymerization techniques to date. However, using the conventional chlorosilane approach, the synthesis of star−block copolymers in this category has long been a challenge, most likely due to difficulties in controlling the degree of linking reaction. This was first circumvented by Quirk et al. when they introduced a novel concept of the living coupling reaction as a unique pathway to the synthesis of A_2B_2-type star−block copolymers.[16] They prepared A_2B_2-type star−block copolymers, where A is polystyrene and B is polyisoprene or polybutadiene, via living coupling reactions of living poly(styryl)lithium with 1,3-bis(1-phenylethenyl)benzene (or meta-double diphenylethylene, MDDPE) (Chart 1) followed by sequential monomer addition to the living coupled product.[16−19] Shortly after this work, Mays succeeded in the synthesis of A_2B-type star−block copolymers using methylchlorosilane as a coupling agent.[20] A similar technique has recently been extended to the preparation of ABC-,[21] ABCD-,[22] and A_2B_2-type[22−24] star−block copolymers by Hadjichristidis et al. Numerous examples of star−block copolymers

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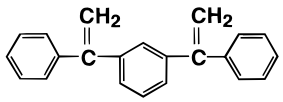
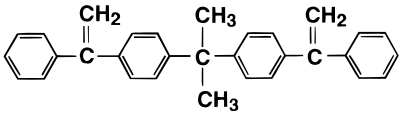
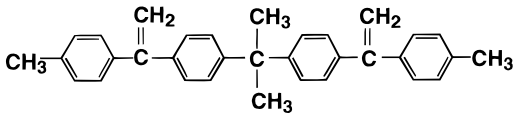
Chart 1



MDDPE



BDPEP



BDTEP

synthesized using chlorosilane compounds have been well delineated in a recent review article by Tselikas et al.[4]

In the first paper of this series,[25] we reported the coupling reaction of living polyisobutylene (PIB) using bis(diarylethenyl) compounds, such as 2,2-bis[4-(1-phenylethenyl) phenyl]propane (BDPEP) or 2,2-bis[4-(1-tolylethenyl)phenyl]propane (BDTEP), as coupling agents (Chart 1). It was demonstrated that living PIB reacts quantitatively with these coupling agents to yield stoichiometric amounts of bis(diarylalkylcarbenium) ions, which was further confirmed by the quantitative formation of diarylmethoxy functionalities at the junction of the coupled PIB. Since the resulting stable and fully ionized diarylalkylcarbenium ions have successfully been employed for the controlled initiation of second monomers such as *p*-methylstyrene, α-methylstyrene, isobutyl vinyl ether, and methyl vinyl ether, it was proposed that this living coupling reaction of living PIB can be a viable pathway to the synthesis of PIB-based A_2B_2 star−block copolymers. In this paper, we report the first example of amphiphilic A_2B_2 star−block copolymers, where A is PIB and B is poly(methyl vinyl ether) (PMeVE), by a living cationic process involving the living coupling reaction of living PIB followed by the chain ramification reaction of methyl vinyl ether (MeVE) at the junction of the living coupled PIB. Since a linear diblock copolymer with 80 wt % PMeVE composition (IB_{90}-*b*-$MeVE_{340}$) has already been prepared and characterized,[26] an A_2B_2 star−block copolymer with same total M_n and composition ((IB_{45})$_2$-*s*-($MeVE_{170}$)$_2$) was planned in this study. A linear diblock copolymer with the same segmental lengths (IB_{45}-*b*-$MeVE_{170}$) as the star−block copolymer was also prepared to complete studies in the architecture/property relationships.

Experimental Section

Materials. 2,2-bis[4-(1-tolylethenyl)phenyl]propane (BDTEP) was synthesized according to the procedure reported previously.[27] Methyl vinyl ether (MeVE, 98% from Aldrich) was purified by passing the gaseous monomer through a calcium hydride column and condensed at −80 °C. All other chemicals and solvents were purified as described previously[25−27] or used as received.

Procedures. Polymerizations were carried out either in 75 mL test tubes or in a 500 mL three-neck flask under a dry ([H_2O] < 1.0 ppm) nitrogen atmosphere in an MBraun 150-M glovebox (Innovative Technology Inc.). Model reactions for the synthesis of A_2B_2 star−block copolymers were carried out using a difunctional initiator which closely models the living coupled PIB. This difunctional initiator was prepared by the coupling reaction of 2 equiv of 2-chloro-2,4,4-trimethylpentane ((TMP)-Cl) with BDTEP in hexane (Hex)/methylene chloride (CH_2Cl_2) (40/60, v/v) solvent mixture at −80 °C in the presence of $TiCl_4$ and a proton trap, 2,6-di-*tert*-butylpyridine (DTBP). After a 90 min coupling reaction, the Lewis acidity was moderated to the reactivity of MeVE by the addition of titanium (IV) ethoxide ($Ti(OEt)_4$). In this way, a weaker Lewis acid, $TiCl_n(OEt)_{4-n}$, is formed, where n (<4) is manipulated by stoichiometry; thereby a more nucleophilic counterion is generated which is necessary for the living polymerization of MeVE.[26] After 5−15 min, MeVE was introduced to the coupled (TMP)Cl with BDTEP ((TMP)$_2$BDTEP) at −80 °C. After 10 min, the temperature was raised to 0 °C to accelerate MeVE polymerization.

The synthesis of A_2B_2 star−block copolymers was carried out in three steps. In the first step, living PIB was prepared by the (TMP)Cl/$TiCl_4$/-80 °C system using a Hex/CH_2Cl_2 (50/50, v/v) solvent mixture in the presence of DTBP. At ∼100% conversion of IB (30 min), the coupling reaction of living PIB was carried out by adding a stoichiometric amount of BDTEP dissolved in CH_2Cl_2 to the reactor, and concurrently the solvent polarity was increased to 40/60 (v/v) Hex/CH_2Cl_2. Upon addition of BDTEP solution, the characteristic dark red color of diarylalkylcarbenium ions developed instantaneously. Finally, after the Lewis acidity tuning, the chain ramification reaction of MeVE at the junction of the living coupled PIB was commenced by the addition of MeVE. At predetermined time intervals, the reaction mixtures were quenched with prechilled methanol and then poured into excess 10% ammoniacal methanol.

The terminated polymer solution was allowed to stand overnight under the hood and the remaining products were dried in vacuo for 24 h. The products were dissolved in CH_2Cl_2 and the solution was filtered to remove inorganic salts. Further purification was carried out by passing the prefiltered solution through a silica gel column.

Characterization. Molecular weights were measured using a Waters HPLC system equipped with a model 510 HPLC pump, model 410 differential refractometer, model 441 absorbance detector, on-line multiangle laser light scattering (MALLS) detector (MiniDawn, Wyatt Technology Inc.), model 712 sample processor, and five Ultrastyragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. THF was used as a carrier solvent in a flow rate of 1 mL/min. The detector signals were simultaneously recorded on a Macintosh computer for the absolute molecular weight and molecular weight distribution determination by MALLS using ASTRA software (Wyatt Technology Inc.). Refractive index increments (dn/dc) of star−block copolymers were calculated from the individual dn/dc of PIB and PMeVE and their relative compositions determined by ^{1}H NMR spectroscopy.

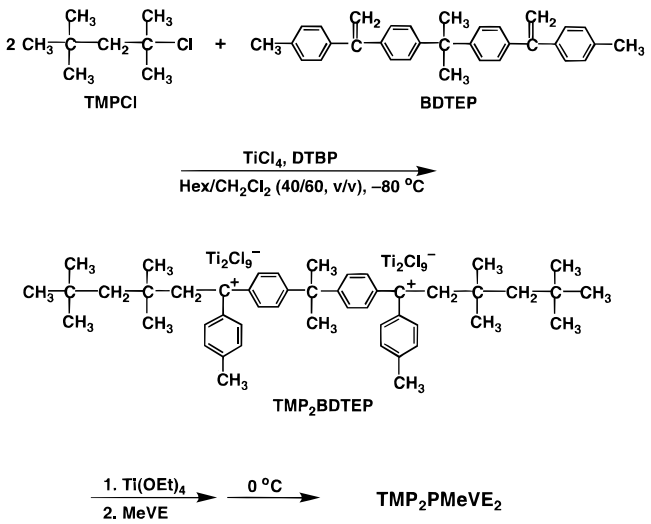
Fractionation of an amphiphilic A_2B_2 star−block copolymer was carried out using column chromatography according to the procedure reported by Pernecker and Kennedy.[28]

^{1}H NMR spectroscopy for structural analysis was carried out on a Bruker 250 MHz spectrometer using $CDCl_3$ (Cambridge Isotope Laboratories, Inc.) as a solvent.

The glass transition temperatures (T_g) of A_2B_2 star−block and linear diblock copolymers were determined using a DuPont 910 differential scanning calorimeter at a scan rate of 20 °C/min in a nitrogen atmosphere. Samples were cooled slowly at 2.5 °C/min after first scans and T_g values were taken on second scans.

Surface tension measurements were carried out on a SensaDyne 6000 surface tensiometer (Chem-Dyne Research Co.) using the maximum bubble pressure method, and nitrogen was used as an inert gas at a bubble rate of 1/s. Data were collected on a personal computer using SensaDyne 6000 software program (Chem-Dyne Research Co.). The critical micelle concentration (cmc) was determined by plotting surface tension vs concentration.

Scheme 1



Average particle sizes of linear and star−block copolymers were measured in aqueous solution above cmc in terms of the mean diameter of the volume distribution by laser light scattering (an ultrafine particle analyzer, Microtrac, Leeds and Northrup).

Results and Discussion

Model Reaction for the Synthesis of A_2B_2 Star−Block Copolymer. To find optimum conditions for the synthesis of A_2B_2 star−block copolymers, MeVE polymerization was studied using a difunctional initiator which mimics the living coupled PIB. This difunctional initiator was prepared by the coupling reaction of (TMP)Cl with BDTEP, as shown in Scheme 1. Since, with IB units ≥2, there is no significant difference in reactivities of polyisobutenyldiphenylcarbenium ions toward nucleophiles,[29] the coupled (TMP)Cl with BDTEP ($(TMP)_2$BDTEP) would have a reactivity very similar to that of the living coupled PIB. For the living polymerization of MeVE using difunctional diarylalkylcarbenium ions, experimental conditions which were found to be successful for the living polymerization of MeVE involving monofunctional diarylalkylcarbenium ions[26] were employed.

In the first series of experiments, the ratio of [Ti$(OEt)_4$]/[$TiCl_4$] was varied from 0.3 to 1.4 in order to find suitable nucleophilic counterions for MeVE polymerization. This tuning of Lewis acidity was found necessary for the living polymerization of MeVE and to effectively decrease the extent of complexation between Lewis acid and PMeVE, which significantly affects conversions of MeVE polymerization.[26,30] After 15 min, MeVE was added to $(TMP)_2$BDTEP and temperature was raised to 0 °C, by placing the reactors in an ice bath, to accelerate the MeVE polymerization. The results in the MeVE polymerization with various ratios of [Ti$(OEt)_4$]/[$TiCl_4$] are summarized in Figure 1. Using [Ti$(OEt)_4$]/[$TiCl_4$] ratios of 0.3−0.6, the reaction mixtures became cloudy with yellow precipitates upon MeVE addition at −80 °C. These yellow precipitates turned to brownish violet at 0 °C. After being quenched with prechilled methanol and purification, the products exhibited an orange yellow color. The observed discoloration during the polymerization can be attributed to the termination reaction via β-proton elimination followed by dealcoholation due to relatively weak nucleophilicity of the resulting counterions.[30,31] A conjugated

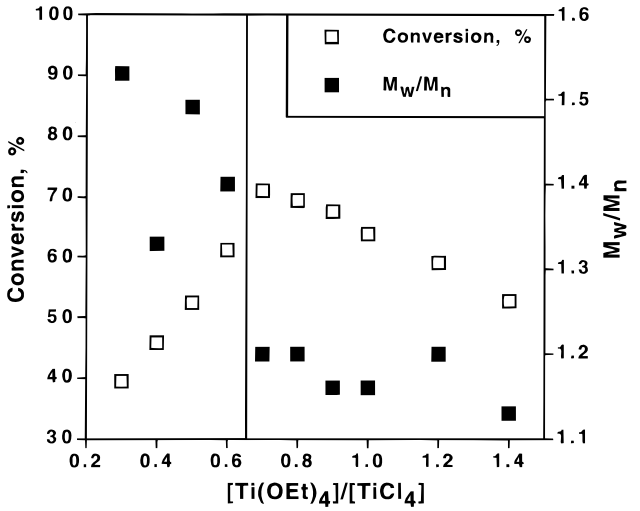


Figure 1. Conversion or M_w/M_n vs [Ti$(OEt)_4$]/[$TiCl_4$] plot in the polymerization of MeVE. Polymerization conditions: [(TMP)-Cl] = 0.004 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.003 M, [BDTEP] = 0.002 M, and [MeVE] = 0.7 M in Hex/CH_2Cl_2 (40/60, v/v) at 0 °C for 7 h.

diene structure (δ = 5.3−6.2 ppm) from ^{1}H NMR spectra of the products further confirmed that termination is operational with relatively strong Lewis acid and this termination process occurs via β-proton elimination followed by dealcoholation. GPC traces of the products exhibited broad and multimodal distribution. On the basis of conversion data, it is concluded that termination via dealcoholation is more significant with lower [Ti$(OEt)_4$]/[$TiCl_4$] ratios, i.e., with less nucleophilic counterions.

Using higher ratios of [Ti$(OEt)_4$]/[$TiCl_4$] (≥0.7), the reaction mixtures exhibited transparent and straw yellow color, if any, without precipitates and this color disappeared when quenched with prechilled methanol. With a [Ti$(OEt)_4$]/[$TiCl_4$] ratio of 0.7, the highest conversion and relatively high number-average molecular weight (M_n) were obtained. Above this ratio, the conversion decreased with increasing [Ti$(OEt)_4$]/[$TiCl_4$] ratio. This indicates that there exists an optimum ratio of [Ti$(OEt)_4$]/[$TiCl_4$] which provides a fast polymerization rate without inducing chain-breaking reactions. This observation is consistent with previous results obtained in the α-methylstyrene polymerization using diphenylalkylcarbenium ion as an initiator and $TiCl_n(OR)_{4-n}$ as a co-initiator where R is ethyl, isopropyl, or butyl.[32] The absence of termination via β-proton elimination was confirmed by the absence of conjugated diene structures from ^{1}H NMR spectra of the products. While molecular weight distributions (M_w/M_n) of PMeVEs obtained with these ratios were relatively low (<1.2), GPC traces exhibited bimodal distributions with small tail at higher elution volume.

It was postulated that this bimodal distribution might have resulted from the abrupt increase in temperature which may accelerate the propagation rate relative to the crossover or initiation rate. To increase the crossover rate relative to the propagation rate, after 15 min of Lewis acidity tuning at −80 °C followed by MeVE addition, the temperature was slowly raised to 0 °C over a period of 30 min. Using three ratios of [Ti$(OEt)_4$]/[$TiCl_4$] (=0.7, 1.0, and 1.4), MeVE polymerization and its kinetics were studied. Even when the temperature was slowly raised to 0 °C, similar results were obtained; M_w/M_ns of PMeVEs were relatively low (<1.2) but GPC

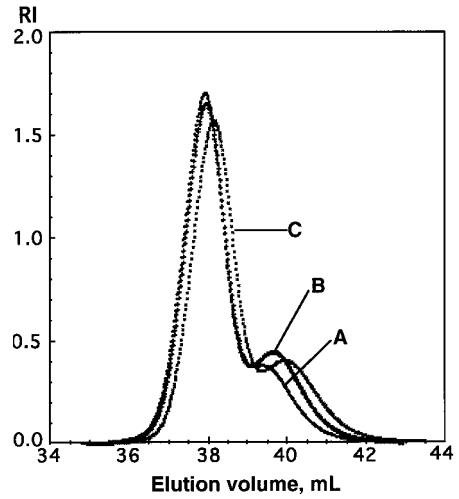


Figure 2. GPC traces of PMeVEs obtained with $[Ti(OEt)_4]/[TiCl_4] = 0.7$ (A), 1.0 (B), or 1.4 (C). Polymerization conditions: $[(TMP)Cl] = 0.004$ M, $[TiCl_4] = 0.036$ M, $[DTBP] = 0.003$ M, $[BDTEP] = 0.002$ M, and $[MeVE] = 0.7$ M in Hex/CH_2Cl_2 (40/60, v/v) at 0 °C for 15 h.

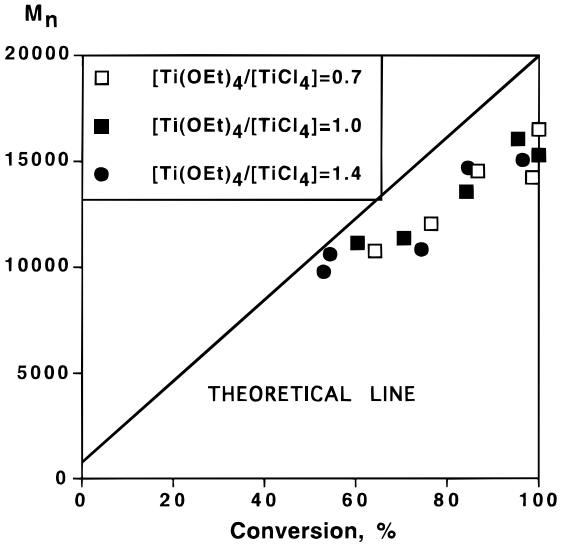


Figure 3. M_n vs conversion plot in the MeVE polymerization. Polymerization conditions: same as in Figure 2.

traces still exhibited bimodal distributions as can be seen in Figure 2. $\ln([M]_o/[M])$ vs time plots exhibited sinuous patterns due to the change in the polymerization rates resulting from the temperature increase in the beginning of the polymerization. As shown in Figure 3, lower than theoretical M_ns were obtained in all three cases. These results strongly suggest there exists initiating species other than $(TMP)_2BDTEP$ under these experimental conditions. Since bimodal distribution is more significant when the ratio of $[Ti(OEt)_4]/[TiCl_4]$ is increased, the decoupling of (TMP)Cl seemed to occur during the Lewis acidity tuning and a monofunctional initiator associated with decoupling reaction might be responsible for the observed bimodal distribution.

It has been reported that capping reactions of living PIB with diarylethylenes are equilibrium reactions which are sensitive to temperature, solvent polarity, Lewis acidity and electron-donating ability of *para*-substituents.[33] Since a stronger Lewis acid is more favorable to move this equilibrium toward the capped product, minimum amounts of $Ti(OEt)_4$ seemed necessary during the Lewis acidity tuning to prevent the possible decoupling reaction. In the meantime, it was also found that the reaction of $Ti(OEt)_4$ with $TiCl_4$ is instantaneous; i.e., the Lewis acidity tuning occurs instantaneously.[34] In this regard, the time interval between the Lewis acidity tuning and the addition of MeVE should be short to avoid the possible decoupling reaction. In the next sets of experiments, a $[Ti(OEt)_4]/[TiCl_4]$ ratio of 0.7 was used and less than 5 min, instead of 15 min reaction time, was allowed before MeVE addition. Using these experimental conditions, as shown in Figure 4, linear and theoretical growth of M_ns with increased conversion was obtained indicating the absence of polymerization by initiating species other than $(TMP)_2BDTEP$. GPC traces of PMeVEs exhibited monomodal and narrow distributions ($M_w/M_n \sim 1.1$) as shown in Figure 5, and M_w/M_ns decreased with increased conversions as often observed in cationic polymerizations.

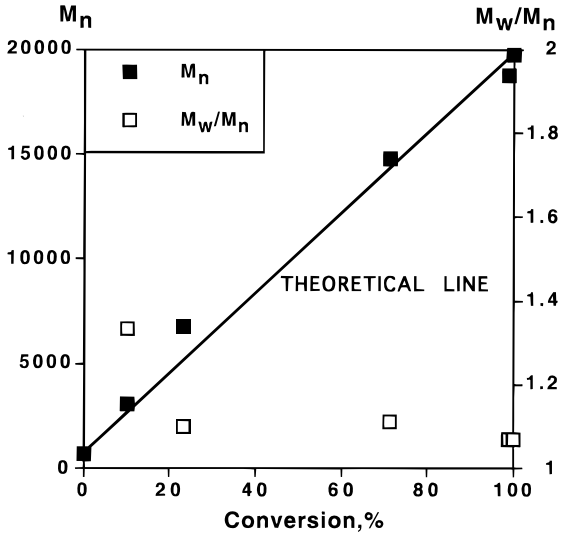


Figure 4. M_n vs conversion plot in the MeVE polymerization with $[Ti(OEt)_4]/[TiCl_4] = 0.7$. Polymerization conditions: $[(TMP)Cl] = 0.004$ M, $[TiCl_4] = 0.036$ M, $[DTBP] = 0.003$ M, $[BDTEP] = 0.002$ M, and $[MeVE] = 0.7$ M in Hex/CH_2Cl_2 (40/60, v/v) at 0 °C. Temperature was raised to 0 °C over a period of 30 min after ~5 min of the Lewis acidity tuning followed by MeVE addition at −80 °C.

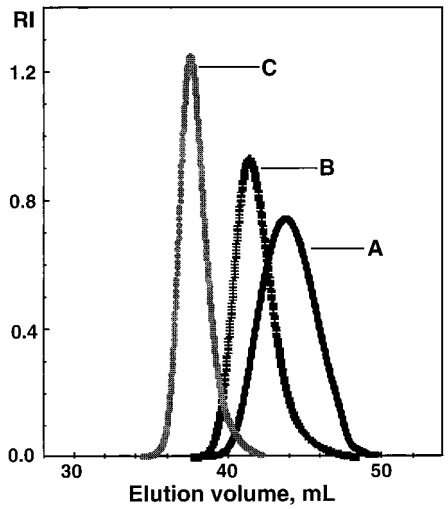


Figure 5. GPC traces of PMeVEs obtained with $[Ti(OEt)_4]/[TiCl_4] = 0.7$ (A, $M_n = 3100$ and $M_w/M_n = 1.33$ after 1 h; B, $M_n = 6700$ and $M_w/M_n = 1.10$ after 1.5 h; C, $M_n = 19\,800$ and $M_w/M_n = 1.07$ after 15 h).

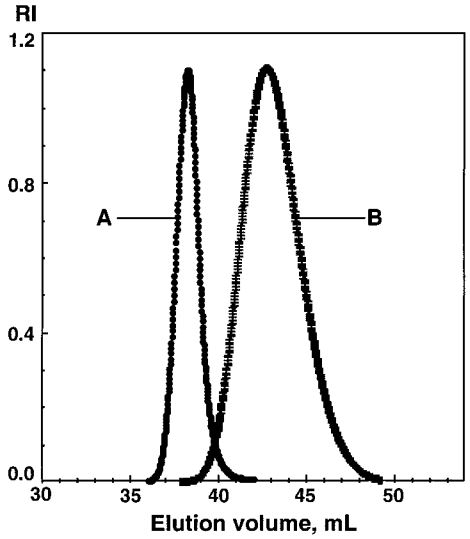


Figure 6. GPC traces of IB_{45}-*b*-$MeVE_{170}$ (A) with $M_n = 1.3 \times 10^4$ and $M_w/M_n = 1.05$ and its precursor PIB homopolymer (B) with $M_n = 2.5 \times 10^3$ and $M_w/M_n = 1.25$.

Synthesis of AB Linear Diblock or A_2B_2 Star−Block Copolymers. The significant effect of tuning time on the crossover reaction was also observed when the synthesis of a PIB-*b*-PMeVE diblock copolymer (IB_{45}-*b*-$MeVE_{170}$), which has same segmental lengths as the planned star−block copolymer (($(IB_{45})_2$-*s*-$(MeVE_{170})_2$), was carried out in conditions similar to those previously reported except for the tuning time (5 min instead of 15 min). Figure 6 shows GPC traces of the original PIB and a PIB-*b*-PMeVE diblock copolymer. Using a 5 min tuning time, tailing at a higher elution volume was completely absent from the GPC trace of IB_{45}-*b*-$MeVE_{170}$, indicating the crossover is virtually quantitative under given conditions. Therefore, it is concluded that the fine-tuning of Lewis acidity is a crucial step for the structural integrity of the resulting A_2B_2 star−block or AB diblock copolymers.

On the basis of results in the model reaction, the synthesis of A_2B_2 star−block copolymers with 80 wt % PMeVE composition (($(IB_{45})_2$-*s*-$(MeVE_{170})_2$), which is expected to be water-soluble,[26] was carried out in three steps as shown in Scheme 2. In the first step, living PIB was prepared in Hex/CH_2Cl_2 (50/50, v/v) solvent mixture. After ~100% conversion of IB, the coupling reaction of living PIB was carried out by adding a stoichiometric amount of BDTEP dissolved in CH_2Cl_2 to the reactor containing living PIB, and concurrently the solvent polarity was increased to 40/60 (v/v) Hex/CH_2Cl_2. Finally, the chain ramification reaction of MeVE at the junction of the living coupled PIB was commenced by the addition of MeVE after the Lewis acidity tuning. Aliquots of the reaction mixture were withdrawn from the reactor and quenched with prechilled methanol. GPC traces of a crude A_2B_2 star−block copolymer and its precursors are shown in Figure 7, and a summary of characterization is given in Table 1. The coupled PIB (B in Figure 7) exhibited doubled M_n and lower M_w/M_n than the original PIB (A in Figure 7) indicating a quantitative coupling reaction of living PIB by BDTEP as demonstrated previously.[25] While the GPC trace of an A_2B_2 star−block copolymer (C in Figure 7) exhibits negligible but detectable tailing at higher elution volume, both a nearly monomodal distribution and close to theoretical M_n ($M_{n,th} = 25\,000$) of the crude product prove that the living coupling

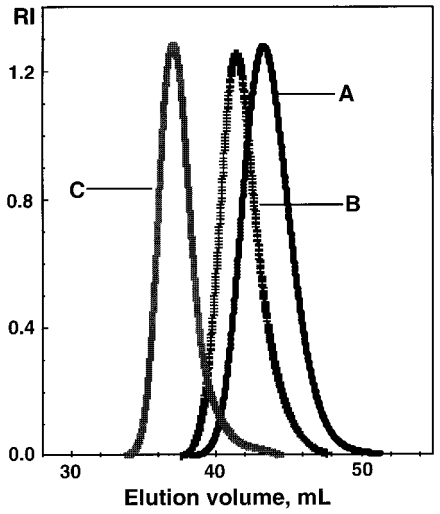


Figure 7. GPC traces of the original PIB (A), the coupled PIB (B), and an A_2B_2 star−block copolymer (C). IB polymerization conditions: [(TMP)Cl] = 0.004 M, [$TiCl_4$] = 0.036 M, [DTBP] = 0.004 M, [IB] = 0.17 M in Hex/CH_2Cl_2 (50/50, v/v) at −80 °C for 30 min. Coupling reaction conditions: [(TMP)Cl]/[BDTEP] = 2 in Hex/CH_2Cl_2 (40/60, v/v) at −80 °C for 90 min. MeVE polymerization conditions: [MeVE]/[(TMP)Cl] = 175 and [$Ti(OEt)_4$]/[$TiCl_4$] = 0.7 at 0 °C for 15 h.

Scheme 2

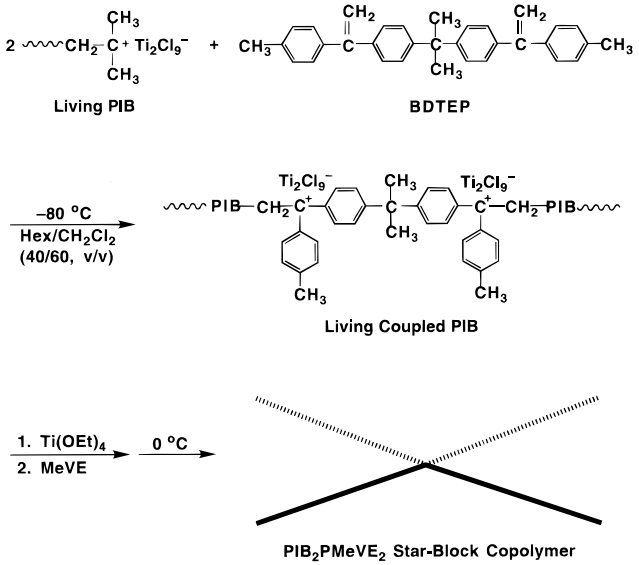


Table 1. GPC Results of an A_2B_2 Star−Block Copolymer and Its Precursors

sample	$10^{-3}M_n$	M_w/M_n
original PIB (A)	2.5	1.24
coupled PIB (A_2)	5.7	1.14
PIB_2PMeVE_2 (A_2B_2)[a]	22.6	1.19
PIB_2PMeVE_2 (A_2B_2)[b]	25.3	1.12

[a] Before fractionation. [b] After fractionation.

reaction, by a living cationic process, is a powerful tool for the synthesis of A_2B_2-type star−block copolymers.

For the structural analysis using ^1H NMR spectroscopy, an A_2B_2 star−block copolymer with low segmental M_ns ($M_{n,PIB} = 2500$ and $M_{n,PMeVE} = 3400$) was also prepared. Figure 8 shows ^1H NMR spectrum of an A_2B_2 star−block copolymer with low segmental M_ns. Almost quantitative coupling reaction of living PIB as well as chain ramification reaction of MeVE was confirmed by

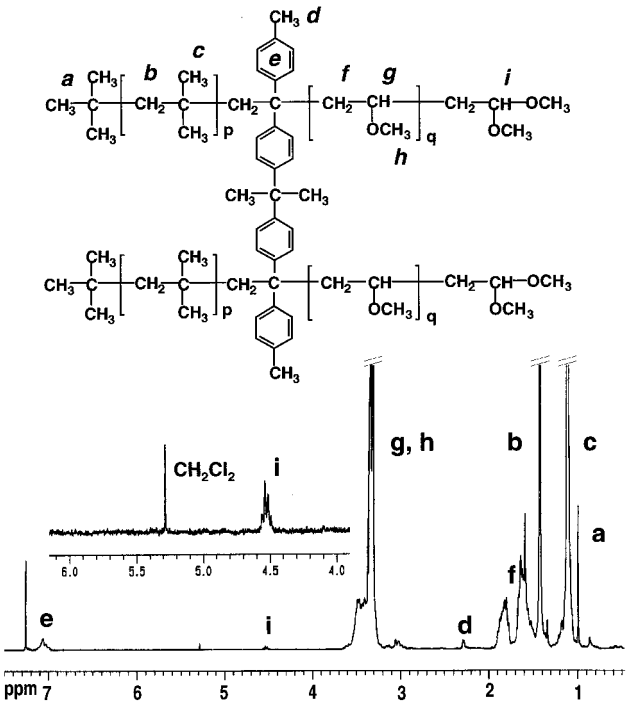


Figure 8. 250 MHz ^{1}H NMR spectrum of an A_2B_2 star−block copolymer. $M_{n,PIB}$ = 2500 (by GPC) and $M_{n,PMEVE}$ = 3400 (by ^{1}H NMR).

comparison of integration areas of chain end groups. For example, the integration ratio of the resonance signal for methyl protons of PIB headgroup (peak *a*) over the resonance signal for *p*-methyl protons of BDTEP (peak *d*) is close to theoretical value of 3 (observed, 2.97), indicating virtually quantitative coupling reaction of living PIB by BDTEP. The integration ratio of resonance peak *d* over peak *i*, corresponding to acetal methine protons of the PMeVE end group, also proves almost stoichiometric reinitiation of MeVE by the living coupled PIB (theoretical, 3, and observed, 2.91). The absence of a conjugated diene structure (δ = 5.3−6.2 ppm) further indicates the absence of termination during PMeVE polymerization. However, when the chain ramification reaction of MeVE was carried out at room temperature, otherwise under the same conditions, the ^{1}H NMR spectrum of the product exhibited broad resonance peaks at δ = 5.3−5.9 ppm which are characteristic of a conjugated diene structure indicating termination during PMeVE polymerization via β-proton elimination at elevated temperature.[30]

Characterization of A_2B_2 Star−Block Copolymer. Fractionation of an A_2B_2 star−block copolymer (C in Figure 7) was carried out on a silica gel column using pentane and THF as eluents as described by Pernecker and Kennedy.[28] A summary of results in the fractionation is given in Table 2 and Figure 9. Analyses by GPC and ^{1}H NMR spectroscopy of each fraction with a sufficient amount (>10 mg) proved this separation method is very effective for amphiphilic block copolymers for which a conventional fractionation method using solvent/nonsolvent is not applicable. The chemical composition of each fraction was calculated using ^{1}H NMR spectroscopy and this was used for the d*n*/d*c* calculation of each fraction. Using pentane, which is a good solvent for PIB segment, as an eluent, PIBs with little or no MeVE segment were obtained. At elution volume of 350 mL (no. 7 in Table 2), THF was detected by smell and the color of the product was yellow. Characterization by ^{1}H NMR spectroscopy revealed strong resonance signals for PIB and the presence of unreacted diarylethylene moieties at δ = 5.4 ppm. Complex resonance signals at δ = 3.5−5.0 ppm, which are assignable to neither PIB nor PMeVE segments, were also observed, most likely due to the presence of PIB with eliminated PMeVE segments. From fraction 8 to 11, a pure and colorless A_2B_2 star−block copolymer was eluted. M_ns of fractions 8−11 were close to the theoretical value ($M_{n,th}$ = 25 000) with ∼80 wt % of PMeVE composition and their distributions were narrower than that of the crude A_2B_2 star−block copolymer. The product obtained at the final stage of fractionation (no. 12 in Table 2) exhibited higher content of PMeVE (91 wt %) with much lower M_n and broader molecular weight distribution. Considering the PIB homopolymer detected in the early stage of the fractionation, this structural impurity can be possibly attributed to the block copolymers with higher composition of PMeVE arising from decoupling of living PIB. Based on the weights of fractions, the purity of the crude A_2B_2 star−block copolymer was calculated to be ≥93.5%.

The pure A_2B_2 star−block copolymer ($(IB_{45})_2$-*s*-$(MeVE_{170})_2$) was further characterized by DSC as shown in Figure 10. Two T_gs at −60 and −20 °C were observed, indicating the presence of two microphases. Interestingly, the T_gs of both segments were about 10 °C higher than those of their homopolymers ($T_{g,PIB}$ = −73 °C and $T_{g,PMeVE}$ = −31 °C), which was not observed with a linear diblock copolymer, IB_{90}-*b*-$MeVE_{340}$.[26] At a first glance, it appeared this upward shift of both T_gs might be related to the steric hindrance to segmental motions in the star architectures; however, this can be possibly accounted for by the different method for sample preparation, since a linear diblock copolymer, IB_{45}-*b*-$MeVE_{170}$, prepared in this work (A in Figure 6) also exhibited upward shifts of both T_gs (−60 and −20 °C).

As expected, the star−block copolymer, $(IB_{45})_2$-*s*-$(MeVE_{170})_2$, was also soluble in water similar to its linear counterpart with same total M_n, IB_{90}-*b*-$MeVE_{340}$. The surface tension in aqueous solution of $(IB_{45})_2$-*s*-$(MeVE_{170})_2$ was measured as a function of concentration at 25 °C. Figure 11 shows the surface tension vs concentration plots for $(IB_{45})_2$-*s*-$(MeVE_{170})_2$ and IB_{45}-*b*-$MeVE_{170}$. The critical micelle concentrations (cmc) determined from surface tension measurements are listed in Table 3, along with average particle sizes measured above the cmc. Interestingly, $(IB_{45})_2$-*s*-$(MeVE_{170})_2$ exhibited an order of magnitude higher cmc than its linear diblock counterparts such as IB_{90}-*b*-$MeVE_{340}$ or IB_{45}-*b*-$MeVE_{170}$. Moreover, $(IB_{45})_2$-*s*-$(MeVE_{170})_2$ exhibited a slightly higher surface tension (∼42 dyn/cm) above its cmc than IB_{90}-*b*-$MeVE_{340}$ and IB_{45}-*b*-$MeVE_{170}$ which exhibited identical surface tension (∼39 dyn/cm), independently of chain length, above their cmcs. While, to our best knowledge, no report has been made on the architectural effects on the micellar properties of amphiphilic block copolymers, these results may indicate that block copolymers with star architectures have less tendency to micellization than their corresponding linear block copolymers.

Comparing average particle sizes of two linear diblock copolymers listed in Table 3, the influence of chain length on the particle size can be seen; IB_{45}-*b*-$MeVE_{170}$ exhibits a much smaller size than IB_{90}-*b*-$MeVE_{340}$ (41

Table 2. Fractionation of an A_2B_2 Star−Block Copolymer on a Silica Gel Column[a]

no.	eluent	vol (mL)	W_i (g)	ΣW_i (g)	W_i (%)	ΣW_i (%)	$10^{-3}M_n$ (M_w/M_n)
1	pentane	50	0.0013	0.0013	0.03	0.07	
2	pentane	100	0.0356	0.0369	1.99	2.06	2.5 (1.38)
3	pentane	150	0.0315	0.0684	1.76	3.83	2.5 (1.53)
4	pentane	200	0.0018	0.0702	1.10	3.93	
5	pentane	250	0.0025	0.0727	0.14	4.07	
6	pentane	300	0.0007	0.0734	0.04	4.11	
7	THF	350	0.0043	0.0777	0.24	4.35	
8	THF	400	0.0823	0.1600	4.60	8.95	25.2 (1.12)
9	THF	450	0.7672	0.9272	42.92	51.87	25.3 (1.12)
10	THF	500	0.5908	1.5180	33.05	84.93	24.5 (1.17)
11	THF	550	0.2304	1.7484	12.89	97.82	24.1 (1.18)
12	THF	600	0.0372	1.7856	2.08	99.90	16.7 (1.37)
13	THF	650	0.0043	1.7899	0.24	100.14	
14	THF	700	0.0035	1.7934	0.20	100.34	
15	THF	750	0.0005	1.7939	0.03	100.36	

[a] Total amount of polymer loaded in the column: 1.7874 g.

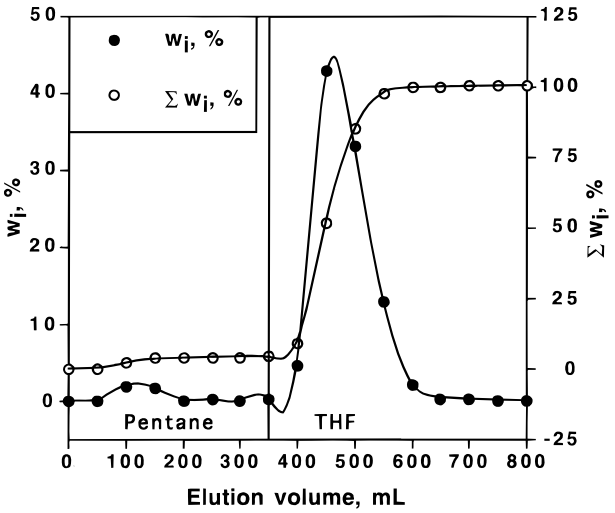


Figure 9. Chromatogram of the fractionation of an A_2B_2 star−block copolymer (C in Figure 7) on a silica gel column.

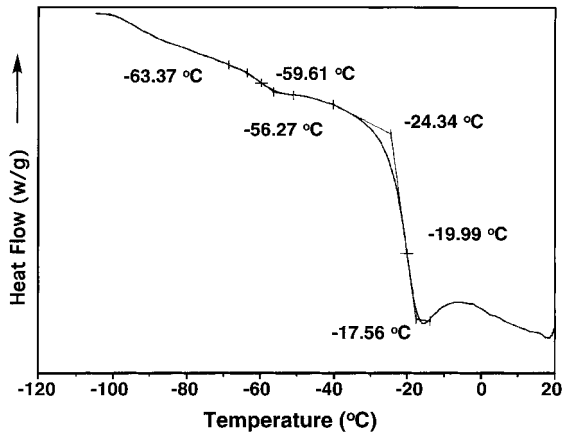


Figure 10. DSC thermogram recorded during the second heating scan of A_2B_2 star−block copolymer (no. 9 in Table 2).

nm vs 154 nm) in aqueous solution above the cmcs. It is also interesting to note that $(IB_{45})_2$-*s*-$(MeVE_{170})_2$ exhibits an average particle size comparable to that of a linear diblock copolymer with same total M_n (IB_{90}-*b*-$MeVE_{340}$).

Conclusions

A simple and expedient pathway to the synthesis of A_2B_2-type star−block copolymers with higher structural integrity has been developed via the living coupling reaction of living PIB followed by the chain ramification reaction of a second monomer. Since diarylalkylcarbenium ions, which are generated during the living coupling reaction, have successfully been employed for the living polymerization of cationic monomers such as vinyl ethers and styrenic monomers, this living coupling reaction should be a general process for the synthesis of A_2B_2 star−block copolymers with a variety of monomers.

While no evidence was observed for the architectural effect on the thermal properties such as the glass transition, preliminary results in the solution properties of star−block or linear block copolymers suggest the presence of the strong interplay between block architectures and micellar properties in aqueous solution. Further reseach involving different characterization techniques should be carried out to advance our understanding of the architecture/property relationships.

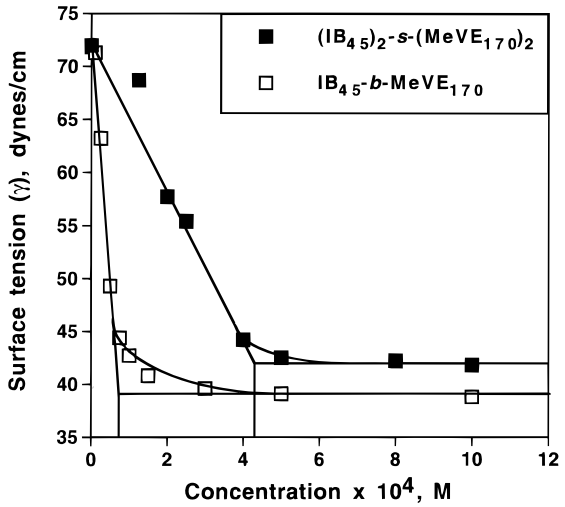


Figure 11. Surface tension vs concentration plots at 25 °C. cmc = 4.25×10^{-4} M for $(IB_{45})_2$-*s*-$(MeVE_{170})_2$ and 7.5×10^{-5} M for IB_{45}-*b*-$MeVE_{170}$.

Table 3. Characterization of a Star−Block or a Linear Diblock Copolymer in Water at 25 °C

sample	$10^{-3}M_n$	$10^5 \times$ cmc, M	average particle size,[a] nm
$(IB_{45})_2$-*s*-$(MeVE_{170})_2$	25.3	42.5	177
IB_{90}-*b*-$MeVE_{340}$	25.0	2.5[b]	154
IB_{45}-*b*-$MeVE_{170}$	13.3	7.5	41

[a] Measured at 0.001 M and within ± 5% experimental error. [b] From ref 26.

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