Macromolecules
ARTICLE

Macromolecules **2009**, *42*, 7309–7317 **7309**
DOI: 10.1021/ma9006768

Synthesis of Dendritic Polystyrenes from an Anionic Inimer

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Received March 30, 2009; Revised Manuscript Received August 9, 2009

ABSTRACT: An anionic inimer (a monomer with an initiating site) is prepared by monoaddition of *sec*-butyllithium and 1,3-bis(1-phenylethenyl)benzene (MDDPE) in tetrahydrofuran (THF) at low temperature. The selectivity of monoaddition is high, yielding nearly quantitative formation of the inimer. The inimer is able to initiate the polymerization of styrene, forming different architectures of the products in THF and cyclohexane. In the former, linear product with larger-than-expected molecular weight is obtained whereas, when the solvent is switched from THF to cyclohexane, dendritic polymer is obtained through the copolymerization of the inimer and styrene. The resulting products are characterized by size exclusion chromatography equipped with a multiangle light scattering detector and a viscometer. Smaller radius of gyration and intrinsic viscosity are measured for the dendritic product. The mechanism of forming dendritic structure by the solvent-switching process is discussed according to Müller's theory.

Introduction

A common approach to synthesize hyperbranched (or dendritic) vinyl polymers is by self-condensing vinyl polymerization (SCVP) of inimer, i.e., a monomer with latent initiating moiety first synthesized by Fréchet and co-workers.[1,2] For many years, this protocol has been successfully applied for the syntheses of a variety of hyperbranched polymers through various polymerization mechanisms, such as cationic polymerization,[1] TEMPO-mediated radical polymerization,[2−4] atom transfer radical polymerization (ATRP),[5,6] reversible addition−fragmentation chain transfer process (RAFT) mediated radical polymerization,[7,8] metal-catalyzed "living" radical polymerization[9] and group transfer polymerization.[10] There are, however, very few reports on the synthesis of hyperbranched polymers from anionic inimer.[11,12] Baskaran has prepared hyperbranched polymers by SCVP of the reaction products of *sec*-butyllithium (*sec*-BuLi) and diisopropenylbenzene[11,12] or divinylbenzene.[12] Although it is believed that the polymerization involves an inimer intermediate, the product is contaminated by small amounts of gels as indicated by the reported broad signals in HPLC analysis.[11] This is because a stoichiometric reaction is difficult to achieve in the preparation of inimer, despite rapid mixing of the reactants, since the anion can initiate *in situ* polymerization of divinyl monomers.[13]

In the present work, we report the synthesis of dendritic polystyrenes using an anionic inimer, the monoadduct of *sec*-BuLi and 1,3-bis(1-phenylethenyl)benzene (MDDPE). The chemistry of anionic addition toward 1,1-diphenylethylene (DPE) derivatives has been widely used in macromolecular design.[14,15] It is known that the two double bonds of MDDPE are equivalent to anionic addition in nonpolar solvents,[14−18] while monoaddition has been achieved by using excessive MDDPE in reaction with polystyryllithium (PSLi) in polar solvent.[14,19,20] Nevertheless, stoichiometric reaction between *sec*-BuLi and MDDPE has never been reported. The stoichiometry is important because the resulting monoadduct is further used *in situ* as an inimer to copolymerize with styrene to prepare dendritic polystyrene. We have recently succeeded in high yield preparation of monoadduct using equal molar amount of *sec*-BuLi and MDDPE in tetrahydrofuran (THF). Therefore, the synthesis of dendritic polymers starting with monoadduct as inimer becomes feasible. We should mention here that there are a number of publications on the synthesis of dendritic,[21] arborescent,[22] and dendrimer-like[23,24] polymers by anionic polymerization through either convergent coupling reaction,[21] grafting of polymeric anion to a main chain ("grafting-to"),[22] or iterative functionalization coupling reactions.[23,24] These syntheses are not through SCVP of inimer and are therefore different from the present work.

Experimental Section

Materials. Styrene (National Pharmaceutical, ≥99%) was distilled over di-*n*-butylmagnesium ($MgBu_2$) (Aldrich, 1.0 M in heptane) before use. Cyclohexane (Feida, 99.5%) and tetrahydrofuran (THF) (Feida, 99.5%) were refluxed over sodium (Na) and distilled from the adduct of *sec*-BuLi and DPE (DPELi) before use. *sec*-Butyllithium (*sec*-BuLi) (Acros, 1.3 M solution in cyclohexane/heptane) and methyllithium (Acros, 1.6 M solution in diethyl ether) were used as received. Methyltriphenylphosphonium bromide (Lancaster, >98%) and 1,3-dibenzoylbenzene (Aldrich, 98%) were vacuum-dried at 50 °C for 12 h. MDDPE was synthesized according to a previous method.[25] The product was a clear oil. Yield: 50% (purity 99% by HPLC). ^1H NMR ($CDCl_3$): δ (ppm) = 7.36 (m, 14 H, aromatic), 5.47 (m, 4 H, $=CH_2$). GC-MS: 99%, m/z = 282.

Polymerizations. All of the reactions were performed in a flask connected to the vacuum line, nitrogen inlet, sampling ampule, and distillation apparatus. The glass apparatus was dried by three cycles of flaming/N_2-purging/evacuating and rinsed with a dilute solution of *n*-BuLi in cyclohexane, then purified cyclohexane, several times before polymerization. All reactions were conducted in nitrogen.

A solution of MDDPE (0.076 g, 0.27 mmol) in cyclohexane (1 mL) was mixed with dry THF (20 mL) at −78 °C and titrated with dilute DPELi solution until a light red color was sustained.

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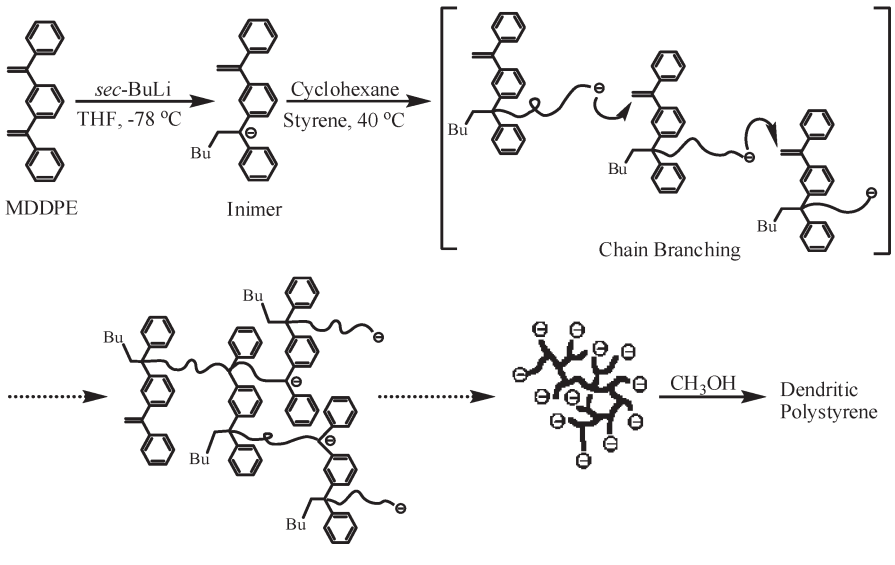
Scheme 1. Synthesis of Dendritic Polystyrene Using an Anionic Inimer



sec-BuLi (0.27 mmol, 0.2 mL of cyclohexane/heptane solution) was injected to the system using a syringe. The reaction was completed within 10 min. Then a small amount of the resulting dark-red solution was withdrawn and terminated with degassed methanol. The purity of the product was determined by HPLC to be 98%.

The above prepared inimer was used to initiate *in situ* styrene polymerization. After the reaction of MDDPE and *sec*-BuLi, THF was distilled out to dryness by cooling the receptor flask with liquid nitrogen while keeping the reaction flask below 5 °C in a water/ice bath. Then cyclohexane (30 mL) and styrene (4.5 g, 0.04 mol) were distilled over DPELi and MgBu$_2$, respectively, into the reaction flask. The reaction proceeded at 40 °C for 5 h and was terminated using degassed methanol. The polymerization product was precipitated from methanol and dried in vacuum at 50 °C for 48 h. $M_{n,GPC} = 4.1 \times 10^4$ g/mol, $M_w/M_n = 2.49$, $M_{w,MALLS} = 20.5 \times 10^4$ g/mol.

For the system without solvent switching, styrene (3.60 g, 0.04 mol) was distilled over MgBu$_2$ into the reaction flask directly after the synthesis of the inimer. The reaction was terminated after 30 min. $M_{n,GPC} = 3.67 \times 10^4$ g/mol, $M_w/M_n = 2.42$, $M_{w,MALLS} = 9.76 \times 10^4$ g/mol.

Model Reaction I (Batch Polymerization Initiated by the Inimer in THF). After the preparation of inimer in THF (*sec*-BuLi: 0.35 mmol; MDDPE: 0.10 g, 0.35 mmol; THF: 30 mL), two batches of freshly distilled styrene (each 0.90 g, 8.6 mmol) was charged into the reaction flask, with polymerization times for each batch 30−60 min at −78 °C, followed by termination with methanol. The GPC results of the products are $M_{n,GPC} = 9.60 \times 10^3$ g/mol, $M_w/M_n = 2.08$ (for the first batch polymerization), and $M_{n,GPC} = 2.05 \times 10^4$ g/mol, $M_w/M_n = 2.24$ (for the second batch polymerization).

Model Reaction II (Addition Reaction of PSLi toward Inimer in THF). A solution of PSLi (preparation: styrene: 0.90 g, 8.6 mmol; *sec*-BuLi: 0.48 mmol; THF: 20 mL, −78 °C, 10 min) was dropped into a solution of inimer (*sec*-BuLi: 0.27 mmol; MDDPE: 0.08 g, 0.27 mmol; THF: 20 mL) with vigorous stirring at −78 °C. The reaction was deactivated by degassed methanol after 1 h, resulting in a product with $M_{n,GPC} = 2.0 \times 10^3$ g/mol and $M_w/M_n = 1.15$ determined by GPC.

Model Reaction III (Solvent Switching after Polymerization in THF). After the polymerization of styrene (0.9 g, 8.6 mmol) in THF initiated by inimer (*sec*-BuLi: 0.35 mmol; MDDPE: 0.10 g, 0.35 mmol; THF: 20 mL), the resulting mixture containing PSLi ($M_{n,GPC} = 1.10 \times 10^4$ g/mol, $M_w/M_n = 1.68$) was distilled to remove THF to dryness. Then cyclohexane (30 mL) was distilled over DPELi into the reaction flask to redissolve PSLi and the residual inimer. The reaction proceeded at 40 °C for another 5 h and was terminated using degassed methanol. The product was analyzed by GPC with $M_{n,GPC} = 1.41 \times 10^4$ g/mol and $M_w/M_n = 1.93$.

Model Reaction IV (Addition Reaction of PSLi toward Inimer in Cyclohexane). A solution of inimer in cyclohexane was prepared first in THF (*sec*-BuLi: 0.27 mmol; MDDPE: 0.08 g, 0.27 mmol; THF: 20 mL), followed by solvent switching through distillation of THF and cyclohexane (30 mL). Then a solution of PSLi in cyclohexane (preparation: styrene: 0.90 g, 8.6 mmol; *sec*-BuLi: 0.48 mmol; cyclohexane: 20 mL, 40 °C, 2 h) was mixed with the above inimer solution with vigorously stirring at 40 °C. The reaction was deactivated by degassed methanol after 3 h, giving a product with $M_{n,GPC} = 2.40 \times 10^3$ g/mol and $M_w/M_n = 1.09$ determined by GPC.

Characterization. High-performance liquid chromatography (HPLC) was performed on an instrument composed of a Waters 515 pump, a C-18 column (Symmetry ShieldP RP-18, 5.0 μm, 4.6 × 250 mm), and a UV detector (254 nm). Acetonitrile/water (83/17, v/v) was used as eluent (1.0 mL/min) at 40 °C. ^{1}H NMR and ^{13}C NMR measurements were carried out on a Bruker (500 MHz) NMR instrument, using CDCl$_3$ or deuterated DMSO as the solvent and tetramethylsilane as the interior reference. Gas chromatography/mass spectroscopy (GC-MS) was performed on a Finnigan Voyager instrument in electron impact mode (70 eV). GPC analysis was performed through three Waters Styragel columns (pore size 10^2, 10^3, and 10^4 Å), calibrated by narrow polystyrene standards, equipped with three detectors: a DAWN HELEOS (14°−154°) (Wyatt multi-angle laser light scattering detector, He−Ne 658.0 nm), ViscoStar (Wyatt), and Optilab rEX (Wyatt). THF was used as the eluent at a flow rate of 1.0 mL/min at 35 °C.

Results and Discussion

The syntheses of inimer and dendritic polystyrene are outlined in Scheme 1. The inimer is a monoadduct of *sec*-BuLi with MDDPE. Note that this monoadduct cannot undergo SCVP since the DPE anion is not able to initiate the polymerization of the residual double bond. Nevertheless, the inimer should be able to copolymerize with styrene because DPE anion can initiate the polymerization of styrene and the initiated polystyrene anion can add to the residual double bond. Dendritic structure will be formed after a series of initiation−addition−initiation cycles.

Synthesis of Anionic Inimer. The monoadduct is synthesized in nearly quantitative yield in THF through the stoichiometric addition of *sec*-BuLi toward MDDPE. The key

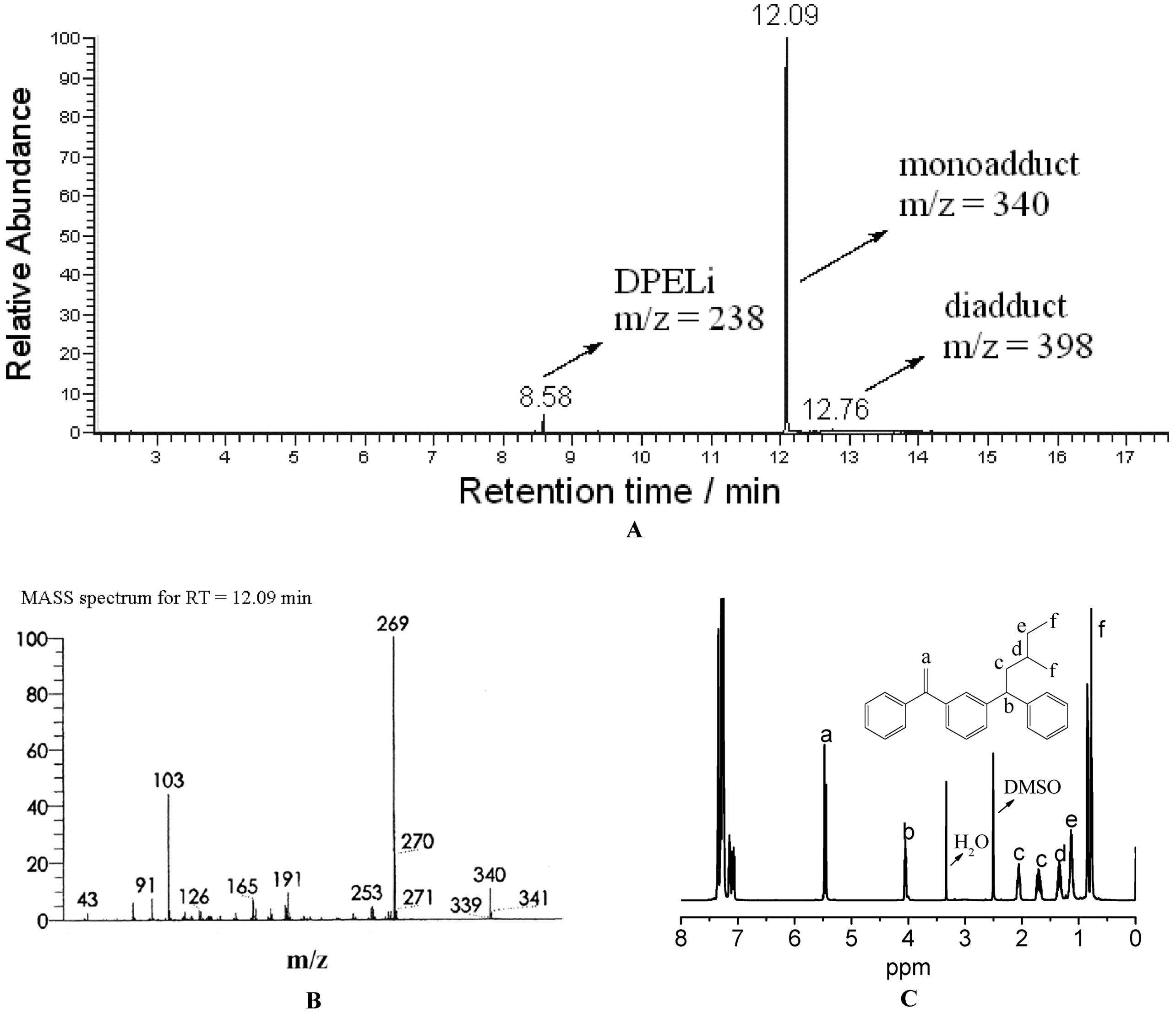


Figure 1. Characterization of the monoadduct (inimer) of *sec*-butyllithium (0.35 mmol, 0.30 mL cyclohexane/heptane solution) and 1,3-bis(1-phenylethenyl)benzene (0.10 g, 0.35 mmol) by gas chromatography−mass (GC-MS, A and B) and proton nuclear magnetic resonance (^{1}H NMR, in DMSO-d_6, C) spectroscopies.

factor to the success of monoaddition is the control of solvent polarity. Upon injection of *sec*-BuLi, the reaction solution becomes dark red immediately. The addition reaction is very quick and completes within 10 min. The reaction is so specific that diadduct formation is negligible even in slight excess of *sec*-BuLi. Figure 1 shows the characterization results by GC-MS and ^{1}H NMR. GC-MS shows a high peak of monoadduct at RT = 12.09 min, which constitutes 96% of the products and shows molecular ion at 340 *m*/*z*. The other two small peaks at RT = 8.58 and 12.76 min come from (1,1-diphenyl-3-methyl)pentyllithium (DPELi, adduct of *sec*-BuLi and DPE, used for rinsing the flask) and diadduct, respectively, as indicated by their molecular mass at 238 and 398 *m*/*z* (Supporting Information). The monoadduct is isolated by column chromatography. The ^{1}H NMR spectrum shows clearly the vinylic protons at 5.5 ppm and the methine proton at 4.0 ppm. The integrations of these protons, together with those of aromatic and alkyl protons, correlate very well with the molecular structure of the monoadduct.

The nearly quantitative formation of the monoadduct in the present work is different from the diadduct formation reported in the literature.[14,16−18,26] This is a consequence of different solvent polarity. In this work, the solvent is THF in which carbon anions are generally more dissociated due to the solvent separation of the counterions (Li^+). The selectivity in the addition reaction is due to electrostatic repulsion between the resulting DPE anion and the approaching anion of *sec*-BuLi, impeding the addition of second molecule of *sec*-BuLi. In the literature,[14,16−18,26] however, the solvent is a nonpolar hydrocarbon in which the ion pairs are more tightly contact due to the low dielectric constant of the solvent. In addition, the repulsive force can be further balanced by the association of ionic species (polystyryllithium exists as dimer in cyclohexane but as unassociated form in THF[27]), resulting in a large fraction of diadduct in nonpolar solvent.

It is well established that the two vinyl groups of MDDPE are equivalent toward anionic addition since the first anion can not be delocalized to the second double bond.[14,16−18] The 1,4-isomer of bis(1-phenylethenyl)benzene, PDDPE, shows more selectivity in reaction with organolithium.[16] Therefore, it would be more reasonable to use PDDPE in the preparation of monoadduct. Nevertheless, the result in the present work demonstrates that the key factor to control the addition reaction style is the solvent polarity. The results

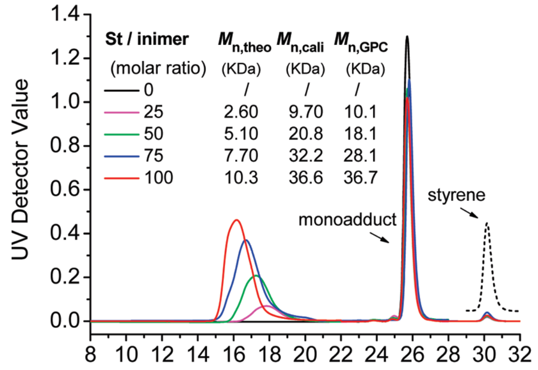


Figure 2. Gel permeation chromatography (GPC) results of polymerization solutions of styrene initiated by the inimer at various feed ratios of styrene to inimer. The polymerizations are conducted in tetrahydrofuran (THF) at −78 °C for 30 min. $M_{\mathrm{n,theo}}$, $M_{\mathrm{n,cali}}$, and $M_{\mathrm{n,GPC}}$ are number-averaged molecular weights of theoretical calculation based on the molar ratio of monomer and inimer, theoretical calculation based on the molar ratio of monomer and the consumed inimer, and GPC determined results, respectively.

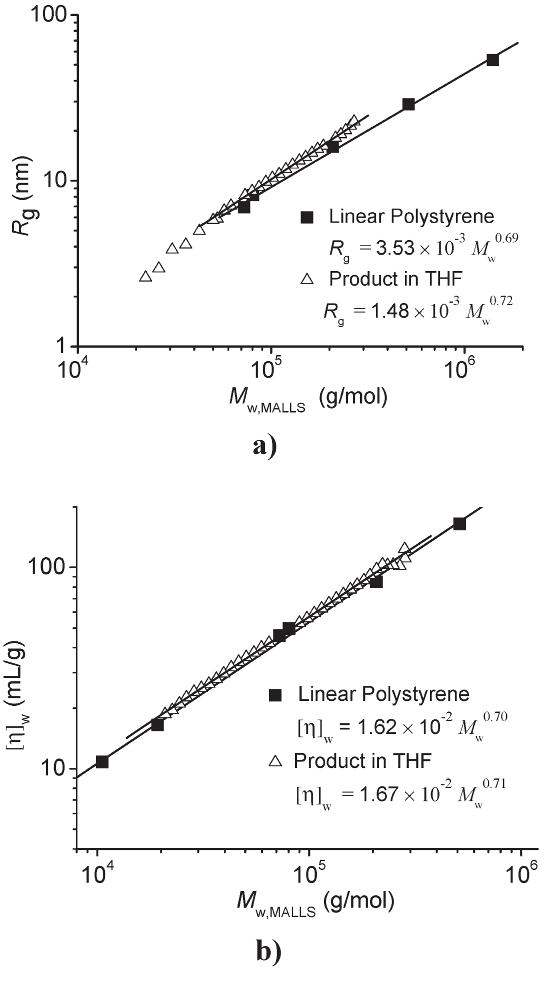


Figure 3. Molecular weight dependence of radius of gyration, R_g (a), and intrinsic viscosity (b) for products prepared in tetrahydrofuran (THF) (△) and linear polystyrene standard (■).

are not in conflict with those in ref 16 since the solvent is different.

Polymerization Conducted in THF. The freshly prepared inimer solution in THF is used *in situ* to initiate the polymerization of styrene. Figure 2 shows the GPC results with fixed injection amount of the reaction mixture after the polymerization completes. The product exhibits broad but monomodal distribution, with number-average molecular weights ($M_{\mathrm{n,GPC}}$) much larger than the theoretical values ($M_{\mathrm{n,theo}}$) derived from the feed ratio of monomer to anionic species. Although these phenomena are typical for SCVP of inimer[28] or copolymerization of inimer and monomer,[29] a close analysis of the product by light scattering and viscometry detector connected to the GPC system reveals that the product has a linear structure. As shown in Figure 3, the radius of gyration, R_g, and intrinsic viscosity, $[\eta]$, of the product are very close in magnitude and in molecular weight dependence to those of commercial linear polystyrene standard.

In search for the reason why branching has not occurred, it is necessary to discuss the reaction mechanism. There are three elementary reactions that are crucial for the formation of dendritic product, i.e., the initiation of styrene by DPE anion (including the initial and various resulting species during addition reaction), the propagation of initiated chains, and the addition of living chains toward the residual double bond in MDDPE moiety (in either inimer or macromolecule) (Scheme 2):

Unlike conventional SCVP, there is no reaction between inimer molecules. If we consider an assumption that all the initiation reactions have equal rate constants, k_i, and so do the addition reactions, the kinetic model can be written as

$$\mathrm{DPE}^- + M \xrightarrow{k_i} M^-$$

$$M^- + M \xrightarrow{k_p} M^-$$

$$M^- + \mathrm{DPE} \xrightarrow{k_{\mathrm{add}}} \mathrm{DPE}^-$$

in which M and DPE represent monomer (styrene) and diphenylethylene moieties, respectively, with the superscript meaning active centers. k_i, k_p, and k_{add} are rate constants of initiation, propagation, and addition reactions. The kinetics can be expressed by the following differential equation:

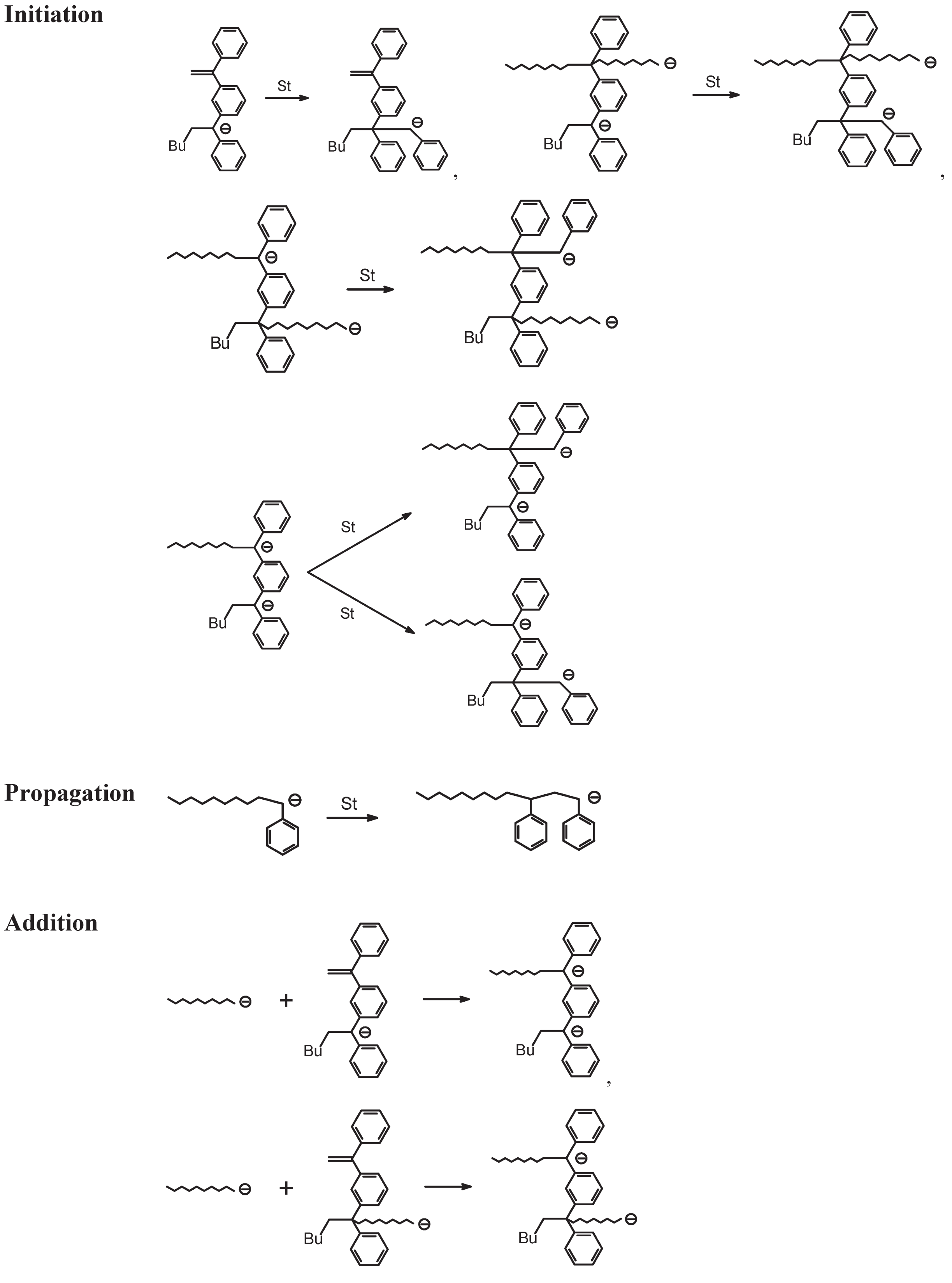
$$\frac{\mathrm{d[M]}}{\mathrm{d}t} = -[\mathrm{M}](k_{\mathrm{i}}[\mathrm{DPE}^-] + k_{\mathrm{p}}[\mathrm{M}^-]) \qquad (1)$$

$$\frac{\mathrm{d[inimer]}}{\mathrm{d}t} = -[\mathrm{inimer}](k_{\mathrm{i}}[\mathrm{M}] + k_{\mathrm{add}}[\mathrm{M}^-]) \qquad (2)$$

In order to analyze the above equations, we need to know the relative rates of the elementary steps, which can be inferred from the following model reactions. In the following section, we should keep in mind that all discussions are qualitative. This is due to not only the unavailability of various rate constants but also the possible coexistence of various aggregating anionic species caused by residual THF in the flask even after the solvent switching process.

First, the initiation ability of the inimer is investigated by GPC-monitoring the residual inimer in the final reaction mixture for systems with different ratios of monomer to inimer. As shown in Figure 2, a large fraction of inimer (~75% based on the peak areas of the remaining and the initial inimer) has remained after the full consumption of monomer for all systems. Keeping in mind that both initiation and addition reactions consume inimer, we conclude that the initiation ability of the inimer is certainly low and, furthermore, the sum of initiation and addition rates is lower than the propagation rate. It is also noted in Figure 2 that the GPC measured molecular weights, $M_{\mathrm{n,GPC}}$, are quite close to the calibrated theoretical value, $M_{\mathrm{n,cali}}$, based merely on the

Scheme 2. Elementary Reactions for the Formation of Dendritic Product in the Copolymerization of Styrene and the Anionic Inimer



fraction of initiated inimer, indicative of a simple anionic polymerization of styrene with slow initiation by the inimer.

The slower initiation in relative to propagation is further verified by batch polymerization in THF (model reaction I), in which the second batch of monomer is added in order to see whether the chain extension takes place on polymer or on inimer. Figure 4 shows the GPC result. It is obvious that further polymerization mainly takes place on polymeric anion while the inimer concentration remains almost constant (compare the red and blue lines). This demonstrates again that the propagation rate is much faster than the initiation rate.

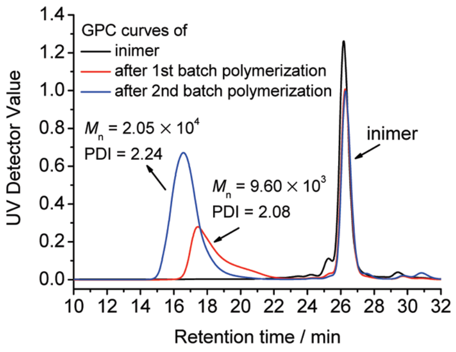


Figure 4. Gel permeation chromatography (GPC) profiles of the reaction mixtures in tetrahydrofuran (THF) by batch feed of styrene: 1 mL (red) and further 1 mL (blue) monomer. Reaction conditions: *sec*-BuLi, 0.35 mmol (0.30 mL cyclohexane/heptane solution); 1,3-bis(1-phenylethenyl)benzene (MDDPE), 0.10 g, 0.35 mmol; temperature, −78 °C.

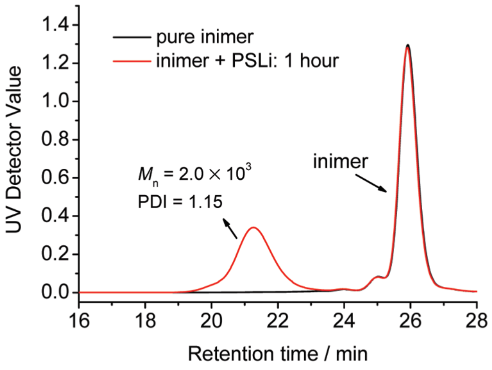


Figure 5. Gel permeation chromatography (GPC) profiles of the reaction mixtures of polystyryllithium (PSLi) with the inimer, the monoadduct of *sec*-BuLi and 1,3-bis(1-phenylethenyl)benzene (MDDPE) in tetrahydrofuran (THF). Preparation of PSLi: styrene: 0.90 g, 8.6 mmol; *sec*-BuLi: 0.48 mmol; −78 °C, 10 min. Preparation of inimer: *sec*-BuLi: 0.27 mmol; MDDPE: 0.08 g, 0.27 mmol; −78 °C.

Second, the addition reaction is investigated by mixing the inimer and excessive PSLi (molar ratio 1:1.8) in THF without monomer (model reaction II). GPC traces in Figure 5 show that there is no addition reaction occurring after 1 h of mixing, which is due to the electrostatic repulsions between DPE$^-$ of the inimer and the approaching polystyrenyl anion.

Unfortunately, it is difficult to determine quantitatively these rate constants due to very fast polymerization rate and infeasible continuous sampling during anionic reaction. Nevertheless, it is possible to give a qualitative analysis of the reaction model. According to Müller's theoretical results for copolymerization of inimer and conventional monomer,[29] if an inimer prefers to initiate monomer rather than initiate the vinyl group of another inimer, in the meantime the homopolymerization rate of monomer is remarkably larger than the copolymerization rate, the reaction will lead to the formation of linear macroinimer possessing telechelic vinyl group and active center which can undergo further SCVP. In the present work, the inimer cannot initiate the residual DPE of another inimer although the initiation efficiency to styrene is also quite low. Meanwhile, once a chain is initiated, its propagating rate is remarkably larger than the addition rate toward DPE moiety. Consequently, the product is linear polystyrene macroinimer with an α-DPE group and an *ω*-living anion. We have expected that, upon prolonging the reaction time after the monomer has been consumed up, the macroinimer would undergo polycondensation through addition of polystyryl anion to DPE terminus of another chain, forming polymer species of multiple molecular weights. Nevertheless, this does not occur as demonstrated by the unchanged GPC profile in Figure 4 for a reaction time up to 2 h, which may be a consequence of relatively low reactivity between anion and DEP termini. Low diffusibilities of the termini may also hamper polycondensation reaction.

We have attempted to characterize the product synthesized in THF, e.g., the sample with M_n = 9600 g/mol in Figure 4, by ^{1}H NMR (Supporting Information). Indeed, there are weak signals at 5.1 and 5.3 ppm which are assigned to vinylic proton of terminal DPE moieties. However, the ratio of signal-to-noise is low for scanning number up to 128, impeding quantitative functionality analysis.

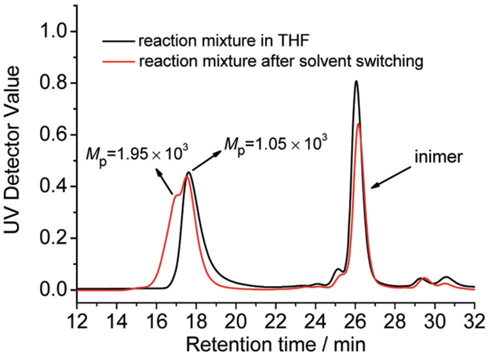


Figure 6. Gel permeation chromatography (GPC) profiles of styrene polymerization initiated by the inimer before (black) and after (red) solvent switching (no monomer). Reaction conditions: *sec*-BuLi, 0.35 mmol; 1,3-bis(1-phenylethenyl)benzene: 0.35 mmol; styrene: 0.90 g, 8.6 mmol.

It is interesting to observe that, when we switch the solvent from THF to cyclohexane, polymer species with double molecular weight is formed (model reaction III). Figure 6 shows GPC result of a model reaction, in which solvent-switching is performed after the complete consumption of monomer, followed by further heating at 40 °C for 5 h without monomer. A new peak of double molecular weight clearly appears which is ascribed to polycondensation between termini of the linear products originally formed in THF. This indicates that the anion reactivity toward DPE moiety is higher in nonpolar solvent, although the reason is not known. It is also noted in Figure 6 that the intensity of the inimer peak is reduced due to further addition of PSLi to the residual DPE moiety in the inimer. This agrees with the fact that diadduct is usually formed in nonpolar solvent.[14,16−18]

Polymerization Conducted in Cyclohexane. According to the reaction scheme, a set of comparable rates of initiation, propagation, and addition is desired for successful synthesis of dendritic products. Nevertheless, in THF the propagation rate far exceeds the initiation and addition rates. A well-known fact is that anionic polymerization in nonpolar solvents, such as cyclohexane, is much slower than that in THF.[27] Model reactions in the above section show that the addition reaction is also promoted in cyclohexane. Therefore, after the preparation of the monoadduct, THF is distilled out at a temperature below 5 °C for ~15 min, and cyclohexane is distilled over DPELi into the reaction flask. The distillation of THF at low temperature is to avoid the decomposition of anionic species by the solvent. Stanetty et al.[30] reported that *n*-BuLi at 0 °C in THF had a half-life of ~1039 min. The DPE anion in the reaction of the present work is expected to be more stable than *n*-BuLi. Therefore, the decomposition of inimer within 15 min is negligible.

By the solvent switching, the dark-red solution becomes orange in color upon feeding of styrene, indicating the initiation by the inimer. This is in contrast to the reaction in THF, in which the dark-red color remains for the whole period. The reaction stands for 5 h in order to ensure a complete conversion of the monomer as measured by GPC (UV detector). In a system with larger concentration of monomer (15% g/g), pseudogel is formed during the polymerization due to the aggregation of branched species with multi-organolithium functionalities. The gel becomes fluid immediately after termination by methanol. Figure 7 shows GPC traces of the final products for systems with various feed ratios of monomer to inimer. Remarkably, the inimer is consumed up within 5 min for all systems. The fast conversion of inimer agrees with the theoretical predictions by Müller and co-workers.[29] All the products exhibit broad and multimodal molecular weight distributions. The molecular weight increases along with the feed ratio of monomer to inimer, also in line with the theoretical results in ref 29. However, a quantitative comparison with theory is impossible because, at the later stage of the polymerization, the molecular weight is very sensitive to a tiny increase of monomer conversion, which is difficult to control in practice.

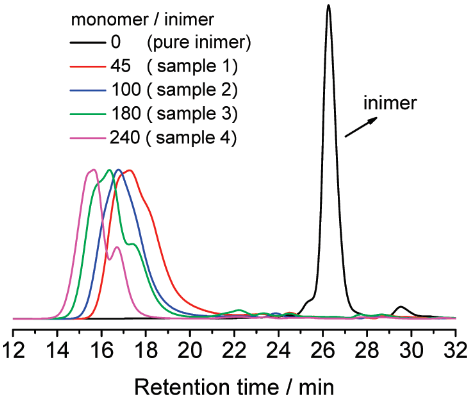


Figure 7. Normalized gel permeation chromatography (GPC) results on polymerization solutions of styrene initiated by the inimer at various feed ratios of styrene to inimer. The polymerizations are conducted in cyclohexane at 40 °C for 5 h.

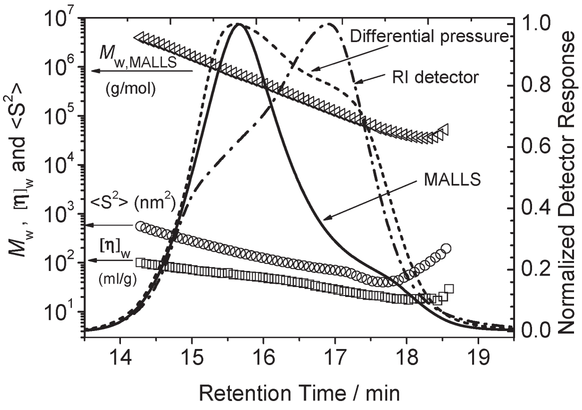


Figure 8. Normalized gel permeation chromatography (GPC) profiles by different detectors: RI, MALLS, and viscometry, and the measured $M_{w,MALLS}$, mean-square radius of gyration $\langle S^2\rangle$, and intrinsic viscosity, $[\eta]_w$, against retention time for the dendritic polystyrene.

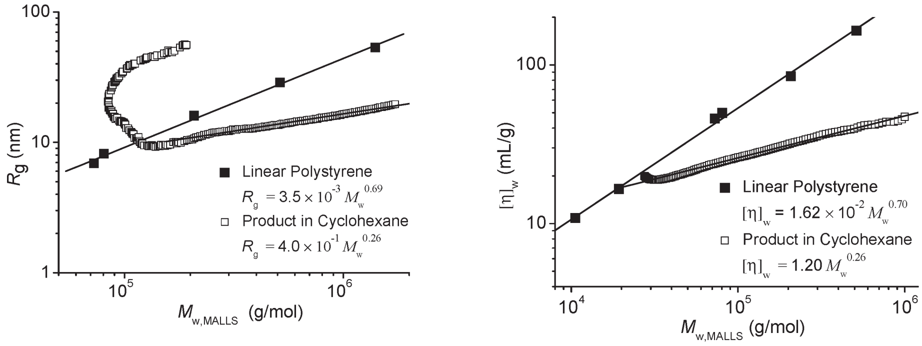
The polymerization product in cyclohexane is analyzed by GPC-MALLS-viscometry measurement. Figure 8 shows normalized GPC profiles of a product (no. 3 in Table 1) recorded by various detectors connected to the GPC system. The profiles are broad multimodal distributions typical for dendritic polymers. The dependences of R_g and $[\eta]_w$ on molecular weight are obtained by calculating these values for every point of the profiles, with each point being considered a narrow disperse fraction separated online by GPC columns. The results are plotted in Figure 9 in double-logarithmic style, in comparison with those of linear polystyrene standards. It is interesting to note a "U-shaped" curve of $R_g \sim M_w$ for the product in cyclohexane. This unusual "U-shaped" curve has been reported many times for highly branched polymers[31-36] and ascribed to delayed elution of extremely large molecular weight species entangled in GPC column packing,[35,36] i.e., at late elution time the elute is composed of normal smaller molecular weight species and delayed larger molecular weight species. Nonetheless, the data before the delayed elution, e.g., at $M_w > 2 \times 10^5$ g/mol in Figure 9, can be used to get the information of chain branching since it is reported that good GPC separation can be achieved in this region as determined by thermal FFF (field flow fractionation)-MALLS measurements.[36] The data before the delayed elution give obviously lower values of R_g and $[\eta]_w$ for product in cyclohexane than the linear standard at the same molecular weight. Furthermore, the dependences of R_g and $[\eta]_w$ on molecular weight at this region are nearly linear that can be fitted to the equation $R_g = kM_w^{\nu}$[37] and the Mark–Houwink–Sakurada equation $[\eta]_w = k'M_w^{\alpha}$ (mL/g),[38] respectively. The slopes of the fitting lines, 0.26 and 0.26 for the dependences of R_g and $[\eta]_w$ on molecular weight, are distinctly lower than those of the product in THF and linear standard, respectively. All these results illustrate that dendritic polystyrene is prepared through the solvent-switching process.

The difference of polymerization behavior in THF and cyclohexane is a consequence of kinetically controlled reaction process. First, the polymerization rate of styrene in the latter is much slower than in the former because the propagating anions are more aggregated in hydrocarbon solvent. In general, it takes 2–5 h to complete the polymerization in the latter whereas only 10 min is necessary in the former. Second, the ratio of initiation and propagation rate constants seems to be in an appropriate range in nonpolar

Table 1. Polymerization Conditions and the Characterization Results of the Products

run[a]	MDDPE[b] (mmol)	styrene (g)	$M_{n,theo} \times 10^{-3}$ (g/mol)	$M_{n,GPC} \times 10^{-3}$ (g/mol)	$M_{w,GPC} \times 10^{-3}$ (g/mol)	M_w/M_n (GPC)	$M_{w,MALLS} \times 10^{-3}$ (g/mol)	$[\eta]_w$ (mL/g)	g' [c]
1	0.40	1.8	4.50	8.80	18.3	2.18	35.1	12.2	0.49
2	0.27	2.7	10.0	28.0	48.4	1.73	86.6	25.1	0.54
3	0.27	4.5	16.7	41.0	102.1	2.49	205.0	42.6	0.44
4	0.20	4.5	22.5	66.0	109.6	1.66	235.3	48.2	0.52
5	0.35	0.9	2.60	10.1	18.1	1.78	25.5	19.9	1.01
6	0.35	1.8	5.10	18.8	38.5	2.02	44.3	29.4	1.01
7	0.35	2.7	7.70	28.1	69.3	2.45	75.2	42.1	1.00
8	0.35	3.6	10.3	36.7	89.4	2.42	97.6	50.1	1.00

[a] Samples 1–4: polystyrenes synthesized by solvent switching process; samples 5–8: polystyrenes synthesized in THF. [b] The feed moles of BuLi are equal to those of MDDPE in all runs. [c] $g' = [\eta]_{w,branched}/[\eta]_{w,linear}$.



a) **b)**

Figure 9. Molecular weight dependence of radius of gyration, R_g (a), and intrinsic viscosity (b) for products prepared in cyclohexane (solvent switching) (□) and linear polystyrene standard (■).

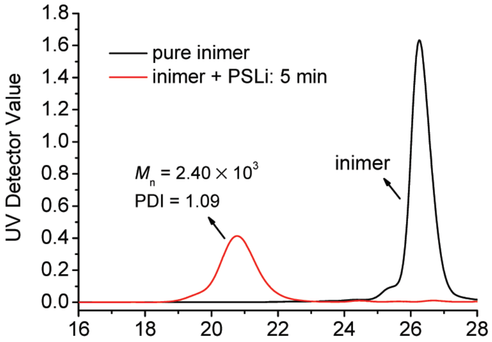


Figure 10. Gel permeation chromatography (GPC) profiles of the reaction mixtures of polystyryllithium (PSLi) with the inimer in cyclohexane. Preparation of PSLi: styrene: 0.90 g, 8.6 mmol; *sec*-BuLi: 0.48 mmol; temperature: 40 °C; cyclohexane. Preparation of inimer: *sec*-BuLi: 0.27 mmol; 1,3-bis(1-phenylethenyl)benzene: 0.08 g, 0.27 mmol; temperature: −78 °C; tetrahydrofuran.

solvent. Quirk and co-workers[39] have reported a value of $k_i/k_p = 0.12$ as measured for styrene polymerization initiated by PS-DPELi in cyclohexane. The value of k_i/k_p in the present work may be close to that measured by Quirk because of the similar reaction conditions. Finally, the addition of the propagating chains toward inimer is fast as observed in model reaction IV between PSLi and the inimer in cyclohexane, shown in Figure 10. After 5 min, the inimer has disappeared completely, which is in sharp contrast to the result of the same model reaction in THF shown in Figure 5.

Table 1 summarizes the polymerization and characterization results of products with and without the solvent-switching process. The branched structure is illustrated by contraction factor $g' = [\eta]_{\text{dendritic PS}}/[\eta]_{\text{linear PS}}$.[40,41] An average value of $g' \approx 0.5$ is obtained for samples from the solvent-switching system while the value for the product of polymerization in THF is 1.0. These distinct values indicate that the polymerization proceeds in different ways between the two systems. We have intended to control the branching ratio by varying the feed molar ratio of inimer to monomer. However, no effect was observed since all of the contraction factors are around 0.5. Thus, it seems that g' value is insensitive to the branching ratio varying in the range of the present work.

Conclusion

Dendritic polystyrenes are prepared by copolymerization of styrene and an anionic inimer through a solvent-switching process. The inimer is synthesized by quantitative monoaddition of *sec*-BuLi and MDDPE in THF. The high purity of inimer, free of residual divinylic species, leads to highly branched product free of gel in the further copolymerization in cyclohexane. The products show reduced radius of gyration, R_g, and intrinsic viscosity, $[\eta]_w$, as compared with linear polystyrene because of the more compact conformation. Owing to the versatility of anionic reactions, the present approach can be used to prepare dendritic polymers with various terminal functionalities, which is currently under investigation.

It is expected that dendritic polydienes can be prepared using the same process. However, our preliminary result indicates that isoprene polymerization initiated by the inimer gives only linear product even with the solvent switching process. This may be a consequence of different rates of kinetic steps in styrene and isoprene systems. Therefore, it seems that the method explored in the present work is, in current view, quite specific for styrene polymerization.

Acknowledgment. The financial support by BASF Co. is highly appreciated. We thank Dr. Bruchmann, ZKT, BASF, Ludwigshafen, and Dr. Ma Lian, BASF (China) Co. Ltd., for their helpful discussions. J.H. and Y.Y. thank the MOE fund of FANEDD (200324) and NSFC program "Excellence in Research Groups" (20221402) and (20674008). Part of this work was orally presented on JKIS2008. J.H. thanks the helpful discussions with Professor Akira Hirao, Nikos Hadjichristidis, and Toyama Higashihara.

Supporting Information Available: HPLC and ^{13}C NMR data of the inimer, GC-MS of minor components, and ^{1}H NMR data of the product in THF. This material is available free of charge via the Internet at http://pubs.acs.org.

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