Synthesis of Graft Copolymers with “V-Shaped” and “Y-Shaped” Side Chains Via Controlled Radical and Anionic Polymerizations

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ABSTRACT: A combination of nitroxide-mediated radical polymerization and living anionic polymerization was used to synthesize a series of well-defined graft (co)polymers with “V-shaped” and “Y-shaped” branches. The polymer main chain is a copolymer of styrene and p-chloromethylstyrene (PS-co-PCMS) prepared via nitroxide-mediated radical polymerization. The V-shaped branches were prepared through coupling reaction of polystyrene macromonomer, carrying 1,1-diphenylethylene terminus, with polystyryllithium or polyisoprenyllithium. The Y-shaped branches were prepared through further polymerization initiated by the V-shaped anions. The obtained branches, carrying a living anion at the middle (V-shaped) or at the end of the third segment (Y-shaped), were coupled in situ with pendent benzyl chloride of PS-co-PCMS to form the target graft (co)polymers. The purified graft (co)polymers were analyzed by size exclusion chromatography equipped with a multiangle light scattering detector and a viscometer. The result shows that the viscosities and radii of gyration of the branched polymers are remarkably smaller than those of linear polystyrene. In addition, V-shaped product adopts a more compact conformation in dilute solution than the Y-shaped analogy. © 2007 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 45: 4013–4025, 2007
Keywords: anionic polymerization; graft copolymers; macromonomer; nitroxide-mediated radical polymerization

INTRODUCTION

A new trend in living anionic polymerization is the synthesis of polymers with nonlinear structures such as star, graft, arborescent, dendritic, and dendrimer-like polymers.1–20 Owing to the living nature of anionic polymerization, the structure of subunits in these polymers, such as arms, branches, and grafts, and so forth can be well controlled in terms of molecular weight and polydispersity. It is also possible to make topological tailoring on the subunits using reactions of anion with some functional compounds. These architectural parameters are very important in the study of structure–property relationship.

Specifically, graft (co)polymers with a diversity of architectures such as conventional graft and its block copolymer with linear segments,21–26 star-graft,26,27 block-graft,25,28,29 and centipede-type graft30–36 structures were synthesized by anionic polymerization. These synthetic works...
employed various methodologies. Hadjichristidis and coworkers developed a chlorosilane coupling technique since a long time, which was then intensively applied in their group to synthesize a variety of polymers with comb-like, star-like, comb-on-comb, double combs, “centipedes,” block-comb/graft, and barbwire-like architectures. These syntheses were fulfilled mostly through a macromonomer strategy. Hirao and coworkers employed coupling chemistry of polymer anion with benzyl halide to prepare high-density branched polymers carrying two branch chains in each repeating unit (“V-shaped” branches). The same coupling chemistry was previously used by Gauthier and coworkers to prepare uniformly branched or arborescent polymers. Lu and coworkers used the addition reaction of polymeric anion toward pendent 1,1-diphenylethylene (DPE) moiety of a poly styrene main chain to synthesize high-density comb-like structure. Most recently, the coupling reaction of anion with alkylaldehyde and chlorosilane finds their way in the synthesis of dendritic or dendrimer-like structures through either divergent or convergent process. Meanwhile, the synthesis of arborescent and graft copolymers with controlled structural parameters was also reported by other living polymerization methodologies.

In a previous work, we have reported the synthesis of ABC-type miktoarm star copolymers using 1,3-bis(1-phenylvinyl)benzene (m-DDPE) as the linking precursor. A key step of the procedure is the coupling of poly styrene macromonomer, formed by monoaddition of polystyryllithium toward m-DDPE, with poly isoprenyllithium to produce PS-b-PI diblock copolymer carrying an anionic center, or a V-shaped anion. By controlling the reaction conditions, we were able to obtain quantitative yield of macromonomer and the coupled product. The resulting V-shaped anion can initiate the polymerization of the third monomer to produce star-like, or “Y-shaped” anion (Scheme 1). In the present work, we extended the synthetic work to the synthesis of graft (co)polymers with V-shaped or Y-shaped branches via coupling reaction of aforementioned polymer anions with the pendant benzyl chloride groups of copolymers of styrene and p-chloromethylstyrene (PS-co-PCMS) produced by nitroxide-mediated radical polymerization (NMRP). A number of graft (co)polymers with well-defined V-shaped or Y-shaped branches were obtained (Scheme 2). To our knowledge, graft polymers with precisely Y-shaped branches have never been reported.

**EXPERIMENTAL**

**Materials**

Styrene (China National Pharmaceutical, >99%) and isoprene (Alfa Aesar, 99%) were stirred over calcium hydride, distilled, and stored under nitrogen atmosphere at 4 °C. These monomers were redistilled over di-n-butylmagnesium (MgBu₂ for styrene) (Aldrich, 1.0 M in heptane) and polystyryllithium (isoprene) before use. p-Chloromethylstyrene (Aldrich, 90%) was freshly distilled over calcium hydride and stored under nitrogen atmosphere. Methanol (Shanghai Ling Feng Chemical Reagent Co., 99.5%) was degassed by freeze-pump-thaw process and stored in ample at 4 °C. 2,2′-Azobisisobutyronitrile (AIBN, Shanghai 4th Factory of Chemicals, 99%) was recrystallized from methanol. 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) (Aldrich, 98%) was used as received. Cyclohexane (Shanghai Feida, 99.5%) and tetrahydrofuran (THF) (Shanghai Feida, 99.5%) were refluxed over sodium in the presence of benzophenone until a purple color was attained. These solvents were redistilled from 1,1-diphenylethyllithium [DPELi, adducts of sec-butyl lithium (sec-BuLi) and DPE] or PSLi in a vacuum line before use. sec-BuLi (Acros, 1.1 M in cyclohexane/heptane) and methyllithium (Acros, 1.6 M in diethyl ether) were used as received. The concentration of sec-BuLi was analyzed by double titration. Methyltriphenylphosphonium bromide (Lancaster, >98%) and 1,3-dibenzoylbenzene (Aldrich, 98%) were vacuum-dried at 50 °C for 12 h. m-DDPE was synthesized from 1,3-dibenzoylbenzene via the Wittig reaction of methyltriphenylphosphonium bromide and methyllithium in ether according to the synthetic route applied by Schulz and Hocker to obtain a clear oil in 50% yield (purity 99.2% by high performance liquid chromatography).

**H NMR (CDCl₃):** δ (ppm) 7.36 (m, 14 H, aromatic), 5.47 (m, 4 H, =CH₂), GC–MS: 99.1%, m/e = 282. ELEM. ANAL.: Calcd. for C₂₂H₁₈: C, 93.6%; H, 6.4%. Found: C, 93.0%; H, 6.5%. FT-IR (NaCl): ν = 3080 cm⁻¹ (=CH₂), 1610, and 1493 cm⁻¹ (aromatic ring). UV–vis (cyclohexane): λ_max (by second derivative) = 223, 234, 252, 258, 264, 267, 271, 284, and 292 nm.
Copolymers of Styrene and \( p \)-Chloromethylstyrene

In a typical copolymerization of styrene and \( p \)-chloromethylstyrene, styrene (100.0 g, 0.97 mol), \( p \)-chloromethylstyrene (16.1 g, 0.11 mol), TEMPO (0.49 g, 3.10 mmol), and AIBN (0.34 g, 2.10 mmol) were placed into a 250-mL round-bottom flask, sealed with a rubber septum. After three freeze–pump–thaw cycles, the flask was placed in an oil bath at 125 °C, samples were taken for analysis at predetermined time. Twelve hours later, the polymerization was quenched with liquid nitrogen. The resulted copolymer was dissolved in toluene and precipitated in methanol several times. The copolymer was dried under vacuum until constant weight. \( M_w \)_{MALLS} = 23.0 \times 10^3 \text{ g/mol}, \( M_w \)_{GPC} = 20.3 \times 10^3 \text{ g/mol}, \( M_w / M_n = 1.20 \), Conversion: 58.7%.

Synthesis of Graft Copolymers Carrying V-Shaped and Y-Shaped Branches

All the reactions were performed in glass apparatus consisting of round-bottom flasks connected to the vacuum line, equipped with inert
gas (Ar or N₂) inlet and a rubber septum. Before polymerization, the glass apparatus was dried by three cycles of flaming/N₂-purging/evacuating, then rinsed with a dilute solution of sec-BuLi in cyclohexane. All the reactions were conducted under N₂ atmosphere.

**Synthesis of PS Macromonomer**

An orange solution of polystyryllithium \( (M_n,\text{GPC} = 5.1 \times 10^3 \text{ g/mol}, M_w/M_n = 1.06) \), prepared by anionic polymerization of styrene \( (1.80 \text{ g, 0.02 mol}) \) in cyclohexane \( (35 \text{ mL}) \) at \( 35^\circ \text{C} \) initiated by sec-BuLi \( (0.3 \text{ mL, 0.4 mmol, cyclohexane/heptane solution}) \), was slowly added to the \( m\)-DDPE \( (0.14 \text{ g, 0.50 mmol}) \) solution in THF \( (100 \text{ mL}) \) under vigorous stirring at \( -78^\circ \text{C} \). Upon mixing, the solution turned dark-red immediately, indicating the addition of PSLi to the double bond of \( m\)-DDPE. The polymerization ran for 5 h, and terminated by degassed methanol. The polymer was precipitated in large amount of methanol, filtered for three times, and then vacuum dried at \( 50^\circ \text{C} \) for 48 h until constant weight. Yield: 97%. \( M_n,\text{GPC} = 5.3 \times 10^3 \text{ g/mol}, M_w/M_n = 1.06; M_n,\text{NMR} = 4.8 \times 10^3 \text{ g/mol}. \)

**Synthesis of V-Shaped Branches**

The obtained PS macromonomer \( (1.75 \text{ g, 0.36 mmol}) \) was dissolved in cyclohexane \( (30 \text{ mL}) \) and titrated with a dilute solution of DPELi until a pale yellow color persisted for nearly half an hour. The solution was added to a solution of polyisoprenyllithium \( (M_n,\text{GPC} = 4.9 \times 10^3 \text{ g/mol, } M_w/M_n = 1.09) \) in cyclohexane \( (30 \text{ mL}) \) prepared from polymerization of isoprene \( (1.70 \text{ g, 0.03 mol}) \) initiated by sec-BuLi \( (0.38 \text{ mmol, 0.3 mL of cyclohexane/heptane solution}) \) at \( 35^\circ \text{C} \). THF \( (0.6 \text{ mL, } [\text{THF}]/[\text{Li}] = 20) \) was added to the mixture as a polar additive and the color turned red immediately upon mixing, indicating the occurrence of the coupling reaction of polymer anion toward the DPE terminus. The mixture was stirred at \( 30^\circ \text{C} \) for 4 h and an aliquot was taken for gel permeation chromatography (GPC) characterization. \( M_n,\text{GPC} = 10.9 \times 10^3 \text{ g/mol, } M_w/M_n = 1.10. \)

The coupling reaction of polystyryllithium \( (M_n,\text{GPC} = 5.4 \times 10^3 \text{ g/mol, } M_w/M_n = 1.05) \) with PS macromonomer \( (1.75 \text{ g, 0.36 mmol}) \) was carried out at \( 25^\circ \text{C} \) under otherwise identical reaction conditions. \( M_n,\text{GPC} = 12.3 \times 10^3 \text{ g/mol, } M_w/M_n = 1.09. \)

**Synthesis of Y-Shaped Branches**

The earlier obtained V-shaped branches in the coupling reaction of macromonomer with either polyisoprenyllithium or polystyryllithium, with polymer anion in the center, were further used to initiate the polymerization of styrene or isoprene to get the Y-shaped branches with different sequence of PS and PI segments. A typical reaction process was as follows: styrene \( (1.80 \text{ g, 0.02 mol}) \) was added \( \textit{in situ} \) to the mixture of the finished coupling reaction of polyisoprenyllithium \( (M_n,\text{GPC} = 5.4 \times 10^3 \text{ g/mol, } M_w/M_n = 1.05) \) with PS macromonomer \( (1.75 \text{ g, 0.36 mmol}) \) in cyclohexane \( (30 \text{ mL}) \) at \( 30^\circ \text{C} \). An aliquot of the reaction mixture was taken for analysis. \( M_n,\text{GPC} = 15.1 \times 10^3 \text{ g/mol, } M_w/M_n = 1.21. \)

Further polymerization of isoprene \( (1.70 \text{ g, 0.03 mol}) \) initiated by the V-shaped branches was performed in an ice/water bath \( (0^\circ \text{C}) \) under otherwise identical conditions. \( M_n,\text{GPC} = 15.4 \times 10^3 \text{ g/mol, } M_w/M_n = 1.19. \)

**Coupling of V-Shaped and Y-Shaped Polymer Anions with Pendent Benzyl Chloride of PS-co-PCMS**

Before coupling, the reaction solution of V-shaped polymer anion was diluted with threefold
volume of THF at -78 °C, whereas Y-shaped polymer anion was end-capped with DPE (0.16 g, 0.90 mmol) in cyclohexane for 1 h and then in cyclohexane/THF (1/3 v/v) for another 1 h. These solutions were then added to a solution of PS-co-PCMS (0.34 g, 0.02 mmol) in THF (15 mL) with vigorous stir at -78 °C while keeping [Li]/[Cl] = 1.5:1. The reaction of anion with benzyl chloride was evidenced by the immediate color change, from dark red to pale red, after mixing of the two solutions. The excessive anion was finally quenched by degassed methanol. The product was purified by the following fractionation procedure: the crude product was dissolved in toluene to a concentration of 1.3% (3.2 g/250 mL). Methanol (100 mL) was added slowly to the solution under continuous agitation at room temperature until the solution became slightly cloudy. An extra 5 mL of methanol was dropped in. Then the solution was heated up until it became clear, followed by cooling to room temperature overnight. Two phases with clear interface were observed. The concentrated (lower) phase was carefully isolated and the polymers were precipitated in methanol. For the samples containing polyisoprene segment, 2,6-di-tert-butyl-4-methylphenol (BHT, 1% w/v) was used as stabilizer.

Characterization

High performance liquid chromatography 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. 1H NMR measurements were carried out on a Bruker (500 MHz) NMR instrument, using CDCl3 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).

The number-average molecular weight, \( M_n \), and polydispersity index, \( M_w/M_n \), were measured by GPC through three Waters Styragel columns (pore size 10^2, 10^3, and 10^4 Å) in series calibrated by narrow polystyrene standard with molecular weight ranging from 2.20 × 10^3 to 5.15 × 10^5 g/mol. THF was used as the eluent at a flow rate of 1.0 mL/min at 40 °C. The elution of the sample was detected by a Waters 410 RI detector.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) MS was performed on Voyager DE-STR (MALDI-TOF MS) instrument equipped with a 337-nm nitrogen laser. Samples, dithranol (matrix), and silver trifluoroacetate were dissolved in THF with the concentrations of 10, 20, and 10 mg/mL, respectively. These solutions were mixed in the volume ratio of matrix/polymer/salt = 10/2/1. A volume of 0.5 μL of the mixed solution was placed on a copper plate and air-dried at ambient temperature. Mass spectra were acquired in positive reflection mode using an acceleration voltage of 25 kV. External mass calibration was performed using a standard peptide mixture (insulin, thioredoxin). Spectra were obtained by setting the laser power close to the threshold of ionization, and generally 700 pulses were acquired and averaged.

GPC-MALLS-Viscosity-DRI analysis was performed using a Wyatt system equipped with a Water 515 pump, three ME-gel SD Plus columns (10^3, 10^5, 10^6 Å in series), DAWN HELEOS (14–154 Å) (Wyatt multangle LS detector, He–Ne 658.0 nm), ViscoStar (Wyatt viscosity detector), and Optilab rEX (Wyatt RI detector). THF was used as eluent at a rate of 1 mL/min at 35 °C.

Laser light scattering was performed on an ALV/DLS/SLS-5022F spectrometer with a multi-τ digital time correlation (ALV5000) and a cylindrical 22 \( M_w \) UNIPHASE He–Ne laser (\( λ_0 = 632 \) nm) as the light source at 25 °C. Toluene was used as the solvent. The weight average molecular weight (\( M_w \)) and radius of gyration (\( R_g \)) were measured by static LLS with the scattering angle from 20° to 150°. The refractive index increment (dn/dc) was used 0.108, and the concentration (c) of each polymer ranged from 0.8 × 10^{-3} to 2.0 × 10^{-1} g/mL. The hydrodynamic radius (\( R_h \)) was measured by dynamic light scattering (DLS). Hydrodynamic radius distribution \( f(R_h) \) was calculated from the Laplace inversion of the intensity–intensity time correlation function \( G^{(2)}(t,q) \) using the CONTIN program. All DLS measurements were performed at a scattering angle (θ) of 20°.

RESULTS AND DISCUSSION

Synthesis of V-Shaped and Y-Shaped Graft Copolymers

Graft (co)polymer carrying V-shaped and Y-shaped branches were synthesized via the
"grafting-onto" methodology in which the polymer anions were coupled with the pendent benzyl chloride group of the polymer main chain. The synthetic route is outlined in Scheme 1. The process was developed by Hadjichristidis and coworkers in the synthesis of conventional graft, linear-graft diblock, graft-graft diblock as well as graft copolymers carrying diblock side chains.

**Synthesis of the PS-co-PCMS**

The polystyrene polymer main chain, with a fraction of pendent benzyl chloride groups, was synthesized by NMRP in the presence of p-chloromethylstyrene as the comonomer. To obtain narrow disperse product, the feed molar fraction of comonomer was relatively low, 10%, because it was reported that p-chloromethylstyrene can broaden the molecular weight distribution in the case of NMRP. The copolymerization proceeded in a living fashion, as demonstrated by linear growth of molecular weight with monomer conversion and the low polydispersity index of the resulting copolymer (Supporting Information). From 1H NMR spectrum (Supporting Information), the ratio of styrenic and chloromethylstyrenic units was estimated to be 11.4/1. GPC-MALLS result showed that the weight-average molecular weight of PS-co-PCMS was $23.0 \times 10^3$ g/mol with the polydispersity index 1.08. Thus the average number of chloromethylstyrene units in each polymer chain, $N_{Cl}$, is $\sim 17$. The very sample was used as the polymer main chain for further grafting reaction.

**Synthesis of PS Macromonomer**

PS macromonomer with DPE terminus was synthesized by addition reaction of polystyryllithium toward one of the double bonds in $m$-DDPE in polar solvent. The key factor to the success is to control the reaction conditions to obtain monoadduct that is free of diadduct (coupled) product. It was reported that the relative reactivity of the two double bonds of $m$-DDPE depends on the polarity of the solvent. In nonpolar solvents such as cyclohexane and benzene, the two double bonds show equal reactivity and, therefore, diadduct is predominant, as in the syntheses of dilithium initiator, A2B2 star polymers, and cyclic polymers. The coupling efficiency is as high as 87% even in threefold molar excess of $m$-DDPE in cyclohexane. However, in polar solvent such as THF or THF/cyclohexane mixture, the same reaction leads to 90–95% yield of monoadduct.

Therefore, the preparation of macromonomer was conducted in THF/cyclohexane (3/1 v/v). The results of GPC in Figure 1 and MALDI-TOF MS in Figure 2 clearly show no sign of...
coupled product, demonstrating the exclusive formation of monoadduct. MALDI-TOF MS shows an interval of two neighboring peaks, 104.12 g/mol, which is equal to the molecular weight of styrenic repeating unit. The peak value, for example 4825.70 g/mol, corresponds to those polymer chains with 42 styrenic repeating units, for example, C4H9(C8H8)42C22H19/Ag⁺ = 4824.40 g/mol, within the range of system error, ±0.15%. In addition, the signals are free of side peaks, indicating high efficiency of the monoadduct formation. MALDI-TOF MS result is in consistence with 1H NMR shown in Figure 3, from which a functionality of 95% was estimated by the ratio of the signal area of methyl group (derived from sec-BuLi fragment at 0.46–0.83 ppm) and the remaining double bond (from m-DDPE at 5.21–5.53 ppm), as well as the methine proton appeared at chemical shift of 3.47 ppm.

**Synthesis of V-Shaped and Y-Shaped Branches**

The V-shaped branches were synthesized by coupling reaction of PS macromonomer with another polymer chain, polystyryllithium or polyisoprenyllithium, following the process developed by Quirk and coworkers, in which stoichiometric reaction was achieved with the aid of THF ([THF]/[Li] = 20, molar ratio). The presence of THF promoted the rate of coupling reaction as indicated by the immediate color change from pale yellow to dark red upon THF addition. The resulting V-shaped polymer anion was used to initiate further polymerization of styrene or isoprene to prepare Y-shaped branches. Figures 4 and 5 show the GPC monitoring the whole process of the grafting reaction. From curves a, b, and c in both figures, the efficiency of the coupling reaction is evident, with slightly tailing effect because of uncoupled PS macromonomer and polyisoprenyllithium. Curve d in Figure 5 shows further increase in molecular weight caused by polymerization of styrene initiated by the V-shaped anion to form a three-arm star polymer anion, the Y-shaped branches. However, a broadening effect was observed from curves c to d in Figure 5, which was attributed to slow initiation of the third arm by DPELi moiety of V-shaped precursor. Indeed, Quirk and Lee reported that the crossover initiation of styrene by DPELi functionality was slow. In addition, there is also possibility for occasional termination of V-shaped branches by impurity in the third monomer. Therefore, the tailing of the Y-shaped branches is due to uninitiated and/or terminated V-shaped branches, together with those residual species coming from the preceding coupling reaction. The content of Y-shaped branches was roughly estimated to be 92% from the area of the main symmetric peak after

![Figure 3](image-url)  
**Figure 3.** 1H NMR of PS macromonomer. The reaction conditions are identical to those in Figure 1.
fitting curve d to Gaussian function in Origin® software (Fig. 5 dashed lines. Note: the contaminating species were shown presumably in one side peak in the fitting). Therefore, the relative content of Y-shaped functionality is high in the final product despite the presence of various species.

**Coupling of V-Shaped and Y-Shaped Polymer Anions to PS-co-PCMS**

The prepared V-shaped and Y-shaped branches were grafted *in situ* onto polystyrene main chain through the nucleophilic attack of polymeric anion toward the pendant benzyl chloride group of the main chain. To eliminate the side reaction such as lithium-halide exchange, the solvent for coupling reaction was switched from cyclohexane to THF/cyclohexane (v/v), and the reactivity of polymeric anion was lowered, if necessary, by end-capping with DPE. Furthermore, ~50% excess of polymer anions was used to ensure that all chlorine was replaced by the branches.

The coupling process was monitored by GPC. Curves c, d, and e in Figure 4 represent GPC traces of V-shaped polymer anion, the PS-co-PCMS main chain, and the resulting crude graft copolymer, respectively. It is clear that the excess V-shaped polymer chains exist in the crude product. Through fractionation, these excess chains were easily removed and narrow disperse graft product, $M_w/M_n = 1.18$, was obtained, as shown by curve f in Figure 4. Similar results were obtained in the synthesis of Y-shaped graft copolymers, except that the polymer anion was end-capped with DPE, as indicated by curves d and e in Figure 5.

A series of graft (co)polymers with V-shaped and Y-shaped branches were synthesized with various sequences of PS and PI segments as shown in Scheme 2 and the characterization of these graft (co)polymers are summarized in Table 1. The number of branches per molecule can be estimated from the weight-average molecular weights of the branches, the main chain, and the final graft (co)polymers.

![Figure 5. Gel permeation chromatograms (GPC) traces of the synthesis of Y-shaped graft copolymer S-g-(Y-ISS).](image)

A representative $^1$H NMR spectrum was shown in Figure 6 for S-g-(Y-ISS). Because PI segment was prepared before addition of THF, the content of 1,4-enchainment of polyisoprene segment is as high as 90%, as estimated by signal intensities at chemical shifts of 4.68–5.13 ppm. However, for those samples in which PI segment was prepared after THF addition ([THF]/[Li] = 20, molar ratio), for instance S-g-(Y-SSI), only 45% 1,4-enchainment of polyisoprene was observed by $^1$H NMR.

**Dilute Solution Properties of the Graft (co)Polymers**

It is well established that the branched polymers exhibit different solution properties, such as reduced viscosity and more compact globular structure, than their linear counterparts. The V-shaped and Y-shaped graft copolymers were

analyzed by GPC-MALLS-Viscosity-DRI measurement, using a dilute solution of 4–5 × 10⁻³ g/mL. The analysis takes the advantage of online GPC separation of the samples into numerous slices, which are then subject to MALLS and intrinsic viscosity measurements.

Figure 7 shows representative profiles for the normalized response intensities of different detectors against retention time. These profiles closely overlap and show symmetric monomodal distribution of the purified graft polymer. The dependence of $M_w$ on retention time (or elution volume) is nearly linear within the whole range, whereas the mean square radius of gyration, $<S>^2$, becomes rather scattered at low molecular weight tail because of the accuracy limit of...

<table>
<thead>
<tr>
<th>Sample</th>
<th>First Block $^a$</th>
<th>$M_w,MALLS$ ($×10^3$ g/mol)</th>
<th>$M_w/M_n$ (GPC)</th>
<th>$M_w/GPC$ ($×10^3$)</th>
<th>$M_n,GPC$ ($×10^3$)</th>
<th>$η_w$ (mL/g)</th>
<th>BF $^e$ (%)</th>
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<tr>
<td>S-$g$-(V-SS)</td>
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<td>11.2</td>
<td>1.06</td>
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<td>1.06</td>
<td>13.1</td>
<td>9.4</td>
</tr>
</tbody>
</table>

$^a$ For example, sample S-g-(Y-ISS) means a graft copolymer with PS as polymer main chain and ISS star copolymer as ‘‘Y-shaped’’ branches.

$^b$ Represents the PS macromonomer in ‘‘V-shaped’’ and ‘‘Y-shaped’’ graft polymers.

$^c$ The coupling product of polystyryllithium or polyisoprenyllithium with PS macromonomer.

$^d$ PS-$co$-PMS copolymer with $M_w,MALLS = 23.0 × 10^3$ g/mol was used as polymer main chain in all cases.

$^e$ Branching functionality was given by the relationship: $BF = N_{branch}/N_{Cl} = [(M_w,Graft – M_w,Backbone)/M_w,Branch]/N_{Cl}$.

Figure 6. $^1$H NMR of S-$g$-(Y-ISS) graft copolymer.
MALLS. Thus, only those values larger than 100 nm$^2$ were used in the following analysis.

Figure 8 depicts $R_g$s as a function of molecular weight for both V-shaped and Y-shaped graft homopolystyrene. The $R_g$s of linear polystyrene standard with different molecular weight are also included as the reference. The fitting straight line for the linear polystyrene gives a slope 0.70, which is larger than those reported in the literature. The larger value is possibly due to higher temperature in the present measurement.

Figure 8 shows that, under the same conditions, the absolute size decrease in the order of PS > S-g-(Y-SSS) > S-g-(V-SS). This indicates that, while both graft polymers display compact structure, the V-shaped product adopts the most compact conformation in dilute solution.

Figure 9 plots the Mark–Houwink–Sakurada (MHS) equation,

$$[\eta]_w = K M_w^{\alpha} (\text{mL/g})$$

for S-g-(V-SS), S-g-(Y-SSS), and linear polystyrene reference. The exponent for linear polystyrene is 0.70, in agreement with those reported in the literature. The exponents for V-shaped and Y-shaped branched polystyrenes are 0.59 and 0.38, respectively, within the range for branched polymers.

The conformation density of graft or branched polymers is often described by contraction factors, $g'$, defined as the ratio of intrinsic viscosities of branched and linear polymers at the same molecular weight. For S-g-(V-SS) and S-g-(Y-SSS), the $g'$ can be written as:

$$g'_V = \frac{[\eta]_{S-g-(V-SS)}}{[\eta]_{\text{linear}}}$$

and

$$g'_Y = \frac{[\eta]_{S-g-(Y-SSS)}}{[\eta]_{\text{linear}}}$$

at the same molecular weight.

Strictly, eq 1 is valid at $\theta$ condition. However, GPC measurement is normally performed in good solvent, such as THF for polystyrene in the present work. Figure 10 shows $g'_V$ and $g'_Y$ for
GPC slices of the samples S-g-(V-SS) and S-g-(Y-SSS), respectively. An average value of $g'_V = 0.28$ and $g'_Y = 0.47$ is obtained for V-shaped and Y-shaped graft polystyrenes, respectively. The lower value in the former again implies that the segments are more crowded in V-shaped structure. In this sense, the third arm of the Y-shaped branches can be viewed as a spacer between polymer main chain and the V-shaped branches, leading to a more loose conformation of the product. It is interesting to note that $g'_V$ is remarkably larger than that obtained by Hirao for high density V-shaped branched polystyrene. This is because the current product has lower segment density than the branched polymers prepared by Hirao.

Figures 11 and 12 show the Zimm plots and DLS results of the two samples, S-g-(V-SS) and S-g-(Y-SSS). From Zimm plots we obtain $M_w = 2.44 \times 10^5$ and $2.07 \times 10^5$ g/mol for S-g-(V-SS) and S-g-(Y-SSS), respectively, with the corresponding $R_g = 11.0$ and 10.3 nm. From DLS results, the average hydrodynamic radius are $R_h = 10.1$ and 9.7 nm for S-g-(V-SS) and S-g-(Y-SSS), respectively. Therefore, both samples give $R_g/R_h \sim 1.0$, indicating sphere-like globular conformations in solution because of their nonlinear structures.

CONCLUSIONS

Well-defined graft (co)polymers carrying V-shaped and Y-shaped branches were synthesized by means of a grafting-onto approach in which V-shaped and Y-shaped polymer anions were coupled to the pendant benzyl chloride of the main chain. The polymer main chain was
prepared by NMRP and the branches by anionic polymerization. Therefore, the molecular parameters, such as the lengths and length distributions of the main chain and the branches, as well as the topological architecture of the branches, can be well-controlled due to the living feature of the polymerization. The products show reduced intrinsic viscosity, $\eta_\infty$, and radius of gyration, $R_g$, because of their nonlinear and more compact structure in dilute solution. In addition, both V-shaped and Y-shaped products show $R_g/R_h \sim 1.0$ in toluene, indicating sphere-like globular conformations.

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REFERENCES AND NOTES