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Reactive Dendronized Copolymer of Styryl Dendron and Maleic Anhydride: A Single Molecular Scaffold

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ABSTRACT: Novel dendronized copolymers bearing reactive anhydride groups along the backbones are reported in this paper. They were synthesized through copolymerizations of styryl macromonomers bearing Fréchet-type dendrons of the first to the fourth generation and maleic anhydride (MAn) through conventional radical polymerization. The dendritic macromonomers were prepared by an accelerated convergent approach, i.e., a reaction of the dendritic bromide of lower generation with a styrene derivative bearing a 3,5-dihydroxybenzyl group. The dendronized copolymers with rather high molar masses were obtained under mild conditions, even for the fourth-generation dendritic monomer as determined by static light scattering (SLS). For example, the degree of copolymerization for the third-generation monomer reached 487. Owing to the reactivity of the anhydride, functional groups, which were buried by the grafted dendrons along the backbone, could be easily introduced as follows: (1) by the hydrolysis under acid conditions, the amphiphilic copolymers with a structure of dendron-*alt*-2COOH were prepared; (2) by reacting with alkyl primary amine, the copolymers with dendron-*alt*-linear alkyl chain were obtained in a quantitatively yields; (3) when reacted with a primary amino dendron of its generation different from the pendent dendron, a series of new dendronized copolymers with their side dendrons grafted in an alternative generation structure were produced. Therefore, the novel reactive dendronized copolymer presented herein can be a single molecular scaffold to be applied in nanomaterials and nanotechnologies of one dimension.

Introduction

Dendronized polymers are linear polymers of their repeating units pendent with dendritic wedges as the bulky side groups along the main chains.[1−3] The most important feature concerning these novel grafted polymers is the conformation of the whole polymers. With increase of the steric repulsion between the bulky side groups along the backbone, the polymer main chains prone to extend and transfer from random coils to rodlike cylinders. When the main chains are longer enough and dendritic wedges are large enough, huge single molecular nanorods have been obtained.[4−8] Since the size and branch number of the side dendron are tailored precisely during the synthesis of dendron by changing generation number, diameter and flexibility of the dendronized polymers can be controlled precisely. These rodlike polymers, together with the cylindrical polymer brushes, have attracted much attention in recent years.[9,10]

The syntheses of dendronized polymers have been achieved through three approaches. The first one is the so-called macromonomer approach, which refers to homopolymerization of the dendritic macromonomer through selected polymerization techniques, such as radical polymerization,[11−13] polycondensation,[14−17] living polymerization,[18] and so on. The advantage of this approach is the uniform structures of the resulting polymers can be guaranteed since every repeat unit bears one dendron. However, it becomes difficult to get the polymers with higher degrees of polymerization (DP) for the dendritic monomers of higher generation due to the steric hindrance. High monomer concentration during the polymerizations was crucial to increase the DP. The second one is the "coupling to" approach, of which to attach dendrons directly to a backbone-to-be polymer containing anchor groups.[19−21] However, its disadvantage is obvious; i.e., it is difficult to ensure completely coverage. Therefore, the coupling chemistry selection and the characterization method on the coupling efficiency are rather important. An extended study has been made by Hawker et al. on the degree of the coverage considering the factors of dendron size and the spacer between two anchor groups along the polymer backbone.[22] The third one is the "grafting from" or divergent approach. Dendrons grow up step by step from the backbone of the polymer, through which extremely long dendronized polymer of high generation can be achieved.[23] Similarly, it has the same problem with the second approach. Some recent review articles have summarized the synthetic strategies in detail.[24,25] Furthermore, dendronized polymers have also been produced through noncovalent interactions.[26]

The interior and the periphery of the dendrimers having different chemistry can supply a single molecular microenvironment, which is used as catalyst support, encapsulation, release, etc.[27−29] This is one of the most interesting features that have attracted researcher's attention since the dendrimers emerged one and half decades ago. Therefore, incorporation of functional groups along the main chains of dendronized polymers can be very important to extend their applications for nanoreactors and one-dimensional nanoparticle arrays being wrapped by dendron wedges. There are two ways to introduce the functional groups on the dendronized polymers. One is introduction of functional groups on the periphery of the polymers.[23] Scrivante et al. have tried to prepare dendronized polymers which carry dendritic polypyridine as side groups by the macromonomer approach for complexation studies.[12] But

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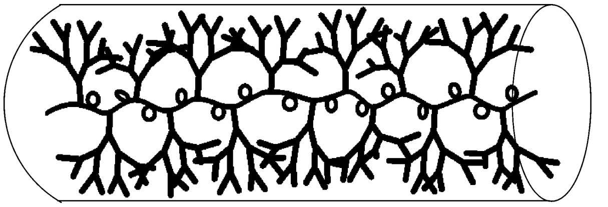
Scheme 1. Cartoon Presentation of Dendronized Copolymer with Reactive Anhydride Groups along the Backbone



polymerization of the third-generation monomer only gave the oligomer. The other one is modifying the backbone of the dendronized polymer, and this may open the possibility to engineer the interior of the polymer. However, to the best of our knowledge, only one example of the dendronized cyclocopolymer bearing pyrrolidinopyridine functional groups was reported recently, and the polymer was used as a catalyst of esterification.[27] The functionalities of the polymer were dispersed randomly along the backbone.

In this paper, we present a family of the dendronized copolymers bearing anhydride groups uniformly distributed along the main chains, as depicted in Scheme 1. It is well-known that copolymerization of maleic anhydride (MAn) and styrene or its derivatives gives alternative copolymers in radical copolymerization. It is likely to incorporate anhydride groups, which are highly reactive, into the backbones of the dendronized polymers through the copolymerization of MAn and the styrene derivatives bearing dendron wedges. Herein, we synthesized the novel dendronized copolymers through the radical copolymerization of maleic anhydride (MAn) and styryl-type macromonomers carrying Fréchet-type polyether dendrons of the first to the fourth generation, respectively. By this way, reactive anhydride groups were easily incorporated alternatively into the backbone with the dendrons pendent. The copolymers with rather high molar masses were obtained even for the third-generation monomer under mild conditions. The functionalization was easily manipulated through chemical reactions of anhydride groups, leading to a series of novel dendronized copolymers with functionalities being buried in the bulky dendrons along the main chain.

Experimental Section

Materials. 3,5-Dihydroxybenzoic acid (97%, Acros), 4-vinylbenzyl chloride (tech 90%, Acros), 18-crown-6 (18-C-6; 99%, Acros), lithium tetrahydroaluminate ($LiAlH_4$; typically 97%, Alfa), sodium hydride (NaH; 60% dispersed in mineral oil, Aldrich), carbon tetrabromide (CBr_4; 99%, Aldrich), 3,4-dihydro-2*H*-pyran (DHP; 99%, Acros), potassium iodide (KI; Beijing Chemicals Co.), anhydrous potassium carbonate (K_2CO_3; AR, Beijing Chemicals Co.), triphenyl phosphine (PPh_3; CP, Shanghai Chemicals Co.), 1-butylamine (CP, Beijing Chemicals Co.), and laurylamine (CP, Beijing Chemicals Co.) were used as received. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. Maleic anhydride (MAn) was recrystallized from benzene. Tetrahydrofuran (THF) was distilled from sodium/benzophenone before use. Chloroform was dried over CaH_2 and distilled before use. Other reagents were used without further purification.

Fréchet-type dendrons, [G-*n*]-Br and [G-*n*]-OH, were prepared according to the literature procedure ([G-*n*] is the generation number of dendron, and X (X = Br, OH) is the functionality of the focal point according to the literature).[30]

Measurement. Polydispersities of polymers, M_w/M_ns, were obtained by SEC equipped with a Waters 515 pump, a Waters 2414 refractive index detector, and a combination of Styragel HT-2, HT-3, and HT-4; the effective molar mass ranges were 100−10000, 500−30000, and 5000−600000, respectively. Linear polystyrene standards were applied as the calibration. The eluent was THF at a flow rate of 1.0 mL/min at 35 °C. A commercial laser light scattering (LLS) spectrometer (ALV/DLS/SLS-5022F) equipped with a multi-τ digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He−Ne laser (λ_0 = 632 nm) was used. The d*n*/d*c* value was measured by a refractometer (Dawn DSP, Wyatt Technology Corp.). All samples were dissolved in THF solvent, and the solutions were filtered through a 0.45 μm PTFE membrane prior to use. The solutions were put in 10 mm diameter glass cells. Static light scattering (SLS) measurements were made from 30° up to 150° at 25.0 °C. The data acquisition was done with the ALV Correlator Control software. MALDI−TOF (matrix-assisted laser desorption and ionization time-of-flight) mass spectrometry was performed on a Bruker Biflex III spectrometer equipped with a 337 nm nitrogen laser. Both matrix 4-hydroxy-α-cyanocinnamic acid (CCA) and sample were dissolved in 1:1 (v/v) acetonitrile:water with 1% trifluoroacetic acid. 0.5 μL of this mixture solution was placed on a metal sample plate and air-dried at ambient temperature. Mass spectra were acquired in positive reflector mode using an acceleration voltage of 19 kV. External mass calibration was performed using a standard peptide mixture. Spectra were obtained by setting the laser power close to the threshold of ionization, and generally 100 pulses were acquired and averaged. FT-IR spectra were recorded by a deuterate triglycine sulfate (DTGS) detector on a Bruker EQUINOX 55 spectrometer and processed by the Bruker OPUS program. THF solution (20 mg/mL) was dropped on KBr flake and dried before tested. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DMX300 spectrometer.

Preparation of Molecules 2, 3, 4, 5, and [G-1]-NH_2. See Supporting Information for details.

Synthesis of Monomer 6 [G-1]. [G-1]-OH (10.0 g, 31.2 mmol) was added to THF (100 mL) solution of sodium hydride (1.62 g, 40.6 mmol). The solution was stirred under nitrogen for 30 min. A solution of 4-vinylbenzyl chloride (5.87 mL, 37.5 mmol) in THF (40 mL) was added, and the reaction mixture was refluxed for 48 h. After the flask was cooled to room temperature, water was added carefully until no bubble escaped. Dilute hydrogen chloride aqueous solution (1 equiv) was added until the pH value reached 5−6. After THF removed by rotary evaporator, the reaction mixture was extracted with dichloromethane, and the combined organic layers were dried over anhydrous sodium sulfate. A kind of viscous oil was obtained after filtration and removal of the solvent. The crude product was purified by column chromatography using petroleum ether/ethyl acetate (16:1 v/v) as eluent. A white powder was obtained; 6.01 g (yield: 44%). ^{1}H NMR ($CDCl_3$) δ: 4.49 (s, 2H, ArCH_2O), 4.52 (s, 2H, CH_2=CHArCH_2O), 5.04 (s, 4H, PhCH_2O), 5.25 (d, 1H, J = 12, CH_2=CH), 5.76 (d, 1H, J = 18, CH_2=CH), 6.56 (s, 1H, Ar*H*), 6.62 (s, 2H, Ar*H*), 6.72 (q, 1H, J_1 = 12, J_2 = 18, CH_2=C*H*), 7.26−7.44 (m, 14H, Ph*H* and CH_2=CHAr*H*). ^{13}C NMR ($CDCl_3$) δ: 70.1 (PhCH_2O), 71.8, 71.9 (CH_2OCH_2), 101.4, 106.6 (Ar*C*), 113.8 (CH_2=CH), 126.3, 127.6, 128.0, 128.6 (CH_2=CHAr*C* and Ph*C*), 136.6, 136.9, 137.9, 140.8 (*C*H=CH_2, Ph*C* and Ar*C*), 160.1 (Ar*C*). Elemental analysis: Calcd for $C_{30}H_{28}O_3$: C, 82.54; H, 6.46. Found: C, 82.64; H, 7.11. MALDI−TOF Mass spectrum: Calcd: [M^+] m/z = 436.2. Found: [M + Na^+]$^+$ = 459.2.

General Procedure for the Synthesis of Monomer 6 [G-2, -3, -4]. A mixture of [G-1]-Br, [G-2]-Br, or [G-3]-Br (2.1 equiv), **5** (1.0 equiv), potassium iodide (2.1 equiv), potassium carbonate (3 equiv), and 18-crown-6 (0.1 equiv) in dry acetone was refluxed under nitrogen for 48 h. The mixture was allowed to cool and evaporated to dryness on rotary evaporator, and the residues were partitioned with dichloromethane and water. The combined organic layers were dried over sodium sulfate and filtered. After removing the solvent, the crude product was purified by column chromatography.

Synthesis of Monomer 6 [G-2]. This was prepared from [G-1]-Br and purified by column chromatography, eluting with 8:1 petroleum ether/ethyl acetate followed by 4:1 petroleum ether/ethyl acetate to give **6** [G-2] as a white powder. Yield: 69%. ^{1}H NMR (CDCl$_3$) δ: 4.48 (s, 2H, ArC*H*$_2$O), 4.51 (s, 2H, CH$_2$=CHArC*H*$_2$O), 4.97 (s, 4H, ArC*H*$_2$O), 5.01 (s, 8H, PhC*H*$_2$O), 5.22 (d, 1H, *J* = 12, C*H*$_2$=CH), 5.73 (d, 1H, *J* = 18, C*H*$_2$=CH), 6.53 (s, 1H, Ar*H*), 6.56 (s, 2H, Ar*H*), 6.59 (s, 2H, Ar*H*), 6.65 (s, 4H, Ar*H*), 6.64 (q, 1H, J_1 = 18, J_2 = 12, CH$_2$=C*H*), 7.28–7.42 (m, 24H, Ph*H* and CH$_2$=CHAr*H*). ^{13}C NMR (CDCl$_3$) δ: 69.8 (Ar*C*H$_2$O), 70.0 (Ph*C*H$_2$O), 71.7 (CH$_2$=CHAr*C*H$_2$O), 71.8 (Ar*C*H$_2$O), 101.3, 101.4, 106.2, 106.5 (Ar*C*), 113.8 (CH=*C*H$_2$), 126.2, 127.5, 128.0, 128.5 (CH$_2$=CHAr*C* and Ph*C*), 136.4, 136.7, 136.9, 137.7, 139.2, 140.7 (*C*H=CH$_2$, Ph*C* and Ar*C*), 159.9, 160.1 (Ar*C*). Elemental analysis: Calcd for $C_{58}H_{52}O_7$: C, 80.91; H, 6.09. Found: C, 81.99; H, 6.36. MALDI–TOF mass spectrum: Calcd: [M$^+$] *m/z* = 860.4. Found: [M + Na$^+$]$^+$ = 883.2.

Synthesis of Monomer 6 [G-3]. It was prepared from [G-2]-Br and purified by column chromatography, eluting with 4:1 dichloromethane/petroleum ether to give **6** [G-3] as a white powder. Yield: 81%. ^{1}H NMR (CDCl$_3$) δ: 4.46 (s, 2H, ArC*H*$_2$O), 4.50 (s, 2H, CH$_2$=CHArC*H*$_2$O), 4.95 (s, 12H, ArC*H*$_2$O), 5.00 (s, 16H, PhC*H*$_2$O), 5.20 (d, 1H, *J* = 12, C*H*$_2$=CH), 5.71 (d, 1H, *J* = 18, C*H*$_2$=CH), 6.54–6.66 (m, 22H, Ar*H* and C*H*=CH$_2$), 7.25–7.40 (m, 44H, Ph*H* and CH$_2$=CHAr*H*). ^{13}C NMR (CDCl$_3$) δ: 69.8 (Ar*C*H$_2$O), 69.9 (Ph*C*H$_2$O), 71.7 (CH$_2$=CHAr*C*H$_2$O), 71.8 (Ar*C*H$_2$O), 101.2, 101.4, 106.2, 106.5 (Ar*C*), 113.7 (CH=*C*H$_2$), 126.2, 127.5, 127.7, 127.9, 128.5 (CH$_2$=CHAr*C* and Ph *C*), 136.4, 136.6, 136.8, 137.6, 139.1, 139.2, 140.7 (*C*H=CH$_2$, Ph*C* and Ar*C*), 159.9, 160.0 (Ar*C*). Elemental analysis: Calcd for $C_{114}H_{100}O_{15}$: C, 80.07; H, 5.89. Found: C, 80.64; H, 6.27. MALDI–TOF mass spectrum: Calcd: [M$^+$] *m/z* = 1709.7. Found: [M + Na$^+$]$^+$ = 1732.0.

Synthesis of Monomer 6 [G-4]. This was prepared from [G-3]-Br and purified by column chromatography, eluting with 4:1 dichloromethane/petroleum ether and gradually increasing to dichloromethane to give **6** [G-4] as a white solid. Yield: 83%. ^{1}H NMR (CDCl$_3$) δ: 4.43 (s, 2H, ArC*H*$_2$O), 4.47 (s, 2H, CH$_2$=CHArC*H*$_2$O), 4.91 (s, 28H, ArC*H*$_2$O), 4.97 (s, 32H, PhC*H*$_2$O), 5.17 (d, 1H, *J* = 12, C*H*$_2$=CH), 5.68 (d, 1H, *J* = 18, C*H*$_2$=CH), 6.47–6.65 (m, 45H, ArH and C*H*=CH$_2$), 7.26–7.42 (m, 94H, Ph*H* and CH$_2$=CHAr*H*). ^{13}C NMR (CDCl$_3$) δ: 69.9 (Ar*C*H$_2$O), 70.0 (Ph*C*H$_2$O), 71.7 (CH$_2$=CHAr*C*H$_2$O), 71.8 (Ar*C*H$_2$O), 101.4, 101.5, 106.3, 106.6 (Ar*C*), 113.8 (CH*C*H$_2$), 126.2, 127.5, 127.7, 127.9, 128.5 (CH$_2$=CHAr*C* and Ph*C*), 136.4, 136.7, 137.7, 139.2, 139.3, 140.6 (*C*H=CH$_2$, Ph*C* and Ar*C*), 160.0 (Ar*C*). Elemental analysis: Calcd for $C_{226}H_{196}O_{31}$: C, 79.65; H, 5.80. Found: C, 78.98; H, 5.91. MALDI–TOF mass spectrum: Calcd: [M$^+$] *m/z* = 3407.4. Found: [M + Na$^+$]$^+$ = 3430.2.

General Procedure for the Copolymerization of 6 [G-1, -2, -3, -4] and MAn: Synthesis of Polymer 7 [G-1, -2, -3, -4]. MAn, **6** [G-1, -2, -3, -4], AIBN, and dry chloroform were placed in a Schlenk flask with a magnetic stir bar and a rubber septum. After degassing by bubbling with nitrogen for 30 min, the reaction was carried on at the appropriate temperature in an oil bath, until the magnetic stir bar could not move, usually in 2–8 h. The polymer was dissolved in chloroform and precipitated in diethyl ether until no monomer remained as analyzed by SEC and ^{1}H NMR. See Supporting Information for details.

General Procedure for the Hydrolysis of the Copolymer 7 [G-1, -2, -3, -4]: Synthesis of 8 [G-1, -2, -3, -4]. The copolymers **7** [G-1, -2, -3, -4] were dissolved in THF at room temperature to give the solutions of concentration of 10 mg/mL in ampules. Concentrated hydrochloric acid aqueous solution (36–38%) was added slowly until the solution became cloudy, and then water of ca. 1/3 weight of the polymer solution was added. After frozen with liquid nitrogen, the ampule was sealed under vacuum. The reaction proceeded at 70 °C in oil bath for 48 h before opening the ampule. After removal of the most solvent, the reaction mixture was precipitated in diethyl ether for two times and hexane for one time. The products were dried in a vacuum overnight. Yield: 71.6% (**8** [G-1]); 45.5% (**8** [G-2]); 51.8% (**8** [G-3]); 94.5% (**8** [G-4]).

General Procedure for the Amidolysis of the Copolymer 7 [G-1, -2, -3, -4]: Synthesis of 9 [G-1, -2], 10 [G-1, -2, -3, -4], and 11 [G-2, -3, -4]. The copolymers **7** [G-1, -2, -3, -4] and butylamine (or laurylamine, or [G-1]-NH$_2$) were added in an ampule with mole ratio of 1:1, and THF was added to make the concentration of **7** to 0.05 mol/L. After sealed under vacuum, the ampule was kept in an oil bath at 70 °C for 48 h. After removal of the most solvent, the reaction mixture was precipitated in ether for two times and hexane for one time. After drying in a vacuum desiccator overnight, white powder was obtained. Yield: >90%. Elemental analysis: (1) Calcd for $(C_{38}H_{41}NO_6)_n$ (**9** [G-1]): N, 2.30; C, 75.10; H, 6.80. Found: N, 2.30; C, 72.68; H, 6.98. (2) Calcd for $(C_{66}H_{65}NO_{10})_n$ (**9** [G-2]): N, 1.36; C, 76.80; H, 6.35. Found: N, 1.35; C, 74.69; H, 6.35. (3) Calcd for $(C_{46}H_{57}NO_6)_n$ (**10** [G-1]): N, 1.95; C, 76.74; H, 7.98. Found: N, 2.03; C, 74.57; H, 7.95. (4) Calcd for $(C_{74}H_{81}NO_{10})_n$ (**10** [G-2]): N, 1.22; C, 77.66; H, 7.13. Found: N, 1.25; C, 76.18; H, 7.04. (5) Calcd for $(C_{130}H_{129}NO_{18})_n$ (**10** [G-3]): N, 0.70; C, 78.33; H, 6.52. Found: N, 0.88; C, 77.43; H, 6.51. (6) Calcd for $(C_{242}H_{225}NO_{34})_n$ (**10** [G-4]): N, 0.38; C, 78.74; H, 6.14. Found: N, 0.56; C, 77.03; H, 6.23.

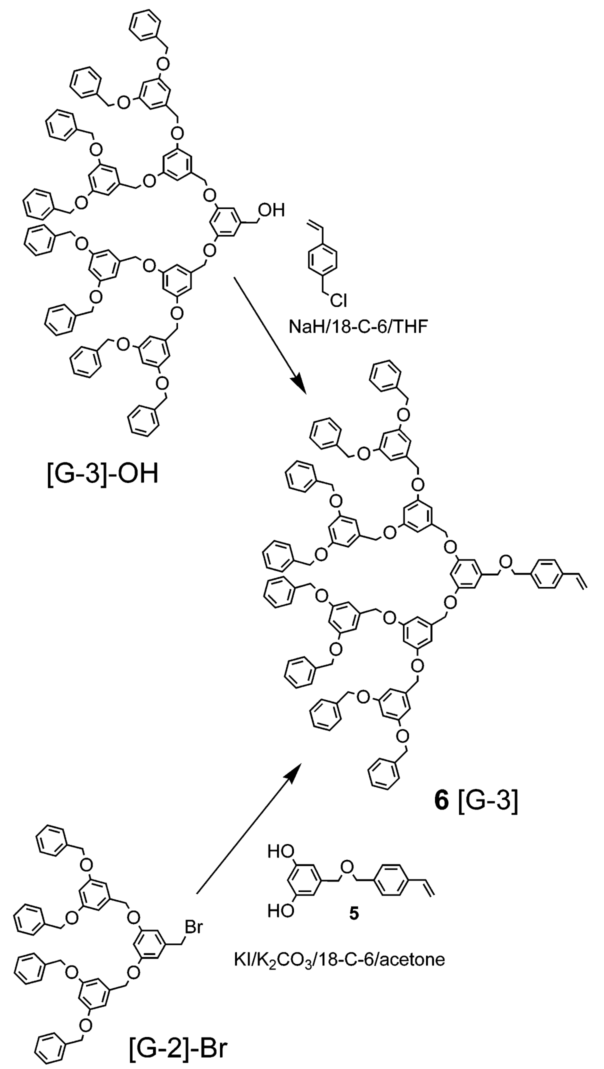
Results and Discussion

Synthesis of Styryl Dendrons. To prepare the styryl dendron, one method is by Williamson reaction of [G-*n*]-OH of Fréchet-type dendron with 4-vinylbenzyl chloride, leading to styryl [G-*n*]-monomer, **6** [G-*n*]. However, it is tedious and time-consuming for the high-generation dendrons. Another choice is to synthesize a styrene derivative **5** that serves as a branching molecule since it bears two hydroxyl groups. By the reaction of **5** and the [G-*n*]-Br dendron, the expected monomer of higher generation, **6** [G-(*n*+1)], can be obtained. This is the so-called accelerated convergent strategy being applied in the literature.[31–33] The advantages of the latter approach are obvious. Increasing generation number and introducing styryl group can be achieved in one step. Therefore, the synthesis is more efficient. Comparison of two methods is exhibited in Scheme 2. The former one was applied to synthesize the first generation monomer, **6** [G-1], whereas the accelerated approach was used to prepare the higher generation monomers, i.e., **6** [G-2], **6** [G-3], and **6** [G-4].

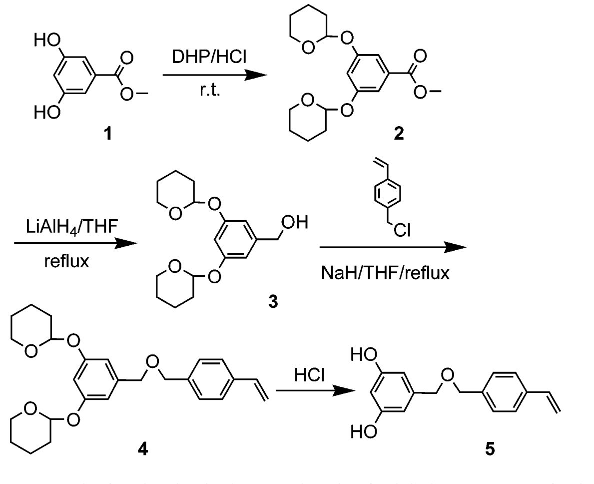
The protection and deprotection technique were applied for preparation of **5** as shown in Scheme 3. Methyl 3,5-dihydroxybenzoate (**1**) reacted with 3,4-dihydro-2*H*-pyran (DHP) catalyzed by concentrated hydrogen chloride. The crude product **2** was used for the next step of reduction with lithium tetrahydroaluminate (LiAlH$_4$) without further purification. The resulted alcohol **3** was used in the following step of etherification directly. Molecule **4** was produced through Williamson reaction of **3** and 4-vinylbenzyl chloride, and the overall yield was as high as 78%. Removal of the protection groups of tetrahydropyran was made by reacting with dilute aqueous HCl, and the product **5** was given. This molecule was unstable in dryness since it became an insoluble material. Therefore, functional monomer **5** was kept in solution of acetone. This phenomenon was reported previously with a similar molecule, 4-hydroxymethylene styrene.[34]

The structures of **6** [G-1, -2, -3, -4] were confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy, element analysis, and MALDI–TOF mass spectrometry, respectively. The ^{1}H NMR spectra of **6** [G-2] are shown in Figure 1 (see Figure S1 in Supporting Information for the spectra of four monomers). The quadruple peaks between 6.68 and 6.61 ppm were assigned to the proton of –C*H*=CH$_2$. The double peaks over 5.76–5.70 and 5.24–5.20 ppm having coupling constant 18 and 12 Hz, respectively, were assigned to the trans and cis protons of –CH=C*H*$_2$, and with the increase of generation the position of the two

Scheme 2. Comparison of Two Approaches for the Synthesis of the Monomer 6 Taking [G-3]-Monomer as an Example



Scheme 3. Synthesis of Branched Molecule 5 Containing Styrene



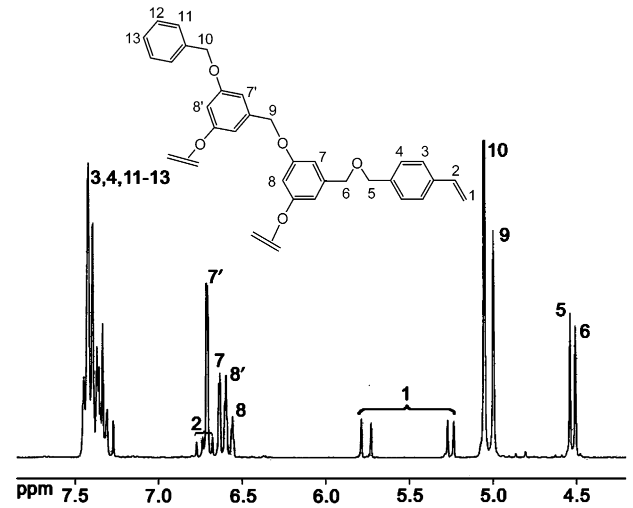


Figure 1. ^{1}H NMR spectrum of **6** [G-2] monomer with assignment.

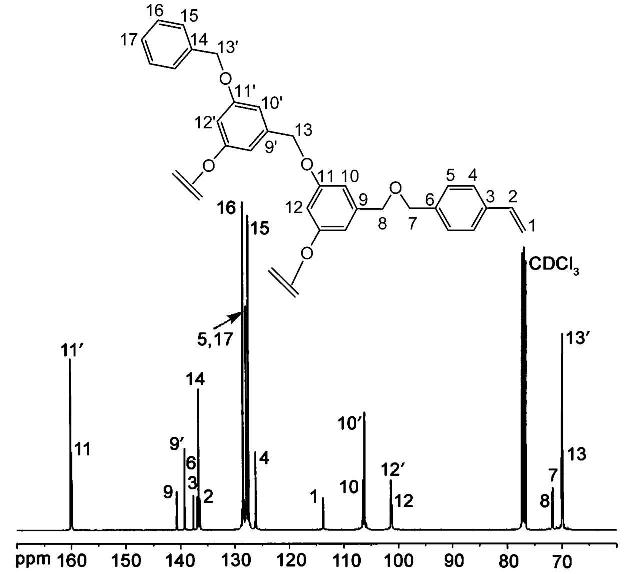


Figure 2. ^{13}C NMR spectrum of **6** [G-2] monomer with assignment.

protons shifted slightly to high field because of the increase of shielding effect due to the electron-donor para-substituent group of styrene. The multipeaks at 7.42−7.28 ppm were attributed to the protons of mono- and 1,4-disubstituent phenyl groups of Fréchet-type dendron, and the proton signals of trisubstituent phenol groups lay in 6.65−6.53 ppm. The carbon signals of the C=C group of styrene were recognized in ^{13}C NMR spectrum of **6** [G-2] at about 113.8 and 136.4 ppm; the other carbon signals could be assigned to the corresponding carbons of the dendron as shown in Figure 2 (see Figure S2 in Supporting Information for the spectra of four monomers).

Size exclusion chromatography (SEC) was applied to characterize the purities of the monomer **6** series from the first to the fourth generation. As demonstrated in Figure 3, very narrow peaks were obtained, indicating the coupling reaction and separation were efficient. The actual molar masses were determined by MALDI−TOF mass spectrometry, and the results corresponded to the theoretical values. As listed in Table 1, the molar masses given by SEC were underestimated comparing to the actual values due to the calibration was made by linear standard polystyrenes.

Copolymerization of 6 [G-1, -2, -3, -4] and MAn Initiated by AIBN. It is known that the copolymerization of styrene and maleic anhydride (MAn) can produce alternating copolymers through a charge-transfer complex (CTC). Styrene derivatives with para-substituent electron-donor groups may increase the

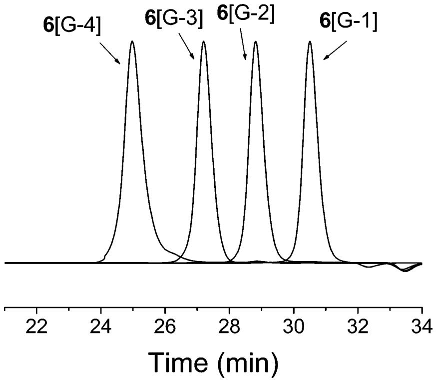


Figure 3. SEC traces for **6** [G-1, -2, -3, -4] monomer.

Table 1. Molar Masses and Polydispersities from SEC and Mass Spectra of 6 [G-1, -2, -3, -4] Monomers

			SEC data	
monomer	molar mass[a]	$[M + Na^+]^+$	M_n	M_w/M_n
6 [G-1]	436.53	459.2[b]	215	1.01
6 [G-2]	861.04	883.2[b]	504	1.02
6 [G-3]	1710.04	1732.0[b]	1162	1.02
6 [G-4]	3407.96	3430.2[b]	3371	1.04

[a] Calculated according to the atom weight. [b] Determined by MALDI–TOF mass spectrometry.

Scheme 4. Radical Copolymerization of 6 [G-1, -2, -3, -4] and Maleic Anhydride (the Sector Represent Fréchet-Type Dendron of [G-1, -2, -3, -4])

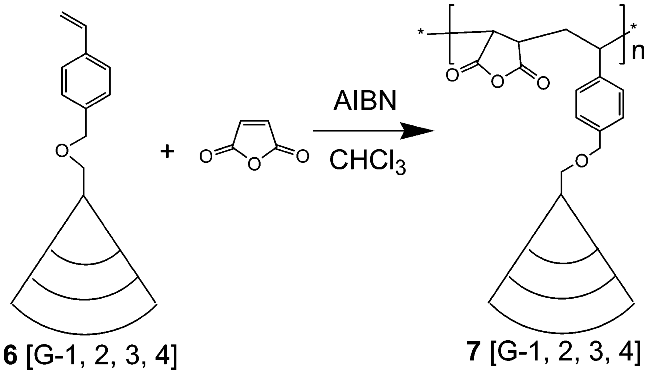


Table 2. Copolymerization Conditions and Results of the Four-Generation Copolymers[a]

sample	feed[b]	conc[c] (mol/L)	temp (°C)	yield (%)	$M_{w\,SLS}$	DP_w[d]
7 [G-1]-1	50:50:2	1.0	50	64	338 100	535
7 [G-1]-2	50:50:2	1.0	50	83	424 000	793
7 [G-2]-1	50:50:2	1.0	50	43	668 100	697
7 [G-2]-2	50:50:2	1.0	50	85	558 900	583
7 [G-3]-1	50:50:4	0.3	60	74	349 900	194
7 [G-3]-2	50:50:4	0.3	50	52	880 500	487
7 [G-4]-1	50:50:4	0.3	60	66	244 900	70
7 [G-4]-2	50:50:5	0.5	60	69	309 000	88

[a] Solvent was chloroform. [b] Molar ratio of [G-*n*]:MAn:AIBN. [c] Concentration of two monomers in solvent. [d] Taking one pair of dendritic monomer **6** [G-1, -2, -3, -4] and one MAn as one repeating unit and calculated from the M_w determined by SLS.

electron density of monomer, favoring to form alternative structure.[35,36] Therefore, the styryl dendrons we designed were likely to have a strong alternating tendency of copolymerization with MAn (Scheme 4). The copolymerizations of the monomer **6** of four generations and MAn were made in chloroform initiated by AIBN at 50 or 60 °C; the results are summarized in Table 2.

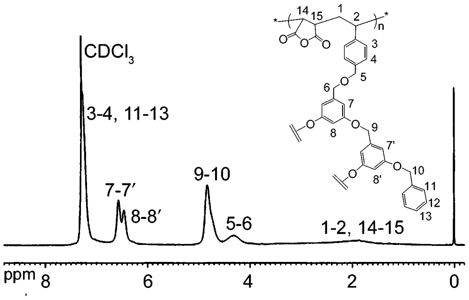


Figure 4. ^{1}H NMR spectrum of **7** [G-2] copolymer with assignment.

As shown in Table 2, the copolymerizations proceeded easily under mild conditions, and the yields were high for a radical polymerization. Since the data were underestimated by SEC analysis with polystyrene as the calibration, absolute molar masses were determined by static light scattering (SLS). The degrees of copolymerizations (DP_ws), defined as one pair of the comonomers, of the **6** for the first and the second generation were over 500, which were rather high. Each copolymerization reaction has been repeated at least for one time and good repeatability was given. The copolymerization of the third-generation monomer with MAn was carried out at different temperature; high DP_w was given at relatively low temperature as shown in Table 2. It should be mentioned that actual polymer length should double the DP_ws since the DP_w used here represented one styrene unit and one MAn unit. Therefore, the dendronized polymers in this system were rather long. However, the DP_w of the copolymers of the fourth-generation monomer and MAn decreased greatly, and average DP_w was ca. 90. The low DP_w for **6** [G-4] was reasonable since the huge size of the monomer would bury its double bond. Moreover, the monomer molar concentrations during the copolymerization were lowered due to the molar mass of **6** [G-4] being very large. These two factors were not helpful to increase the DP_w of **6** [G-4].

The homopolymerizations of the similar monomers with **6** [G-1, -2, -3, -4] were reported by Neubert et al.,[37] which proceeded at higher temperature and at lower initiator concentration. However, the products of the fourth-generation copolymer were oligomers. Comparing with that, the copolymerizations of **6** [G-1, -2, -3, -4] and MAn easily gave the dendronized copolymers with high molar masses in 2–8 h reaction period. The reason for the present results may be attributed to the steric hindrance of the dendrons being reduced by its comonomer (MAn) relative to the homopolymerization of similar styryl dendrons.[37] However, alternative copolymerization was more likely to produce the copolymers of high molar masses since the polymerization of CTC was normally much faster than homopolymerization of styrene.

The ^{1}H NMR spectra of different generation of **7** [G-*n*] copolymers showed not too much difference, but the integral areas were in accordance with the corresponding copolymers. Figure 4 shows the spectrum of **7** [G-2] copolymers with the assignment (see Figure S3 in Supporting Information for the spectra of four copolymers). The broaden peaks were given, and this was typical for dendronized polymers due to the high molar mass and chain stiffness. No vinyl protons could be found, indicating the unreacted monomers were removed completely after the copolymerization. However,

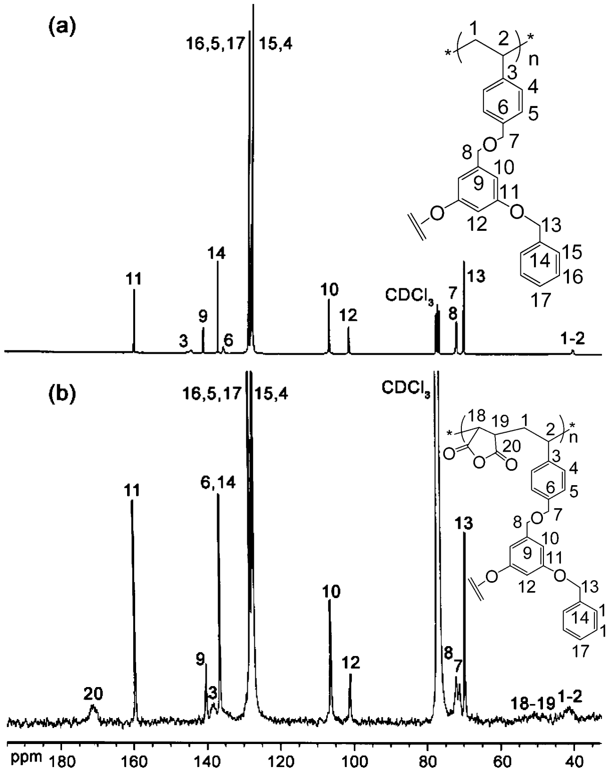
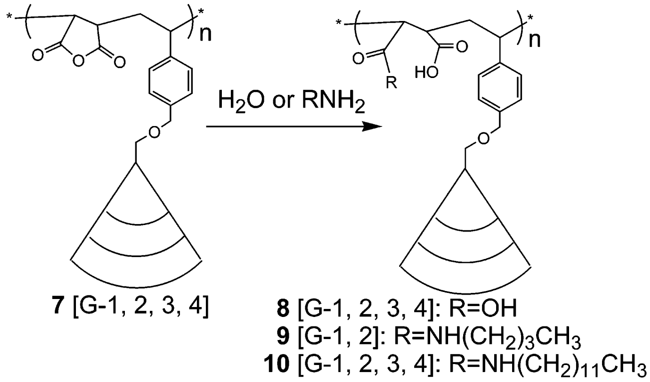


Figure 5. ^{13}C NMR spectrum of homopolymer of **6** [G-1] (a) and copolymer **7** [G-1] (b) with assignment.

Scheme 5. Hydrolysis and Amidolysis of Succinic Anhydride Units of 7 [G-1, -2, -3, -4]



the alternating sequence structure of the copolymers could not be confirmed from the ^{1}H NMR spectrum since the MAn unit only had two protons, which were too weak and also overlapped with other protons in the spectra. Two methods may be used to prove the alternative sequence according to the literature. One was through determining the chemical shift of the carbon of the methylene along the backbones of the St-MAn copolymers according to distortionless enhancement by polarization transfer (DEPT) spectroscopy,[38] but the signal of the carbon of the methylene was too weak to detect for the copolymer of **7** [G-1] due to the high molar mass. The other was through determining the chemical shift of the quaternary aromatic "next to polymer chain" carbon of styrene in the copolymer in ^{13}C NMR spectroscopy.[39] Herein, we applied the latter method to characterize the alternative structure of the copolymer 7 [G-1] because the signals of the copolymers of **7** [G-2, -3, -4] were weak and complicated due to the similar carbon in para-substituent polyether-type dendron of styrene.

For the ^{13}C NMR spectrum of the copolymer of styrene and MAn, the chemical shifts of sequence distribution, nonalternating (111), semialternating (011 + 110), and alternating (010) triad subpeaks of the aromatic "next to polymer chain" carbon of styrene (1 represents the donor monomer styrene; 0 represents the acceptor monomer MAn), lay in 147.5−145, 146−141.5, and 140.5−136.5 ppm, respectively.[39] But for the copolymer **7** [G-1] we should consider the effect of para-substituent dendron of styrene. So we synthesized the homopolymer of **6** [G-1] and tested its ^{13}C NMR spectra. It was found that the position of the aromatic "next to polymer chain" carbon (C$_3$ in Figure 5) lay in 145.6−143.8 ppm; that is to say, the para-substituent induced the position of C$_3$ shifting 1.6 ppm toward high field, so the chemical shift of the alternating triad subpeaks of C$_3$ of **7** [G-1] should lie in 138.9−134.9 ppm. After analyzing the proton broad band decoupling and the gated decoupling ^{13}C NMR spectrum of **6** [G-1] and the DEPT ^{13}C NMR spectra of **7** [G-1], we achieved the assignment as shown in Figure 5. The position of C$_3$ was 138.5 ppm among the alternating period aforementioned. Thus, the conclusion can be made that the copolymer of **7** [G-1] has a strict alternating sequence in microstructure. But for the higher-generation dendronized copolymers of **7** [G-2, -3, -4], the precise assignment of ^{13}C NMR spectra was difficult because the similar carbon in para-substituent polyether-type dendrons of styrene interfered the weak peak of C$_3$.

While we tried to calculate the molar ratio of **6** [G-1, -2, -3, -4] and MAn units in the copolymers **7** [G-1, -2, -3, -4] according to the integral areas of ^{1}H and ^{13}C NMR spectra, we encountered the same problem, i.e., the weak and overlapped signals. As increasing generation the mass proportions of MAn in the copolymers **7** [G-1, -2, -3, -4] decreased dramatically, and the signals became too weak to detect.

Though there was no direct evidence of alternative structure for the copolymers with pendent dendrons in higher generations, the copolymers were likely to be the expected structure on the basis of the following analysis. First, Fréchet-type vinyl monomers at higher generation was difficult to give the homopolymers with high DP in short reaction time due to the bulky dendron shielding the vinyl group.[37] Introduction of a spacer has been tried to increase the DP of the dendronized polymers of Fréchet-type dendron wedges.[40] Second, it is known that MAn cannot radically homopolymerize. Therefore, the dendronized copolymers with high DP readily produced under the molar feed ratio of 1:1 (**7** [G-1, -2, -3, -4]: MAn) could attribute to preferential alternative copolymerizations of the two monomers. The composition of the modified copolymers in followed sections further confirmed the expected structure indirectly.

Hydrolysis of Succinic Anhydrides in Copolymers 7 [G-1, -2, -3, -4]. The functionalization of the succinic anhydride units located along the backbones of the copolymers has been studied extensively. The hydrolysis of the succinic anhydride along the dendronized copolymers is the simplest one, and each unit may produce two COOH groups, as shown in Scheme 5. The reactions were completely as confirmed by FT-IR spectroscopy (Figure 6). The absorption peaks at 1861 and 1779 cm^{-1} of **7** were characteristic bands of anhydride, assigned to asymmetrical and symmetrical $\nu_{C=O}$ of succinic anhydride moieties, respectively. Peaks at 1595, 1498, and 1454 cm^{-1} were the $\nu_{C=C}$ of the

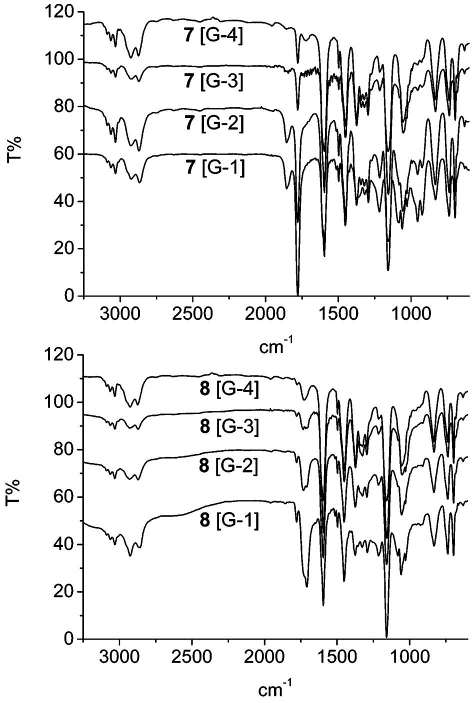


Figure 6. FT-IR spectroscopy of the four-generation copolymers before (**7** [G-1, -2, -3, -4]) and after (**8** [G-1, -2, -3, -4]) hydrolysis.

phenyl groups of the dendrons. The peak at 1159 cm^{-1} was assigned to the $\nu_{\mathrm{C-O}}$ of anhydride or carboxylic acid. The position of corresponding peaks of the copolymer of different generation has no much difference. But with increase of the dendron generation, the characteristic peaks of anhydride at 1861 and 1779 cm^{-1} became smaller relative to those of phenyl moieties. After hydrolysis of anhydride, the characteristic peaks of anhydride at 1861 and 1779 cm^{-1} disappeared and the peaks at 1779 and 1713 cm^{-1} belonging to dicarboxylic acid appeared, indicating that the anhydride moieties have been switched to dicarboxylic acid successfully. And the broad absorbance around 3000 cm^{-1} of carboxylic acid also supported this conclusion. SEC traces of the hydrolyzed samples showed no distinct differences with those of the unhydrolyzed samples.

Amidolysis of Succinic Anhydrides in the Copolymer 7 [G-1, -2, -3, -4]. Primary amine may react with anhydride in a quantitative conversion. The dendronized copolymers were reacted with two kinds of aliphatic amine, 1-butylamine and 1-laurylamine, (Scheme 5). The reactions proceeded completely as demonstrated by FT-IR spectra (Figure 7). After the reaction, the characteristic absorbances of anhydride at 1861 and 1779 cm^{-1} disappeared completely, and the absorbance of amide at 1718 cm^{-1} was observed. Similarly, with the increasing of generation of polyether dendron, the absorbances at 1861, 1779, 1718, and around 3000 cm^{-1} relating to anhydride or aliphatic amide moieties became weaker compared to those of phenyl moieties at 1595, 1498, and 1454 cm^{-1}. In another aspect the protons of aliphatic chains on the polymer **10** [G-1, -2, -3, -4] could be found clearly in ^{1}H NMR spectra (as shown in Figure 8 for **10** [G-1], see Figure S4 in Supporting Information for others). The proton peak of aliphatic alkyl methylenes was at 1.22 ppm while the protons of the methyl at one end was located at 0.86 ppm. This result further demonstrated the introduction of alkyl groups. Above the amidolysis of the anhydride moieties of dendronized copolymer **7** [G-1, -2, -3, -4] with linear aliphatic amine produced the copolymers with a structure of dendron-*alt*-linear alkyl chain.

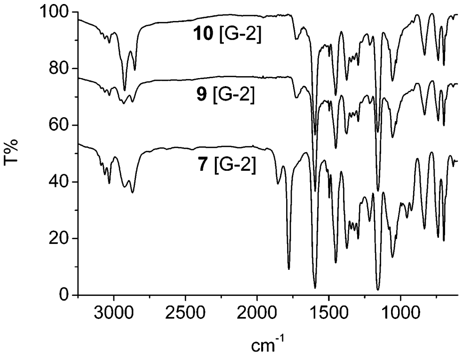


Figure 7. FT-IR spectra of before and after amidolysis of **7** [G-2].

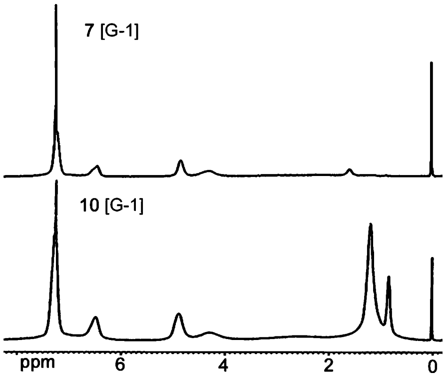
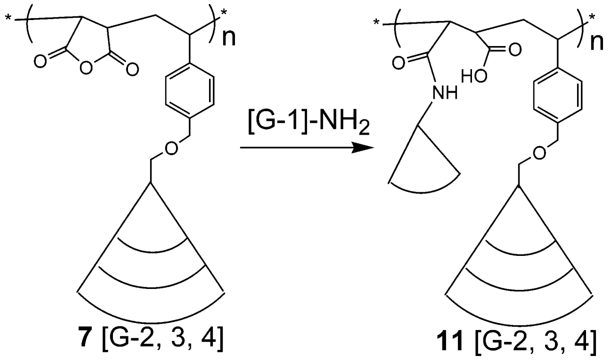


Figure 8. ^{1}H NMR spectrum of **7** [G-1] and **10** [G-1].

Scheme 6. Amidolysis of Succinic Anhydride Units of 7 [G-2, -3, -4] with [G-1]-NH$_2$ and Formation of Different Dendron Hybrid Structure



When the reactive copolymer **7** [G-2, -3, -4] reacted with an amino dendron of the generation different from itself, a new kind of dendronized copolymers with their side dendrons grafted in an alternative generation was produced (Scheme 6). The amidolysis of the anhydride moiety was confirmed from the FT-IR spectrum, in which the absorbances of anhydrides disappeared (Figure 9). However, SEC analysis showed slightly difference before and after the reaction. Introduction of dendritic wedges in these dendronized polymers would increase the stiffness of the copolymer chain.

The composition of the copolymers of MAn and St may be determined by elemental analysis. However, the mass fractions of MAn units in the dendronized copolymers and element content difference were too small to give reliable composition results by elemental analysis,

Table 3. Molar Content of Maleic Anhydride in the Copolymer 9 [G-1, -2] and 10 [G-1, -2, -3, -4] Deduced from the Nitrogen Content

	9[G-1]	**9**[G-2]	**10**[G-1]	**10**[G-2]	**10**[G-3]	**10**[G-4]
N %[a] (calcd/found)	2.30/2.30	1.36/1.35	1.95/2.03	1.22/1.25	0.70/0.88	0.38/0.56
x[b] (calcd/found)	0.28/0.28	0.17/0.17	0.39/0.42	0.24/0.25	0.14/0.18	0.08/0.11
ratio[c]	0.99	1.03	1.12	1.01	1.33	1.49

[a] Nitrogen content of calculated and found values. [b] Weight content of succinic unit in copolymer: $x(\text{calcd}) = M_{\text{succinic unit}}/(M_{\text{succinic unit}} + M_{7[\text{Gn}]})$; $x(\text{found}) = \text{N\% (found in copolymer)/N\% (succinic unit)}$. [c] Ratio of succinic unit: **7** unit $= x \times M_{7[\text{Gn}]}/(1 - x) \times M_{\text{succinic unit}}$.

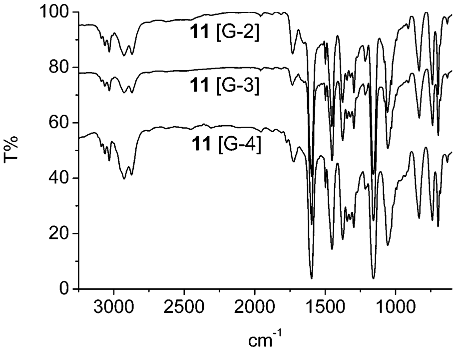


Figure 9. FT-IR spectroscopy of amidolysis products of **7** [G-2, -3, -4] with [G-1]-NH_2.

especially for those copolymers from high-generation monomers. After coupling with the alkylamine, estimation of the composition of two components through elemental analysis became possible since the mass fraction of succinic monoamide increased and elemental content difference of two components became larger. Therefore, elemental analyses were made for the amidolysis products **9** [G-1, -2] and **10** [G-1, -2, -3, -4]. Table 3 lists calculated and found data of nitrogen content, weight content of succinic unit, and ratio of two units in the copolymer **9** [G-1, -2] and **10** [G-1, -2, -3, -4] based on the nitrogen content. We may notice that the found values agreed with the expected ones, and the molar ratios of succinic unit to dendron unit were around 1:1. The ratio for the higher-generation dendron showed a higher difference, owing to the nitrogen contents were too small and analysis error became large.

Conclusion

We have synthesized styryl macromonomers bearing Fréchet-type dendrons of four generations through an accelerated method. Copolymerization of these macromonomers and maleic anhydride (MA) initiated by AIBN proceeded easily in moderate conditions and gave high molar masses as determined by SLS. More interestingly, after modification of anhydrides along the dendronized polymer chain, a series of dendronized polymers of new structures have been produced. In this article, we demonstrated the hydrolysis and amidolysis of anhydride moiety, and new copolymers with their side chain being structures of dendron-*alt*-2COOH, dendron-*alt*-linear alkyl chain, and grafted dendrons of alternative generation were obtained. Therefore, this family of dendronized copolymers can be a powerful scaffold of single molecule for nanotechnologies and nanomaterials. We have also made the amidolysis of maleic anhydride with aminopyridine, and then metal ions such as Cd, Au, Pt, and Pd can be bonded by pyridine groups along the backbone of the dendronized polymers. Therefore, inorganic nanoparticle array may be formed from these single molecules. Furthermore, the copolymerization of these styryl dendrons and maleimide bearing an initiating group for atom transfer radical polymer were prepared as well; linear polymer chains will be grafted from the macroinitiators by controlled radical polymerization to give polymers with interesting structure. These works are ongoing, and the results will be published elsewhere.

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Supporting Information Available: Synthesis of **5**, [G-1]-NH_2, and copolymer **7**; Figures S1−S4 of the ^1H NMR and ^{13}C NMR spectra of monomer **6** of four generations and ^1H NMR spectra of copolymers **7** and **10** of four generations. This material is available free of charge via the Internet at http://pubs.acs.org.

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