

Microporous Thermosetting Film Constructed from Hyperbranched Polyarylate Precursors Containing Rigid Tetrahedral Core: Synthesis, **Characterization, and Properties**

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Porous organic thermosetting film with pore size smaller than 20 Å was constructed through the self-cross-linking reaction from hyperbranched polyarylate precursors with rigid tetrahedral skeleton. Using hydroquinone diacetate as the A_2 monomer and tetrakis(4-carboxyphenyl)silane as the B_4 monomer, the hyperbranched polyarylate precursors were successfully synthesized with high yields, during which the gelation process was efficiently suppressed by heterogeneous polycondensation method by means of the elaborate selection of reaction medium. The control of monomer ratio in the polymerization system led to two types of precursors, i.e., mainly carboxyl-terminated hyperbranched polyarylate (CTHP) and mainly acetoxy-terminated hyperbranched polyarylate (ATHP). They had degree of branching values of 0.53-0.69, molecular weights of 10100-34000 g/mol, inherent viscosities of 0.12-0.18 dL/g, and good solubility in the common solvents. The precursor film, obtained by spin coating from the mixture solution of CTHP and ATHP with equivalent amount of reactive carboxylic group and acetoxy groups, was readily thermally cured via a transesterification reaction to form a cross-linked network, which exhibited excellent thermal stability, good chemical resistance, low birefringence, and low dielectric constant, as well as microporosity, with an average pore size of 11.2 Å and surface area of 158 m^2/g .

Introduction

The development of polymers with specific topologies and architectures has continuously been one of the most interesting subjects in the field of macromolecular engineering, because it provides an original approach to nanoscience and nanochemistry to achieve a range of new and special properties, compared to the conventional polymers.

Dendritic topologies, distinct from the linear type, have been widely explored in academic and industrial fields over the past two decades. Dendritic macromolecules include both dendrimers and hyperbranched polymers, which are composed of successive branch units.¹⁻⁷ In comparison with hyperbranched polymers, dendrimers have more well-controlled and regularly branched structures. However, the large-scale production of dendrimer is difficult, because of the involved multistep

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transformation and chromatographic purification at every step. In contrast, hyperbranched polymers could be easily prepared via a one-pot synthesis. The most common strategy to hyperbranched polymers is the selfcondensation of AB_n $(n \ge 2)$ monomers.⁸⁻¹⁴ Nevertheless, the use of AB_n monomers is limited, because they are usually obtained through tedious synthetic procedures necessary for asymmetric functionality. To further allow for convenient and cost-saving scaleup, researchers have begun to focus toward the polymerization of A2 with B_n (n > 2) monomers, which are all readily available. Among them, the notable examples were reported by Long, Voit, Fréchet, Jikei, and Fossum.^{15–19}

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Article

During the past few years, a new class of macromolecular architecture-termed as polymers of intrinsic microporosity (PIMs), which have pore sizes smaller than 20 Å—have dramatically emerged as a promising approach to nanomaterials.²⁰⁻²⁴ Ascribing to the highly cross-linked network and fully rigid skeleton within structure, their applications can be in the field analogous to zeolites (i.e., catalysis, size-selective absorbents, and gas storage). In addition, for organic polymers, because of their outstanding advantage in processability over inorganic materials, microporous polymer films are significant to expend the applications in some advanced technology fields (e.g., optics, electronics, and membrane separations).²⁵ Recently, PIMs based on soluble polymers have been explored by Budd et al.²⁶⁻²⁹

Relative to linear PIMs, the development of thermosetting microporous thin films will be more attractive, because of their good resistance to solvents and moisture, good dimensional stability, and thermo-oxidative stability. Until now, a series of well-established synthesis strategies—including dioxane-forming polymerization,²¹ Friedel–Crafts reaction,³⁰ reversible chemistry,^{20,31–33} transition-metal-catalyzed cross-coupling reaction, 24,34-37 Schiff base chemistry,³⁸ and *N*-alkylation^{39,40}—have been successfully used to prepare microporous organic networks with high specific surface areas and well-defined pore properties. Nevertheless, most of the full rigid cross-linked

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PIMs reported in the literature are precipitated powders, whereas thermosetting PIM films are almost entirely unexplored with the exception of Economy's thermosetting poly(imide-ester) (BET surface area of 83 m^2/g).⁴¹

In the previous work, we have successfully extended the concept of microporosity into general thermosetting resin via polycyanurate chemistry.⁴² Herein, we make a great effort to prepare microporous thermosetting films based on common hyperbranched polymers of commercial interest, such as polyarylates. For the construction of polyarylate PIM films, the hyperbranched polyarylates play three important roles: first, they serve as building blocks that provide open and accessible cavities; second, upon heating, they act as thermosetting precursors; third, the semirigid ester linkers between branchpoints, rather than full stiff linkers usually used in most microporous networks, could favor the release of internal stresses within the cross-linked network after curing of the precursors.

To this end, a rigid tetrahedral monomer tetrakis-(4-carboxyphenyl)silane, which could efficiently avoid dense chain packing, was first used as B₄ monomer for preparation of fully aromatic hyperbranched polyester. Two types of precursors, i.e., mainly carboxyl-terminated polyarylate (CTHP) and mainly acetoxy-terminated polyarylate (ATHP), were obtained through the polymerization of hydroquinone diacetate (A_2) and tetrakis-(4-carboxyphenyl)silane (B_4) monomers. To further form a cross-linked structure via a transesterification reaction, a self-curable precursor containing equivalent amount of carboxylic acid and acetoxy end groups was thus prepared by simply mixing CTHP with ATHP. Therefore, the chemical component of cured film is only constituted of polyarylate itself, because no other curing agents are added in the system.

In this paper, we conduct a detailed study on the synthesis, characterization of the aforementioned novel hyperbranched precursors, and the preparation of their cured film with intrinsic microporosity. Some interesting effects caused by the unique tetrahedral molecular architecture on optical and dielectric properties of the film are also investigated.

Experimental Section

Materials. Tetrachlorosilane, n-butyllithium, 1,4-dibromobenzene were purchased from J&K Chemical Co., Ltd. Hydroquinone diacetate and diphenyl sulfone were purchased from Shanghai Chemical Reagent Co. Diethyl ether and tetrahydrofuran (THF) were purified by refluxing over sodium with the indicator benzophenone complex. Cyclohexanone was purified by distillation. Diphenyl sulfone was purified by recrystallization from ethanol. The other solvents were reagent grade and used as received.

Instrumentation. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Model 20DXB IR spectrophotometer. Sixty four (64) scans were signal-averaged, with a resolution of 2 cm^{-1} at room temperature. Samples were

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prepared by dispersing the complexes in KBr and compressing the mixtures to form disks.

¹H NMR and ²⁹Si NMR were recorded on 400-MHz Varian Model INOVA NMR spectrometer, with the tetramethylsilane (TMS) as an internal reference.

Thermogravimetric analyses (TGA) was performed on a Netzsch Model TG 209 thermal analyzer both in purified nitrogen and an air atmosphere, and all samples (with masses of \sim 10 mg) were heated from 25 °C to 700 °C at a rate of 10 °C/min, under the gas flow rates of 60 mL/min.

Differential scanning calorimetry (DSC) measurements were conducted with a Netzsch Model DSC 204 instrument. The calorimeter was calibrated with indium metal as a standard. Samples with masses of $\sim 10-14$ mg were used, at a heating rate of 10 °C/min under a flow of nitrogen (20 mL/min). The reported glass-transition (T_g) temperatures corresponded to the midpoint change in heat capacity in the transition region.

Molecular weights and distributions were determined using gel permeation chromatography (GPC), with a Water Associates Model PL-GPC-220 apparatus at room temperature with tetrahydrofuran (THF) as the eluent, at a flow rate of 1 mL/min, calibrated with polystyrene standards.

The inherent viscosities of the samples were measured with an Ubbelohde viscometer at a concentration of 0.5 g/dL in CHCl₃ at 25 ± 0.01 °C.

The atomic force microscopy (AFM) images were recorded with a PicoPlus II microscope (Agilent, USA) at room temperature. The images were recorded in the tapping mode to avoid the possible deformation and indentation of the polymer surface by the tip. The values of root-mean-square (rms) roughness were calculated over the entire captured film area using the accessory software of the instrument.

Nitrogen adsorption-desorption experimentation was conducted using an automated micropore gas analyzer (Autosorb-1-MP, Quantachrome Instruments). Before sorption measurement, the cured film sample was degassed at 150 °C under high vacuum overnight. Apparent surface area was calculated from N_2 adsorption data by multipoint BET analysis.

The out-of-plane and in-plane refractive indices of the thin film were measured with a Sairon Model SPA-400 prism coupler that was equipped with a He–Ne laser light source (wavelength = 632.8 nm) and controlled by a computer. The measurements of the refractive indices were performed in both transverse electric (TE) and transverse magnetic (TM) modes, with the appropriate polarization of the incident laser beam. The TE measurement (in which the electric field was in the film plane) provided the in-plane refractive index, whereas the TM measurement (in which the electric field was out-of-plane) gave the out-of-plane refractive index.

The dielectric constants of the film was evaluated with an optical method based on Maxwell's equation,

$$\varepsilon = 1.1 n_{\rm av}^2$$

where ε is the dielectric constant and n_{av} is the average refractive index.

Preparation of Tetra(4-tolyl)silane (TTS). Tetra(4-tolyl)silane was prepared according to the procedure given in the literature,⁴³ with some modifications. A 1-L four-necked flask equipped with a mechanical stirrer, nitrogen inlet and outlet, a condenser, and a dropper was charged with lithium powder

(13.04 g, 1.94 mol) and anhydrous diethyl ether (250 mL). 4-Bromotoluene (159.55 g, 0.933 mol) in anhydrous diethyl ether (200 mL) was added dropwise over a 8-h period under vigorous stirring under the protection of nitrogen atmosphere. An immediate exothermic reaction caused the ether to start boiling. The mixture was stirred for 4 h, and then 17.7 mL of tetrachlorosilane in 50 mL of anhydrous diethyl ether was added dropwise over a 4-h period. The mixture was stirred for an additional 2 h and quenched by the slow addition of 200 mL of 1 N aqueous HCl at 0 °C. Diethyl ether was removed by rotary evaporation, the solid was filtered off, and then washed with 400 mL of methanol and 200 mL of 1 N aqueous HCl. The crude product was dissolved in chloroform, and the insoluble fraction was filtered off by filtration. Solvent was evaporated to afford a white solid. The crude product was recrystallized twice in cyclohexane and gave as colorless crystals (53.4 g, 87.6%); mp: 236-236.5 °C. ¹H NMR (400 MHz, CDCl3,): d (ppm) 2.45 (s, 12H, Ar-CH₃), 7.15 (d, 8H, Ar-H), 7.42 (d, 8H, Ar-H); IR (KBr, cm⁻¹): 3063 and 3010 (arom. C-H), 2972 and 2863 (Ar-CH₃), 1597, 1499 (arom. C=C), 1445, 1107, and 760 (Si-Ph), 803 (arom. p-subst.).

Preparation of Tetrakis(4-carboxyphenyl)silane (TCS). Tetrakis(4-carboxyphenyl)silane was prepared according to a modified procedure given in the literature.⁴⁴ A 2-L three-necked round-bottom flask in an ice bath was equipped with a thermometer, a mechanical stirrer, and a dropper. To this flask was charged 960 mL of glacial acetic acid and 400 mL of acetic anhydride. Maintaining the temperature below 10 °C, sulfuric acid (60 mL) and TTS (20.8 g) was added successively with stirring. After that, the temperature was increased to 25 °C, and Cr_2O_3 (160 g) was charged in four portions over a 2-h period. The mixture was stirred for additional hour. The product then was decomposed with ice-cold water (1.6 L) and filtered. The green solid was dissolved in dilute aqueous NaOH, and the solution was acidified with 1 N aqueous HCl until the pH reached 1. The resultant white solid was washed with dilute aqueous HCl and distilled water several times. The crude product was recrystallized from acetic acid three times to give tetraacid TCS (17.44 g, 67%); ¹H NMR (400 MHz, acetone- d_6): δ (ppm) 8.12 (d, 8H, Ar–H), 7.75 (d, 8H, Ar–H); ²⁹Si NMR (acetone- d_6 400 MHz, acetone- d_6): δ (ppm) -10.4; IR (KBr, cm⁻¹): 3025 (arom. C–H), 2300–3400, 2666, 2552 (–COOH), 1694 (-C=O, carboxyl), 1600, 1498 (arom. C=C), 1093, 759 (Si-Ph), 708 (arom. p-subst.).

Preparation of CTHP. Tetrakis(4-carboxyyphenyl)silane (0.8 g, 1.61 mmol), hydroquinone diacetate (0.435 g, 1.61 mmol), sodium acetate (0.001 g), and diphenyl sulfone (5 g) were added into a 50-mL three-neck round-bottom flask that was fitted with a condenser, nitrogen inlet tube, and mechanic stirrer, to make a solution of \sim 20% solids content. A slow stream of nitrogen was maintained throughout the entire reaction. The temperature was increased to 200 °C for 1 h and then was increased to 260 °C, at which point acetic acid began to evolve as the reaction byproduct. After 12 h, the mixture became transparent. The polymerization was continued for an additional 30 min until the mixture became viscous. After cooling, the product was precipitated in 50 mL of ethanol, and then it was filtered and washed with hot ethanol for three times to remove diphenyl sulfone and traces of catalyst. The crude product was extracted with DMF, using a Soxhlet apparatus for 24 h, and the insoluble solid (cross-linked polymers) was discarded. The clear filtrate was poured into an excess of ethanol.

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The polymer obtained was dried at 100 °C under a vacuum to constant weight. Yield: 70%. ¹H NMR (400 MHz, DMSO- d_6): δ (ppm) 13.2 (s, COOH), 8.40-8.20 (m, Ar-H), 8.13-8.00 (m, Ar-H), 7.90-8.00 (m, Ar-H), 7.50-7.10 (m, Ar-H), 1.39 (s, CH₃); ²⁹Si NMR (100 MHz, DMSO- d_6): δ (ppm) -10.05-10.35; IR (KBr, cm⁻¹): 3400–2300, 2960, 2880, 1763, 1737, 1700.

Preparation of ATHP. Tetrakis(4-carboxyyphenyl)silane (0.8 g, 1.61 mmol), hydroquinone diacetate (1.739 g, 6.44 mmol), sodium acetate (0.001 g), and diphenyl sulfone (10 g) were added into a 50-mL three-neck round-bottom flask that was fitted with a condenser, nitrogen inlet tube, and mechanic stirrer, to make a solution of $\sim 20\%$ solids content. A slow stream of nitrogen was maintained throughout the entire reaction. The temperature was increased to 200 °C for 1 h, and then was increased to 260 °C, at which point acetic acid began to evolve as the reaction byproduct. After 8 h, the mixture became transparent. The polymerization was continued for an additional hour until the mixture became viscous. After cooling, the product was precipitated in 50 mL of ethanol, and then it was filtered and washed with hot ethanol for three times to remove diphenyl sulfone and traces of catalyst. The crude product was extracted with DMF using a Soxhlet apparatus for 24 h, and the insoluble solid was discarded. The clear filtrate was poured into an excess of ethanol. The polymer obtained was dried at 100 °C under a vacuum to constant weight. Yield: 75%. ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 13.2 (s, COOH), 8.41–8.19 (m, Ar–H), 8.12-8.01 (m, Ar-H), 7.89-8.01 (m, Ar-H), 7.48-7.09 (m, Ar-H), 1.40 (s, CH₃); ²⁹Si NMR (100 MHz, DMSO-d₆): δ (ppm) -10.06-10.35; IR (KBr, cm⁻¹): 3400-2298, 2961, 2878, 1765, 1739, 1701.

Preparation of Cured Film. The substrates used in the experiments were highly polished silicon wafers. Organic residue on the surface was removed by successive ultrasonic cleaning with acetone, alcohol, and ion-free pure water. CTHP (0.703 g) and ATHP (1.5 g) were dissolved in DMF (22 mL) to obtain a 10 wt % mixture solution containing equivalent amounts of carboxyl and acetoxy groups. The solution then was filtered through a 0.22-µm Teflon filter and spin-coated on a silicon wafer. The spin-coating speeds were in the range of 1000-2500 rpm. To guarantee the quality of the spin-coated film, the entire spin-coating procedure was conducted in a 1000-class ultraclean room. The resulting film was dried at 60 °C (30 min) and 120 °C (2 h) to remove the residual solvent under vacuum. Thermal cross-linking was then performed in a vacuum oven by stepwise heating at 150 °C for 1 h, 180 °C for 2 h, 220 °C for 5 h, 250 °C for 5 h, and 320 °C for 1 h. Finally, the sample was cooled slowly to room temperature.

Results and Discussion

Synthesis of Monomer and Hyperbranched Polarylates. Among numerous structural motifs for the construction of novel functional nanometer-sized materials, tetrahedral core compounds such as tetraphenylmethane and tetraphenylsilane have intensively aroused considerable interest. A persistent tetrahedral shape would offer possibilities for construction of diamond-like and other intriguing molecular architectures that might be translated to a

macromolecular system with unusual properties.45,46 In this work, tetrakis(4-carboxyphenyl)silane (TCS) was selected as a B₄ monomer to prepare hyperbranched tetrahedral polyarylates. TCS was prepared according to the literature with some modifications: p-bromotoluene was converted to p-tolyllithium and then reacted with tetrachlorosilane to produce tetrakis(4-tolyl)silane,⁴³ and the oxidation of methyls using chromium trioxide gave the corresponding product³³ with an overall yield of 58.7%. The chemical structures were confirmed by FTIR, ¹H NMR, and ²⁹Si NMR spectra.

The $A_2 + B_n$ type of polymerization usually leads to gelation. However, if the propagation can be terminated prior to the gel point, hyperbranched polymers with satisfactory molecular weights can be obtained. Previously, several strategies, including dropwise addition of a diluted monomer solution, partial conversion of functional groups in dilute solution, and the $A_2 + BB'_2$ approach have been reported to delay or even avoid the occurrence of gelation in the $A_2 + B_3$ polymerization;^{17,47-49} however, similar results are difficult to achieve via the same methods in the $A_2 + B_4$ system. According to Flory's theory, for equifunctional polycondensations, the critical conversion (p_c) above which gel particles are formed for the B_4 monomer ($p_c = 0.58$) is much lower than that of the B_3 monomer ($p_c = 0.71$).⁵⁰ Therefore, it is a great challenge to determine the suitable reaction conditions that would enable $A_2 + B_4$ polymerization to yield hyperbranched polymers with high molecular weight. Most recently, Baek et al. found that the gelation could be efficiently avoided in preparation of hyperbranched poly(ether ketone) from $A_2 + B_3$ approach via the solubility difference of monomer in the reaction medium.⁵¹ They ascribed the result to the following two factors: (1) self-regulated feeding of the aryl ether monomers into the system driven by their poor solubility and phase separation from PPA/P2O5 medium; (2) reaction-medium-induced isolation of growing macromolecules promoted by the high bulk viscosity. Thereby, we speculated that other families of hyperbranched polymers can also be realized via the elaborate selection of solvents and control of polymerization condition.

Given the previously mentioned considerations, herein, we tried to synthesis hyperbranched polymers with a rigid tetrahedral core by step-growth heterogeneous polycondensation, based on kinetic control from $A_2 + B_4$ monomers (see Scheme 1). For this purpose, diphenyl sulfone, which is a poor solvent for TCS, was selected as the reaction medium for the esterification reaction between TCS and hydroquinone diacetate. The polymerization was conducted at 260 °C in a fixed concentration of 20 wt %. With the reaction proceeding, the TCS was slowly dissolved into the reaction system and engaged in the polymerization process. It can be clearly observed

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Scheme 1. Synthesis of Hyperbranched Tetrahedral Polyarylate via Polymerization of A₂ and B₄ Monomers



that the heterogeneous mixture turned gradually to homogeneous and transparent solution within 8-12 h. The polymer was precipitated in ethanol, and the collected product was washed with hot ethanol for several times to remove any residual catalyst, unreacted monomers, and low-molecular-weight oligomers. Subsequently, the product was extracted with DMF using a Soxhlet apparatus for 24 h to remove the insoluble fraction. The extract liquid was precipitated in ethanol and the white product was collected and dried at 100 °C under a vacuum to give a yield of 70%-80%. The highyield soluble products demonstrated that the gelation could be suppressed indeed by the slow feeding of the TCS monomer into the polymerization system, because of its poor solubility. In addition, by adjusting the monomer ratio with $A_2/B_4 < 2$, mainly carboxyl-terminated hyperbranched polyarylate (CTHP) could be obtained. Similarly, a monomer ratio of $A_2/B_4 > 2$ led to the mainly acetoxy-terminated hyperbranched polyarylate (ATHP). The polymers showed good solubility in various solvents such as THF, CH₂Cl₂, CHCl₃, acetone, DMF, NMP, DMSO, and DMAc.

Characterization of Hyperbranched Polyarylates. The chemical structures of the hyperbranched polyarylates were analyzed by FT-IR spectra of Figure 1. The presence of aromatic ester groups at 1737 cm⁻¹ provided evidence for the formation of polyarylate. The careful observation of enlarged peak at 1737 cm⁻¹ showed that it consisted of the other two absorptions: the peak at 1700 cm⁻¹ attributed to



Figure 1. FT-IR spectra of the hyperbranched polyarylates ATHP and CTHP.



Figure 2. ¹H NMR spectra of the hyperbranched polyarylates ATHP and CTHP.

the carboxylic acid and that at 1763 cm^{-1} corresponded to the carbonyl stretching of acetate group. For ATHP, the peak at 1763 cm^{-1} was stronger than that at 1700 cm^{-1} , indicating that it was mainly acetoxy-terminated. In contrast, in the FTIR spectrum of ATHP, the absorption at 1700 cm^{-1} was stronger than that at 1763 cm^{-1} . Besides, there was an apparent absorption band at $2500-3600 \text{ cm}^{-1}$ assigned to the vibration of OH in the carboxylic acid group, meaning that the end groups of CTHP were mainly

Table 1. Polymerization Results for the Synthesis of the Hyperbranched Polyarylates via the $A_2 + B_4$ Approach

polyarylate	yield (%)	$\eta inh (dL/g)$	$M_{\rm w}({ m g/mol})$	$M_{\rm n}~({\rm g/mol})$	PDI	$n_{(-COOH)} (mmol/g)$	$n_{(-OCOCH_3)} \text{ (mmol/g)}$	DB	$T_{\rm g}$ (°C)
ATHP	75	0.18	33290	8963	3.71	0.582	0.769	0.69	146
CTHP	70	0.12	10134	5827	1.71	0.741	0.343	0.53	155

carboxyls. This conclusion was further demonstrated by ¹H NMR spectra of Figure 2, where all the peaks were assigned to the protons labeled in the structure of hyperbranched polymer (see Scheme 1). The signals of the aromatic protons in polymers are divided into four groups, i.e., silarylene protons adjacent to aromatic ester linker (a and b), silarylene protons adjacent to carboxyl group (c and d), phenylene protons adjacent to acetate group (g and f), and phenylene protons adjacent to aromatic ester linker (e). In the spectrum of CTHP, the obvious carboxylic proton appeared at 13.2 ppm, whereas this signal was very weak for ATHP. Moreover, using cyclohexane as an internal standard (at 1.39 ppm), the content of terminal carboxylic acid group and acetoxy group could be calculated using the integral areas of peaks at 13.2 ppm, corresponding to the carboxylic proton, and at 2.3 ppm, corresponding to the acetate proton, and the results are listed in Table 1, which showed that there were more acetoxy groups than carboxyl groups in ATHP, and the result was opposite for CTHP, agreeing well with the observation of FTIR spectra.

The degree of branching (DB) was calculated according to eq 1, as described by Frey:⁵²

$$DB = \frac{D + T - N}{D + T + L - N} = \frac{2D}{2D + L}$$
(1)

where N refers to the number of molecules, and D, T, and L refer to the number of dendritic, terminal, and linear units in the polymer, respectively. Usually, DB is determined from ¹H NMR or ¹³C NMR spectra by comparing the integral area of the peak of the respective unit in the hyperbranched polymer. However, in our study, because of the tetrahedral symmetric character of the branched unit in the hyperbranched polyarylates, no branching signal could be observed from the ¹H NMR spectra. Fortunately, the hyperbranched polymers contain a sp³silicon core, while the Si atom can give an $\sigma - \pi$ conjugation and support the transport of electrons,⁵³ as illustrated in Figure 3. Thus, in the expanded Si signal (at approximately -10 ppm) of the ²⁹Si NMR spectra (Figure 4), the resonance could be resolved into four resonances with slight overlap. The assignments of D_1 , D₂, L, and T signals of these resonances were made in reference to the resolution of quaternary carbons of hyperbranched polymers with sp³-carbon cores, such as pentaerythritol and trimethylol propane in the ¹³C NMR spectra.⁵⁴ For an accurate integration of each resonance, the overlapping peaks were separated by Origin software, using a Gaussian-Lorentzian cross-fitting function. For mainly acetoxy-terminated hyperbranched polyarylate



Figure 3. Illustrations of the sp³-hybridized carbon and silicon cores in the hyperbranched polymers: (a) pentaerythritol or trimethylol propane core, (b) tetraphenylsilane core, and (c) $\sigma - \pi$ conjugation of arylsilane.



Figure 4. ²⁹Si NMR spectra of the hyperbranched polyarylates ATHP and CTHP.

(ATHP), the contents of D_1 , D_2 , T, and L were 29.01%, 13.7%, 19.09%, and 38.2%, respectively, and the calculated DB value, according to eq 1, was 69%. For mainly carboxyl-terminated hyperbranched polyarylate (CTHP), the percentages of D_1 , D_2 , T, and L were 19.91%, 5.43%, 28.92%, and 45.74%, respectively, resulting in its DB value of 53%. These DB values indicated that both polymers exhibited a nearly ideal hyperbranched structure (DB close to 0.5) rather than a linear (DB close to zero) or dendritic structure (DB close to unity).

The molecular weights and distributions of the hyperbranched polyarylates were characterized by GPC, using THF as an eluent. Figure 5 shows the GPC traces, and the results are given in Table 1. The weight-average molecular weights of polymers ATHP and CTHP were 33 290 and 10134 g/mol, respectively, which are comparable to that of hyperbranched polyarlyates prepared from AB_n or $A_2 + B_3$ monomers.⁹⁻¹² Note that, because hyperbranched polymers have a smaller radius of chain gyration than the

⁽⁵²⁾ Hölter, D.; Burgath, A.; Frey, H. Acta Polym. 1997, 48, 30.

 ⁽⁵³⁾ Uhlig, W. Prog. Polym. Sci. **2002**, 27, 255.
 (54) Jena, K. K.; Raju, K. V. N.; Prathab, B.; Aminabhavi, T. M. J. Phys. Chem. B 2007, 111, 8801.



Figure 5. GPC traces of the hyperbranched polyarylates ATHP and CTHP.



Figure 6. DSC curves of the hyperbranched polyarylates ATHP and CTHP.

linear polystyrene standards, the actual molecular weights may be higher than the measured results. Moreover, the low inherent viscosity of 0.12-0.18 dL/g reflected the typical characteristic of hyperbranched polymer. Because of the presence of two types of branching units including D_1 and D_2 units in the structure, hyperbranched polyarylates will lead to increased diversity of structural topologies. Therefore, ATHP and CTHP exhibited the slightly rough GPC traces, indicative of multimodal character, because of the existence of different molecular-weight products with highly irregular structures, and this phenomenon was more obvious for ATHP with relatively higher molecular weight.

As shown in the DSC curves in Figure 6, the T_g values of polymers ATHP and CTHP were 146 and 155 °C, respectively. Even though a rigid tetraphenylsilane core is present, ATHP and CTHP exhibited rather low T_g values, compared to their analogue hyperbranched polyarylate prepared from terephthaloyl chloride (A₂ monomer) and 1,1,1-tris(4-hydroxyphenyl)-ethane (B₃ monomer).⁵⁵ The reason might be ascribed to that the rigid tetrahedral unit could open up the polymer segments, leading to ATHP and CTHP the higher free volume and enhanced segmental motion ability. In addition, it was observed that the T_g value of CTHP was higher than that of the mainly acetoxy-terminated hyperbranched polyarylate (ATHP) because of the much denser intermolecular hydrogen-bonding caused by the carboxylic acid groups in CTHP. However, the T_g increase was not so significant, probably because the CTHP has a lower molecular weight than ATHP.

Preparation of Precursor Film and Its Curing Reaction. Hyperbranched polymers generally have poor film-forming ability, because of the lack of chain entanglement. However, if the large number of terminal functional groups can be reacted with appropriate difunctional compounds and connected via chemical bonds, tough films can be obtained.⁵⁶ In this study, because of the presence of two types of reactive groups, i.e., the carboxylic acid and acetoxy terminal groups in the hyperbranched polyarylate, the self-cross-linking reaction can occur without needing any additional curing agent, which means that the chemical composition of the cured film would be homogeneous and only constituted of pure polyarylate itself. To this end, a reactive precursor with an equivalent amount of two reactive terminal groups was easily prepared by simply mixing polymer ATHP with CTHP in the following weight ratio:

$$\frac{m_{\text{ATHP}}}{m_{\text{CTHP}}} = \frac{\left[n_{(-\text{COOH})} - n_{(-\text{OCOCH}_3)}\right]_{\text{CTHP}}}{\left[n_{(-\text{OCOCH}_3)} - n_{(-\text{COOH})}\right]_{\text{ATHP}}}$$
(2)

where m_{ATHP} and m_{CTHP} are the mass (in grams), whereas $[n_{(-OCOCH_3)} - n_{(-COOH)}]_{ATHP}$ and $[n_{(-COOH)} - n_{(-OCOCH_3)}]_{CTHP}$ (given in units of mol/g) are the net molar number of acetoxy and carboxyl groups per mass unit for the hyperbranched ATHP and CTHP, respectively.

To fabricate a cross-linking film, as illustrated in Figure 7, the DMF solution of precursor was filtered through a 0.25- μ m Teflon filter, and the spin-coating operation was performed in a Class 1000 ultraclean room. The curing process of the precursor was monitored by DSC. As shown in Figure 8, the endothermic peak of curing reaction started at ~200 °C and ended at ~350 °C. Therefore, the cure schedule was set as 1 h at 150 °C, 2 h at 180 °C, 5 h at 220 °C, 5 h at 250 °C, and 1 h at 320 °C to ensure a complete reaction between the carboxylic acid and acetoxy terminal groups. The FTIR spectrum in Figure 9 showed that, after curing, the methyl absorption at 2960 and 2880 cm⁻¹ disappeared. Moreover, there was only a singlet symmetric peak at ~ 1737 cm⁻¹, and the former carbonyl peaks at 1700 cm^{-1} (COOH group) and at 1763 cm^{-1} (OCOCH₃ group) could not be observed, confirming that the curing reaction was complete.

The AFM height image (Figure 10) exhibited that the surface of cured film was smooth with a roughness of \sim 4 nm. The solvent resistance of the film was evaluated by immersing it into various solvents, including

⁽⁵⁵⁾ Fan, Z.; Lederer, A.; Voit, B. Polymer 2009, 50, 3431.



Cross-linked network





Figure 8. DSC scan of the hyperbranched precursor just (a) prior to curing and (b) after curing.

chloroform, THF, NMP, DMSO, DMAc, etc., for 24 h, and no visible change can be observed. The glass transition



Figure 9. FT-IR spectra of the cured film.



Figure 10. AFM image of the surface for the cured film.

of the cured film could not be detected during heating from 100 °C to 400 °C in the DSC thermogram, because of the highly restricted segmental mobility after cross-linking. As illustrated in Figure 11, the cured film exhibited excellent thermal stability with a 5% decomposition temperature ($T_{d5\%}$) of >483 °C. The sharp decomposition curve confirmed the homogeneous network structure of the film.

Thermosetting Film of Intrinsic Microporosity. As shown in the nitrogen adsorption/desorption isotherms for the cured network in Figure 12, the film sample has a high uptake at low relative pressure, exhibiting the characteristics of substantially microporous materials.⁵⁷ The isotherms shows significant hysteresis with desorption curve lying above the adsorption curve, which can be classified as Type 1B. The measured results showed that the cured film has an apparent surface area of 158 m²/g, an average pore size of 11.2 Å, and a total pore volume of 0.1 cm³/g, as calculated from the amount of gas adsorbed at $P/P_0 = 0.99$. The present microporous thermosetting polyarylate film was constructed with the rigid tetrahedral units held together by aromatic ester linkers (Figure 13). Compared with precipitated PIM powders

⁽⁵⁷⁾ Rouqueol, F.; Roquerol, J.; Sing, K. Adsorption by Powders and Porous Solids; Academic Press: London, 1999.

100

90

80





Figure 11. TGA curve of the cured film.



Figure 12. Nitrogen adsorption/desorption isotherms at 77 K for the cured film.

reported in the literature, the amount of microporosity in the studied film was relatively modest. This might be ascribed to the ease of rotation about the ester bonds that enabled the polymer to be densely packed. It could be proposed that, if the semirigid aromatic ester linker was substituted by a full rigid rod one, a large surface area would be obtained. However, such fully rigid networks were unfavorable for the formation of tough films, because of the difficulty in releasing internal stresses induced by the curing reaction. In this regard, it still remains a great challenge to synthesize microporous polymer networks with the excellent combination of film-forming properties, huge surface area, and narrow pore size distribution.

Optical and Dielectric Properties of Cured Film. The optical properties of the thermosetting film were measured by a prism-coupling method. The refractive indices for in-plane and out-plane of the film were 1.4962 and 1.4927, respectively. The microporous structure in the film resulted in much-lower refractive indices than most linear and cross-linked polymers. The birefringence is defined as the difference in refractive indices between in-plane and out-of-plane of a film. For many optical



Figure 13. Rigid tetrahedral core (panel a) in the cured cross-linked network (panel b).

applications such as wave guides, optical fibers, and optical storage elements, the optically isotropic characteristic of a material is very important. The three-dimensional cross-linking structure using highly symmetrical building blocks, i.e., tetraphenylsilane, as branch point imparts isotropic properties to the cured film well, exhibiting a low birefringence of only 0.0035.

The porous materials has been an active research area for development of film with low dielectric constant.⁵⁸ For the modern microelectronic industry with feature size of $< 0.13 \ \mu m$, porous film materials possessing low dielectric constant, uniform porosity, and small porous size (<2 nm), as well as good film formation and excellent thermal stability, are strongly desired. In the present work, the dielectric constant of the thermosetting film can be estimated from the refractive indices, according to the following equation:

$$\varepsilon = 1.1 n_{\rm av}^2$$

where ε is the dielectric constant at 1 MHz and n_{av} is the average refractive index.⁵⁹ As expected, the determined ε value was as low as 2.45. Compared with conventional porous polymeric materials, in the present work, the microporosity was engineered within the thermosetting polyarylate film via the direct polymerization reaction of a precursor containing a specific rigid tetrahedral skeleton, without the use of any porogen, cross-linker, and catalyst, showing promising potential application in integrated circuit (e.g., as an interlayer insulating layer).

Conclusions

In this work, we synthesized a novel class of hyperbranched macromolecular architectures from hydroquinone diacetate as the A₂ monomer and tetrakis(4-carboxyphenyl)silane as the B4 monomer by step-growth heterogeneous polycondensation based on kinetic control. Depending on the monomer feed ratio, two type of polymers-i.e., mainly carboxyl-terminated hyperbranched polyarylate (CTHP) and mainly acetoxy-terminated hyperbranched polyarylate

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(ATHP)—were obtained in good yields. The resulting polymers had degree of branching (DB) values that ranged from 0.53 to 0.69, moderate molecular weights, low inherent viscosity, and good solubility in the common solvent. The self-curable precursor with an equivalent amount of carboxylic acid and acetoxy-terminated groups was prepared by simply mixing the CTHP with ATHP. Thermal curing of the precursor led to a microporous thermosetting film, which own good film formation, excellent thermal stability, good solvent resistance, low birefringence, and low dielectric constant, showing promising potential in the applications such as separation membrane, optical and electronic materials, etc. Acknowledgment. We thank the National Science Foundation of China (through Nos. 50673014 and 20874007) and the Program for New Century Excellent Talents in University of China (through No. NCET-06-0280) for financial support of this research. We appreciate help from Jia You and Hao Yu for the AFM and optical measurements.

Supporting Information Available: This section contains seven figures (Figures S1–S7), including the FTIR and ¹H NMR spectra of compounds TTS and TCS, the ²⁹Si NMR spectra of hyperbranched polyarylates ATHP and CTHP, and the pore size distribution for cured polyarylate film as calculated by the Horvath–Kawazoe (HK) method. This material is available free of charge via the Internet at http://pubs.acs.org.