Macromolecules
ARTICLE

Macromolecules **2009**, *42*, 4099–4109 **4099**
DOI: 10.1021/ma900076z

Facile Polycyclotrimerization of "Simple" Arylene Bipropiolates: A Metal-Free, Regioselective Route to Functional Hyperbranched Polymers with High Optical Transparency, Tunable Refractive Index, Low Chromatic Aberration, and Photoresponsive Patternability

Cathy K. W. Jim,[†] Anjun Qin,[†,⊥] Jacky W. Y. Lam,*[,†] Matthias Häussler,[†] Jianzhao Liu,[†] Matthew M. F. Yuen,[‡] Jang Kyo Kim,[‡] Ka Ming Ng,[§] and Ben Zhong Tang*[,†,⊥]

[†]*Department of Chemistry and* [‡]*Department of Mechanical Engineering and* [§]*Department of Chemical and Biomolecular Engineering, The Hong Kong University of Science & Technology (HKUST), Clear Water Bay, Kowloon, Hong Kong, China, and* [⊥]*Department of Polymer Science and Engineering, Key Laboratory of Macromolecular Synthesis and Functionalization of the Ministry of Education of China, Zhejiang University, Hangzhou 310027, China*

Received January 14, 2009; Revised Manuscript Received April 28, 2009

ABSTRACT: A facile synthetic route to functional hyperbranched polymers is developed. Arylene bipropiolates (HC≡C−CO_2−Ar−O_2C−C≡CH; **1**−**4**) are readily prepared from a one-step esterification reaction between commercially available propiolic acid and arylene diols. Polycyclotrimerizations of **1**−**4** proceed regioselectively in reflux dimethylformamide (DMF), giving hyperbranched poly[1,3,5-tri(aroxycarbonyl)phenylene]s (*hb*-**P1**−*hb*-**P4**) of high molecular weights (M_w up to ∼8.3×10^5) in high yields (up to 82%). The polymers possess perfect 1,3,5-regiostructures and high degrees of branching (DB ∼ 88%). Little weights are lost when the polymers are heated to 390 °C under nitrogen or 380 °C in air. The polymers are highly transparent, allowing almost all light in the entire visible spectral region to transmit through. Thin solid film of *hb*-**P1** shows high refractive indices (RI = 1.6255−1.681) in the wavelength region of 400−1700 nm, extremely high modified Abbé number (ν_D' = 1030.7), and very low optical dispersion (D' = 0.000 97). Its RI values can be modulated and its thin films can be cross-linked by UV irradiation, enabling ready generation of negative photoresist patterns.

Introduction

Study of hyperbranched polymers is a "young" but "hot" area of research. Hyperbranched polymers are expected to show size-, shape-, branch-, and surface-related properties,[1] which may enable them to find an array of technological applications as nanoscale catalysts, chemical sensors, molecular antennae, supramolecular assemblies, micelle mimics, drug-delivery carriers, immunodiagnostic probes, and so forth.[2] Various hyperbranched polymers have been prepared by different synthetic strategies.[3] The most commonly used methods have been the condensation polymerizations of AB_n-type monomers, with A and B being mutually reactive functional groups and $n \geq 2$. The preparations of such multifunctional monomers, however, often require nontrivial synthetic efforts.[4] The monomers are difficult to keep and handle and easy to self-oligomerize during storage. The polymerization reactions are often initiated by in situ deprotection under harsh conditions, and the incomplete deprotection results in the formation of imperfect polymers with low molecular weights (MWs) and degrees of branching (DBs).

Acetylene cyclotrimerization is a century-old reaction for effective transformation of triple bonds to benzene rings. Polycyclotrimerizations of diyne molecules are anticipated to result in the formation of hyperbranched polyarylenes.[5] This simple A_2-type polycyclotrimerization approach will circumvent the synthetic difficulties encountered in the AB_n-type condensation polymerizations and produce stable polymers consisting of robust aromatic rings. This possibility, however, has not been actively explored because alkyne cycloadditions can easily run out of control to yield cross-linked gels.[5,6]

We have embarked on a research program on the development of the polycyclotrimerizations of diynes (**I**) initiated by transition-metal catalysts into a useful synthetic protocol for the construction of hyperbranched polyarylenes (**PI**; Scheme 1).[7] While cross-linking or gelation was involved in the diyne polycyclotrimerization reactions, we succeeded in the preparation of hyperbranched polyarylenes with excellent solubility through optimization of polymerization conditions. The polymers have been found to exhibit a variety of unique properties.[8] They are, for example, highly luminescent with fluorescence quantum yields up to unity, nonlinear optically active when photoexcited by laser pulses, thermally very stable (T_d up to 500 °C), and readily graphitized in high yields upon pyrolysis.

The tantalum-catalyzed diyne polycyclotrimerization, however, has some drawbacks: The catalysts are completely intolerant of polar functional groups, and the polymerization reactions therefore must be conducted under stringently moisture- and oxygen-free conditions. The polycyclotrimerization reactions proceed very rapidly, making the process control very difficult. Although the cobalt-based catalysts can polycyclotrimerize diyne monomers carrying certain functional groups, the resultant polymers generally have lower MWs and poorer optical and photonic properties than those prepared from the tantalum catalysts due to the presence of the catalyst residues in the polymer structures. Moreover, both the Ta and Co catalysts produce hyperbranched polymers

*Corresponding authors. E-mail: chjacky@ust.hk (J.W.Y.L.); tangbenz@ust.hk (B.Z.T.).

Published on Web 05/15/2009

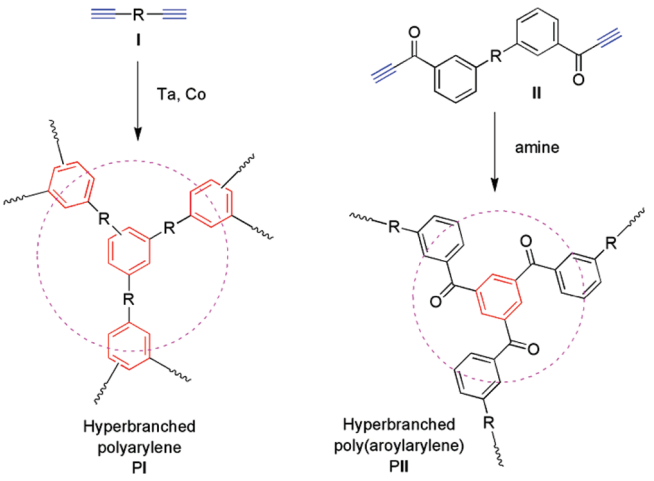
consisting of regiorandom structural units of 1,2,4- and 1,3,5-trisubstituted benzene isomers.

We have recently discovered that the polycyclotrimerizations of aroylacetylenes (**II**) catalyzed by the secondary amines (e.g., piperidine) produce hyperbranched poly(1,3,5-triaroylarylene)s (**PII**) with high DBs in high yields (Scheme 1).[9] The polycyclotrimerization is tolerant to polar functional groups and is strictly regioselective, furnishing polymers comprising of sole structural units of 1,3,5-trisubstituted benzene regioisomers. The aroylacetylene monomers (**II**), however, are difficult to prepare. It takes many steps of reactions to synthesize the monomers and the reactions involve the use of toxic heavy-metal oxidants such as MnO_2 and CrO_3.[9] It would be nice if the polycyclotrimerization can be extended or applicable to the "simple" diyne monomers that can be readily prepared from commercially available starting materials by one-step reaction in one-pot procedure in an environmentally benign fashion.

Careful examination of the molecular structure of monomer **II** reveals that this polymerization works for electron-deficient diynes, whose acetylene triple bonds are linked with electron-withdrawing groups. If the carbonyl linkage between the triple bond and the aromatic ring in the aroylacetylene can be replaced by an ester group, it will make the monomer synthesis much easier. Acetylenecarboxylic acid or propiolic acid **5** is a commercially available reagent and can be readily esterified with arylene diols **6** to give bipropiolates **1**−**4** (Scheme 2). If the bipropiolate monomers can be polymerized, it will pave the way to facile and economic syntheses of functional hyperbranched polymers. A propiolate, however, is less electron-deficient than an aroylacetylene because an ester group is less electron-withdrawing than a carbonyl group, which makes it uncertain whether or under what conditions an arylene bipropiolate will undergo polycyclotrimerization reaction.

In this work, we explore the possibility of regioselectively polycyclotrimerizing arylene bipropiolates **1**−**4**. In this paper, we show that the bipropiolate monomers can be effectively polycyclotrimerized in refluxed *N*,*N*-dimethylformamide (DMF) without adding any external catalysts, producing processable, regioregular, hyperbranched poly[1,3,5-tri(aroycarbonyl)phenylene]s or *hb*-PTACPs (**P1**−**P4**) with high DB values in high yields.[10] Structurally the *hb*-PTACPs are polyesters, but synthetically they are very difficult to access by the conventional polycondensation reactions of $A_2 + B_3$ monomers, with A_2 and B_3 being diol and triacid, respectively. Monomers of trisubstituted benzene derivatives (B_3) are generally difficult to prepare, with that carrying three electron-withdrawing ester groups at the 1,3,5-positions being particularly hard to make due to the well-known deactivating effect of the ester group. To make hyperbranched polymers with high MWs and DBs by the ($A_2 + B_3$)-type polycondensation reactions, strict stoichiometric balance is theoretically required but practically difficult to meet. Moreover, the $A_2 + B_3$ polycondensations are equilibrium reactions, with small MW compounds such as water generated as byproducts. The polycyclotrimerization of the A_2 monomers (**1**−**4**) is free of all these problems and is thus of great value in terms of synthetic methodology development.

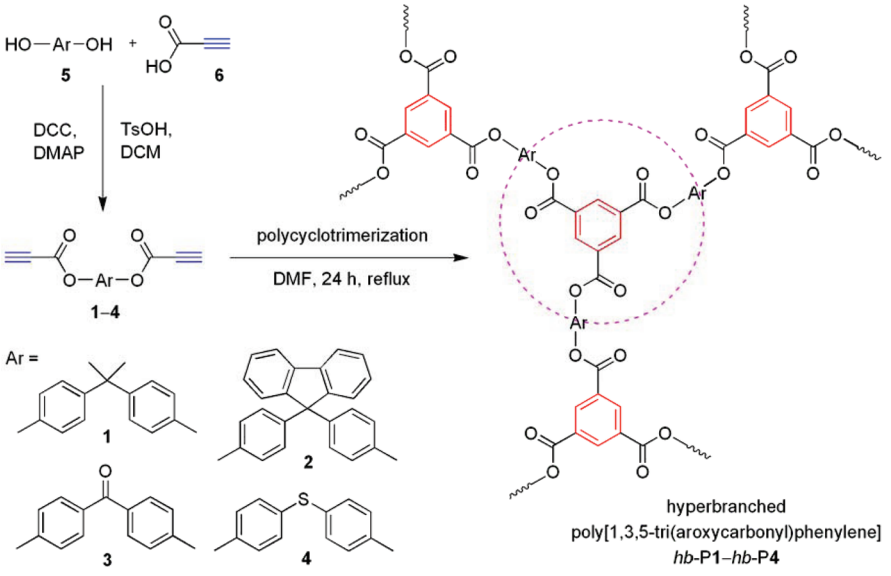
Scheme 1



Experimental Section

General Information. Tetrahydrofuran (THF, Labscan), toluene (BDH), and 1,4-dioxane (Aldrich) were distilled in an atmosphere of dry nitrogen from sodium benzophenone ketyl immediately prior to use. Dichloromethane (DCM) was distilled under nitrogen over calcium hydride. DMF was stirred with calcium hydride overnight, distilled under reduced pressure, and kept under dry nitrogen. Other solvents such as dimethyl

Scheme 2



sulfoxide (DMSO) and triethylamine were purified using standard procedures. Propiolic acid (**6**), bisphenol A (4,4′-isopropylidenediphenol), 4,4′-(9-fluorenylidene)dipheol, 4,4′-dihydroxylbenzophenone, 4,4′-thiodiphenol, 1,3-dicyclohexylcarbodiimde (DCC), 4-(dimethylamino)pyridine (DMAP), *p*-toluenesulfonic acid monohydrate (TsOH), and all other chemicals were purchased from Aldrich and used as received without further purification.

Relative number-average ($M_{n,r}$) and weight-average ($M_{w,r}$) molecular weights and polydispersity indices (PDI or $M_{w,r}/M_{n,r}$) of the polymers were estimated by a Waters Associates gel permeation chromatography (GPC) system equipped with RI and UV detectors. THF was used as eluent at a flow rate of 1.0 mL. A set of monodisperse linear polystyrenes was used as standards for MW calibration. Absolute weight-average molecular weights ($M_{w,a}$) of the polymers were measured by 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 He−Ne laser (λ = 632.8 nm, uniphase) as light source. The RI increment (dn/dc) was determined to be 0.292 mL/g in THF at 25 °C on an Optilab DSP (Digital Signal Processing) refractometer (Wyatt Technology; λ = 632.8 nm, $c \leq$ 1.0 mg/mL).

IR spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX 300 NMR spectrometer using $CDCl_3$, DMSO-d_6, or DCM-d_2 as deuterated solvent. Light transmission spectra were measured on a Milton Roy Spectronic 3000 array spectrophotometer. MALDI-TOF spectra were recorded on a GCT Premier CAB048 mass spectrometer operating in a chemical ionization mode (CI) with methane as carrier gas. Elemental analyses were conducted with an Elementary Vario EL analyzer. Thermogravimetric analysis (TGA) measurements were carried out under nitrogen or in air on a Perkin-Elmer TGA 7 analyzer at a heating rate of 10 °C/min. RI values were measured on a Gaertner L116C ellipsometric thin film thickness measurement system using 1 mW He−Ne laser beam (λ = 632.8 nm) as light source or determined on a J.A. Woollam variable angle ellipometry system with a wavelength tunability from 300 to 1700 nm. To fit the acquired Ψ and Δ curves with the data obtained from the three-layer optical model consisting of crystalline silicon substrate, 2 nm SiO_2 layer, and a uniform polymer film, the Levenberg−Marquardt regression algorithm was employed. The Cauchy dispersion law was applied to describe the polymer layer from visible to IR spectral region.

Monomer Preparation. Arylene bipropiolates **1**−**4** were prepared by esterifications of arylene diols **5** with propiolic acid (**6**) in the presence of DCC, DMAP, and TsOH (cf. Scheme 2). The detailed experimental procedure for the synthesis of monomer **1** is given below as an example. In a 500 mL round-bottom flask were dissolved 3.26 g (14 mmol) of bisphenol A, 8.86 g (43 mmol) of DCC, 0.70 g (5.8 mmol) of DMAP, and 1.08 g (5 mmol) of TsOH in 240 mL of dry DCM/THF (3:1 v/v). The solution was cooled to 0 °C with an ice−water bath, into which 2.0 g (28.6 mmol) of **6** dissolved in 20 mL of DCM/THF (3:1 v/v) was added under stirring via a dropping funnel. The reaction mixture was stirred overnight. After filtering out the solid, the solution was concentrated by a rotary evaporator. The crude product was purified by a silica gel column using chloroform/hexane (1:2 v/v) as eluent.

*Characterization Data for 4,4′-Isopropylidenediphenyl Bipropiolate (**1**).* White solid; yield 53.2% (2.52 g). IR (thin film), ν (cm^{-1}): 3266, 2934, 2124, 1730, 1634. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.26 (d, 2H), 7.05 (d, 2H), 3.06 (s, 1H), 1.67 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 151.0, 148.5, 147.7, 127.9, 120.6, 76.6, 74.3, 42.6, 30.8. HRMS (MALDI-TOF): m/z 333.1080 [(M + H)$^+$, calcd 333.3493]. Anal. Calcd for $C_{21}H_{16}O_4$: C, 75.89; H, 4.85. Found: C, 75.17; H, 5.01.

Other monomers (**2**−**4**) were prepared by the similar procedures, and their characterization data are given below.

*4,4′-(9-Fluorenylidene)diphenyl Bipropiolate (**2**).* White solid; yield 50.7%. IR (thin film), ν (cm^{-1}): 3268, 2125, 1730, 1502. ^{1}H NMR (300 MHz, DMSO-d_6), δ (TMS, ppm): 7.97 (d, 1H), 7.45 (t, 2H), 7.36 (d, 2H), 7.34 (t, 2H), 7.16 (t, 2H). ^{13}C NMR (75 MHz, DMSO-d_6), δ (TMS, ppm): 150.6, 150.0, 148.2, 143.8, 139.5, 128.9, 128.1, 128.0, 126.0, 121.5, 120.7, 81.5, 74.2, 23.3. HRMS (MALDI-TOF): m/z 454.0749 (M$^+$, calcd 454.4722). Anal. Calcd for $C_{31}H_{18}O_4$: C, 81.93; H, 3.99. Found: C, 81.52; H, 3.92.

*4,4′-Benzophenonylene Bipropiolate (**3**).* White solid; yield 52.6%. IR (thin film), ν (cm^{-1}): 3263, 2122, 1732, 1656, 1599. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.88 (d, 2H), 7.32 (d, 2H), 3.15 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 193.9, 152.8, 150.2, 135.4, 131.7, 121.4, 77.4, 73.9. HRMS (MALDI-TOF): m/z 319.0640 [(M + H)$^+$, calcd 319.2797]. Anal. Calcd for $C_{19}H_{10}O_5$: C, 71.70; H, 3.17. Found: C, 71.53; H, 2.99.

*4,4′-Thiodiphenyl Bipropiolate (**4**).* Pale yellow solid; yield 57.3%. IR (thin film), (ν, cm^{-1}): 3273, 2934, 2126, 1732, 1585, 1487. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.37 (d, 2H), 7.13 (d, 2H), 3.90 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 150.6, 149.0, 135.8, 132.3, 122.8, 77.1, 74.0. HRMS (MALDI-TOF): m/z 323.0307 [(M + H)$^+$, calcd 323.3346]. Anal. Calcd for $C_{18}H_{10}O_4S$: C, 67.07; H, 3.13. Found: C, 67.07; H, 3.65.

Polymer Synthesis. All the polymerization reactions were carried out under dry nitrogen using a standard Schlenk technique, unless otherwise specified. A typical procedure for the polymerization of **1** is given below as an example. In a 15 mL Schlenk tube with a three-way stopcock on the side arm was placed 88.7 mg of **1** (0.267 mmol) under nitrogen in a glovebox. Distilled DMF (1.5 mL) was added to dissolve the monomer using a hypodermic syringe. After stirring under reflux for 24 h, the mixture was added dropwise to ∼300 mL of methanol through a cotton filter under stirring. The precipitate was allowed to stand overnight and then collected by filtration. The isolated polymer (*hb*-**P1**) was washed with methanol and dried under vacuum at room temperature to a constant weight.

Characterization Data for hb-P1. Brown powder; yield 68.4% (Table 2, run 2). $M_{w,r}$ 15 600; M_w/M_n 2.4 (GPC, polystyrene calibration); $M_{w,a}$ 832 000 (LLS). IR (thin film), ν (m^{-1}): 2966, 2922, 2872, 1743, 1603, 1504. ^{1}H NMR (300 MHz, DCM-d_2), δ (TMS, ppm): 9.16, 7.91, 7.26, 7.17, 7.03, 6.69, 1.70, 1.67. ^{13}C NMR (75 MHz, DCM-d_2), δ (TMS, ppm): 157.2, 154.9, 149.3, 136.5, 132.0, 128.7, 121.8, 115.5, 43.2, 31.4.

hb-P2. Brown powder; yield 73%. $M_{w,r}$ 14 600; M_w/M_n 3.9 (GPC, polystyrene calibration); $M_{w,a}$ 830 000 (LLS). IR (thin film), ν (cm^{-1}): 3021, 2938, 1742, 1600, 1502, 1447. ^{1}H NMR (300 MHz, DCM-d_2), δ (TMS, ppm): 9.10, 7.79, 7.27, 7.10, 7.04, 6.94, 6.66. ^{13}C NMR (75 MHz, DCM-d_2), δ (TMS, ppm): 164.1, 155.6, 151.9, 150.3, 150.2, 140.8, 136.6, 131.9, 130.0, 128.6, 126.8, 122.2, 122.0, 121.1, 115.8.

hb-P3. Brown powder; yield 66%. $M_{w,r}$ 6900; M_w/M_n 2.4 (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 1736, 1650, 1595, 1499, 1409. ^{1}H NMR (300 MHz, DMSO-d_6), δ (TMS, ppm): 10.57, 9.17, 8.24, 7.93, 7.86, 7.78, 7.75, 7.55, 7.01, 6.13. ^{13}C NMR (75 MHz, DMSO-d_6), δ (TMS, ppm): 193.5, 166.2, 164.2, 163.0, 162.3, 162.0, 160.3, 158.7, 154.9, 135.3, 132.5, 132.1, 131.3, 128.4, 123.7, 117.5, 115.8.

hb-P4. Brown powder; yield 73%. $M_{w,r}$ 14 600; M_w/M_n 3.9 (GPC, polystyrene calibration). $M_{w,a}$ 200 000 (LLS). IR (thin film), ν (cm^{-1}): 2932, 2922, 1741, 1655, 1583, 1487. ^{1}H NMR (300 MHz, DCM-d_2), δ (TMS, ppm): 9.15, 7.95, 7.37, 7.24, 7.14, 7.08, 6.81. ^{13}C NMR (75 MHz, DCM-d_2), δ (TMS, ppm): 164.0, 136.7, 132.9, 129.7, 123.3, 119.8, 119.2, 117.3.

Model Reaction. Triphenyl benzene-1,3,5-tricarboxlate (**10**) was prepared as a model compound by cyclotrimerization of phenyl propiolate (**9**) (Scheme 3). The experimental procedures

Scheme 3

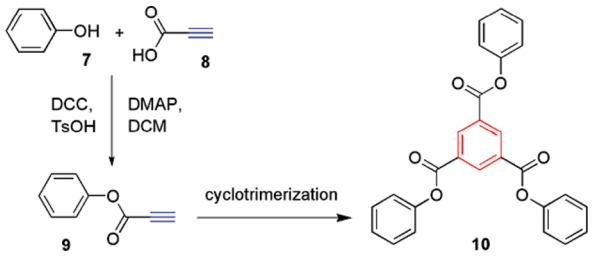


Table 1. Cyclotrimerization of Phenyl Propiolate (9)[a]

run	solvent	catalyst	yield (%)
1	1,4-dioxane	piperidine	25.0
2	toluene	piperidine	21.2
3	toluene/DMF[b]		00.0
4	DMF		34.2
5	triethylamine[c]		

[a] Refluxed under nitrogen for 24 h; [**9**] = 0.178 M; [piperidine] = 5.7 mM. [b] Volume ratio = 1:1. [c] Reaction mixture turned black with heat dissipation immediately after TEA was added.

for the synthesis of **9** and its cycloaddition are similar to those described above for the syntheses of **1** and *hb*-**P1**.

Characterization Data for ***9***. Colorless oil; yield 68.3%. IR (thin film), ν (cm^{-1}): 2931, 2854, 2117, 1732. ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.42 (t, 2H), 7.27 (t, 2H), 7.13 (d, 1H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 151.3, 121.6, 129.1, 125.5, 140.0, 76.8, 73.4.

Characterization Data for ***10***. White solid; yield 34.2% (Table 1, run 4). IR (thin film), ν (cm^{-1}): 1748, 1589, 1487. ^1H NMR (300 MHz, DMSO-d_6), δ (TMS, ppm): 9.04 (s, 1H), 7.52 (t, 2H), 7.38 (m, 3H). ^{13}C NMR (75 MHz, DMSO-d_6), δ (TMS, ppm): 163.0, 150.4, 135.1, 130.9, 129.7, 126.4, 121.9.

Photopatterning. Photo-cross-linking reactions of the polymer films were conducted in air at room temperature using the 365 nm light obtained from a Spectroline ENF-280C/F UV lamp at a distance of 1 cm as light source. The incident light intensity was ~18.5 mW/cm^2. The film was prepared by spin-coating the polymer solution (10% w/w in 1,2-dichloroethane) at 2000 rpm for 1 min on a silicon wafer. The polymer film was dried in a vacuum oven at room temperature overnight. The photoresist patterns ware generated using a copper photomask and taken on an optical microscopy (Olympus B202) using a normal light source.

Results and Discussion

Monoyne Model Reaction. Before studying polycyclotrimerization of bipropiolates, we synthesized a monopropiolate carrying one triple bond (**9**) and utilized it as starting material for a model reaction (Scheme 3). According to our previous study, aroylacetylenes can be cyclotrimerized when refluxed in 1,4-dioxane using piperidine as catalyst.[9b] We thus tried to cyclotrimerize **9** under the same conditions (Table 1, run 1). After 24 h, the solvent was evaporated, and the crude product was purified by silica gel column chromatography using chloroform/hexane (1:1 v/v) as eluent. Product isolation and structural characterization reveal that **10** is the sole product, confirming that **9** can undergo cyclotrimerization in the presence of the base in a regioselective fashion, although the conversion is not so efficient because the reaction conditions have not been optimized. Changing the solvent to toluene has slightly lowered the yield, whereas no product is even isolated when the reaction is carried out in a toluene/DMF mixture. The reaction conducted in DMF gives the best result (Table 1, run 4). Triethylamine fails to initiate the cycloaddition reaction, probably due to its reaction with the acidic ethynyl proton of **9**.

Table 2. Effect of Monomer Concentration on the Polymerization of Monomer 1[a]

run	$[M]_0$ (M)	yield (%)	$M_{n,r}$[b]	$M_{w,r}$[b]	$M_{w,r}/M_{n,r}$[b]	$M_{w,a}$[c]
1	0.120	51.7	5700	14 200	2.5	
2	0.178	68.4	6500	15 600	2.4	832 000
3	0.267	44.8	5800	15 200	2.6	
4	0.534	37.5	5600	15 800	2.8	

[a] Carried out in refluxing DMF for 24 h under nitrogen. [b] Determined by GPC in THF on the basis of a linear polystyrene calibration. [c] Absolute (a) value measured by LLS technique in THF.

Table 3. Time Course for Polymerization of Monomer 1[a]

run	time (h)	yield (%)	$M_{n,r}$[b]	$M_{w,r}$[b]	$M_{w,r}/M_{n,r}$[b]
1	6	19.7	4200	5400	1.3
2	12	22.1	4500	7200	1.6
3	18	55.8	6200	14 200	2.3
4	24	71.3	4800	13 800	2.9
5	36	71.2	4100	10 200	2.5

[a] Carried out in refluxing DMF under nitrogen; $[M]_0$ = 0.178 M. [b] Determined by GPC in THF on the basis of a linear polystyrene calibration.

Diyne Polycyclotrimerization. After confirming that monopropiolate **9** can undergo regioselective cyclotrimerization, we utilized the reaction to synthesize new hyperbranched polymers. We prepared arylene bipropiolates **1**−**4** by esterification reactions of their corresponding diols with propiolic acid in the presence of DCC, DMAP, and TsOH (cf. Scheme 2). All the monomers were fully characterized spectroscopically, from which satisfactory analysis data corresponding to their molecular structures were obtained (see Experimental Section for details).

We attempted to cyclotrimerize **1** by piperidine in 1,4-dioxane but isolated no polymeric product. We tried the reaction in refluxing DMF and succeeded in the transformation of the diyne monomer into its polymer *hb*-**P1** (Table 2, run 1). The active catalytic species for the reaction is believed to be the trace amount of dimethylamine generated from the in situ decomposition of DMF at the high temperature.[11] We increased the monomer concentration by ~1.5-fold and obtained a soluble polymer in a higher yield (~68%). Further increasing the monomer concentration, however, promoted the formation of cross-linking product and hence decreased the yield of soluble polymer.

We followed the time course of the polymerization of monomer **1** in DMF. The yield is generally increased with time and reaches its maximum value of ~72% at 24 h (Table 3). After polymerization for 18 h, the $M_{w,r}$ of the resultant polymer is high enough (14 200) for general purpose applications. It should be pointed out that this relative value is probably considerably underestimated because of the hyperbranched nature of the polymer.[12] Our previous investigations reveal that the underestimation can be very large.[13] The absolute molecular weight ($M_{w,a}$) of *hb*-**P1** may be much higher than the relative value estimated from the GPC analysis ($M_{w,r}$). Indeed, analysis of *hb*-**P1** by a LLS spectrometer gives an $M_{w,a}$ value of 8.32×10^5 (cf. Table 2, no. 2), which is 53-fold higher than its $M_{w,r}$ value.

Temperature exerts a strong influence on the polymerization reaction. Both the yield and molecular weight of the polymer are increased when the temperature is raised from 110 to 130 °C (Table 4). When the temperature is further increased to the boiling point of DMF, the polymerization results are improved significantly, with the polymer yield being ~4 times higher than that obtained at 130 °C.

Table 4. Effect of Temperature on Polymerization of Monomer 1[a]

run	temp (°C)	yield (%)	$M_{n,r}$[b]	$M_{w,r}$[b]	$M_{w,r}/M_{n,r}$[b]
1	110	7.1	3600	5400	1.5
2	130	17.5	4200	6300	1.5
3	153[c]	68.4	4600	11100	2.4

[a] Carried out in DMF for 24 h under nitrogen; $[M]_0$ = 0.178 M. [b] Determined by GPC in THF on the basis of a linear polystyrene calibration. [c] Boiling point of DMF.

Table 5. Polymerizations of Bipropiolate Monomers 1−4[a]

run	monomer	yield (%)	$M_{n,r}$[b]	$M_{w,r}$[b]	$M_{w,r}/M_{n,r}$[b]	$M_{w,a}$[c]
1[d]	**1**	68.4	6500	15 600	2.4	832 000
2[e]	**1**	72.3	4200	13 000	3.1	
3	**2**	73.2	3700	14 600	3.9	830 000
4	**3**	65.9	2900	6 900	2.4	
5	**4**	81.7	3300	5 200	1.6	200 000

[a] Carried out in refluxing DMF for 24 h under nitrogen; $[M_0]$ = 0.178 M. [b] Determined by GPC in THF on the basis of a linear polystyrene calibration. [c] Absolute (a) value measured by LLS technique in THF. [d] Data taken from Table 2, run 2. [e] Conducted in air.

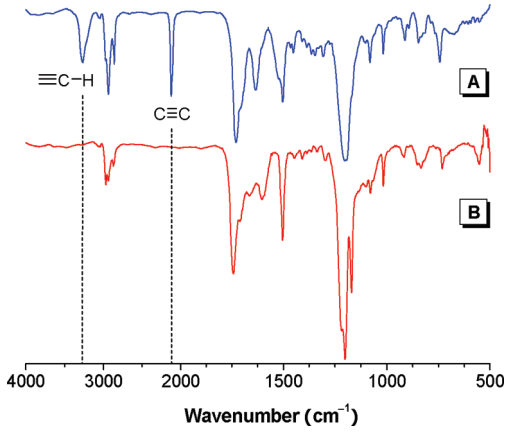


Figure 1. IR spectra of (A) monomer **1** and (B) its polymer *hb*-P**1** (sample taken from Table 2, run 2).

The above investigations enable us to polymerize **1**−**4** under optimal conditions. Table 5 summarizes the polymerization results. All the polycyclotrimerizations proceeded smoothly, giving *hb*-PTACPs in satisfactory yields. Comparing the polymerization results of **1** obtained under nitrogen and in air, it is clear that oxygen and moisture exert little effect on the polymerization reaction (cf. Table 5, runs 1 and 2). This helps simplify the reaction procedures. Similar to the case in *hb*-P**1**, the absolute molecular weights of *hb*-P**2** and *hb*-P**4** are much higher than their relative molecular weights. As no transition-metal catalyst is used in the process, this metal-free polycyclotrimerization enjoys the advantages being less toxic, environmentally friendlier, and economically sounder.

Structure Characterization. In the model reaction, the cyclotrimerization of monoyne **9** gives **10** as the sole product. Diynes **1**−**4** thus must have been polycyclotrimerized in a 1,3,5-regioselective manner. To collect direct structural information, we characterized polymers *hb*-P**1**−P**4** by spectroscopic methods. Examples of the IR spectra of P**1** and its monomer **1** are given in Figure 1. Diyne **1** shows absorption bands at 3266 and 2124 cm^{-1} due to ≡C−H and C≡C stretching vibrations, respectively. All these bands disappear in the spectrum of its polymer, indicating that the acetylene triple bonds have been converted to the benzene rings by the diyne polycyclotrimerization.

The ^{1}H NMR spectra of *hb*-P**1** and its monomer **1** as well as model compound **10** are shown in Figure 2. The acetylene

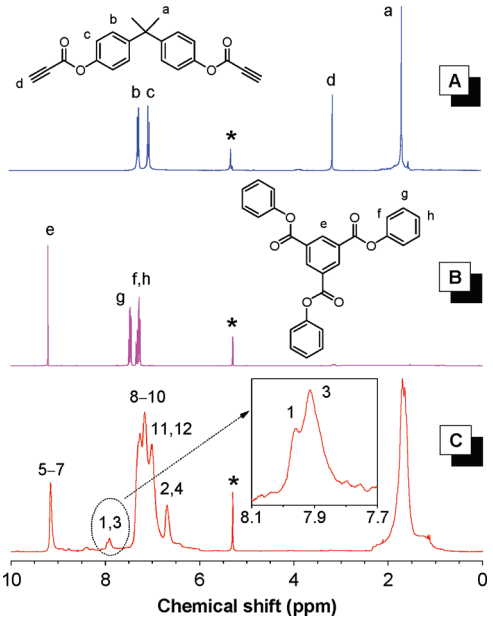


Figure 2. ^{1}H NMR spectra of (A) monomer **1**, (B) model compound **10** (sample taken from Table 1, run 4), and (C) polymer *hb*-P**1** (Table 2, run 2) in DCM-d_2. The solvent peaks are marked with asterisks.

proton of **1** resonates at δ 3.06, which completely disappears after the monomer is subjected to polycyclotrimerization reaction. By comparison with the spectra of monomer **1** and model compound **10**, the resonance peaks in the spectrum of polymer *hb*-P**1** can be readily assigned (cf. Chart 1). The polymerization shifts the resonance of the phenyl protons ortho to the ester group in **1** at δ 7.05 to 7.17 in *hb*-P**1**, while the phenyl protons in the periphery of *hb*-P**1** resonate at δ 7.03. The new peak at δ 9.16 is assigned to the proton resonances of the benzene rings newly formed by the cyclotrimerization polymerization. End-capping of one triple bond in a terminal branch by two triple bonds in one diyne monomer will generate a cyclophane ring, whose aromatic protons should resonate at δ ~9.3 and ~8.7. No such resonance peaks, however, are observed in the spectrum of *hb*-P**1**. Instead, two peaks arising from the resonance of the olefinic unit formed by the alkyne hydroamination (Scheme 4) are detected at δ 7.91 and 6.69 (Figure 2C, peaks 1 and 3).

The ^{13}C spectrum of *hb*-P**1** shows no resonance peaks of the acetylenic carbons of **1** at δ 76.6 and 74.3 (Figure 3). New peaks corresponding to the absorptions of the triphenoxycarbonylphenyl and olefinic carbons are observed at δ 136.5, 132.0, and 115.5 due to the conversion of the acetylene triple bonds of **1** to the benzene rings and double bonds of *hb*-P**1**.

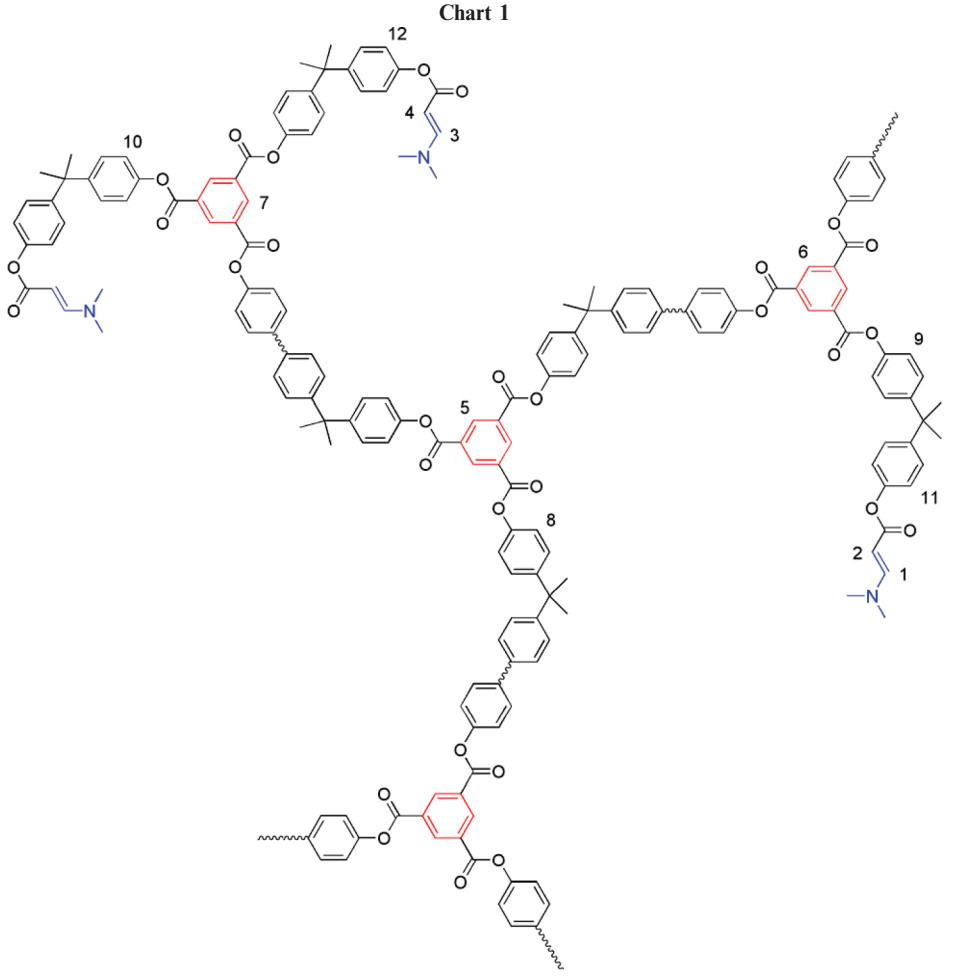
Degree of Branching. As shown in Chart 2, there exist three structural components in *hb*-P**1**: dendritic (D), linear (L), and terminal (T) units. Comparing the ^{1}H NMR spectrum of *hb*-P**1** with those of its monomer and model compound, the following relationships between the contents or fractions (f) of the structural units can be established.

$$\frac{3f_L + 3f_T + 3f_D}{f_L + 2f_T} = \frac{A_{5-7}}{A_{1,3}} \quad (1)$$

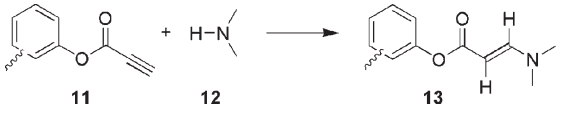
$$f_D + f_L + f_T = 1 \quad (2)$$

where A_{5-7} and $A_{1,3}$ represent the integrals of the areas of resonance peaks (5−7) and (1,3), respectively, as labeled in Chart 1 and panel C of Figure 2. The values can be

Chart 1



Scheme 4



determined from the ^{1}H NMR spectral data, from which, the following equation is deduced:

$$\frac{3f_L + 3f_T + 3f_D}{f_L + 2f_T} = \frac{1}{0.362} \quad (3)$$

Combining eqs 2 and 3 gives eq 4:

$$f_L + 2f_T = 1.086 \quad (4)$$

The peak at δ 7.91 corresponds to the resonance of the olefinic proton capped by the dimethylamino group. Magnification of the peak manifests that it is actually a doublet, and the amount of the olefinic bond in the L unit is ~8-fold lower than that in the T unit. Because there are two such protons in the T unit but only one in the L unit, eq 5 thus holds:

$$\frac{f_L}{2f_T} = \frac{1}{8} \quad (5)$$

From the above equations, f_L is calculated to be

$$f_L = 0.121 \quad (6)$$

According to definition, DB is expressed as[14]

$$DB = \frac{f_D + f_T}{f_D + f_L + f_T} \quad (7)$$

Incorporating eqs 2 and 6 into eq 7 gives the DB value of *hb*-**P1**:

$$DB = 1 - f_L = 0.879 \quad (8)$$

This value is much higher than those of the "conventional" hyperbranched polymer (commonly DB ~ 0.5),[1] which further confirms the hyperbranched structure of the polymer.

Solubility and Stability. All the *hb*-PTACPs are completely soluble in common organic solvents, such as toluene, DCM, chloroform, THF, and dioxane, and can be readily fabricated into tough solid films by spin-coating or solution-casting process. All the polymers are thermally stable. As can be seen from Figure 4A, the temperatures for 5% weight loss or the degradation temperatures (T_d) are near or higher than 300 °C under nitrogen. The T_d value for *hb*-**P2** is particularly high (392 °C), thanks to its bulky, stable fluorenyldiphenyl structural unit. The TGA thermograms of the hyperbranched polymers measured in air (Figure 4B) are similar to those taken under nitrogen, with all the polymers exhibiting high T_d values, indicative of their strong resistance to the thermolysis and oxidation at the high temperatures.

Optical Transparency. Polymers with high optical clarity are promising candidate materials for photonic

applications.[15] As shown in Figure 5, the *hb*-PTACPs absorb little light in the visible spectral region and allows all the light at wavelengths longer than 600 nm to transmit through. This excellent optical transparency is due to the molecular structures of the hyperbranched polymers. Polyesters often show high optical clarity, with poly(methyl methacrylate) (PMMA), poly(ethylene terephthalate) (PET), and polycarbonate (PC) being the best-known and widely used "organic glasses". The ester groups weaken the electronic communications between the aromatic rings in the *hb*-PTACPs and decrease their extents of electronic conjugations, thereby enhancing their optical transparency.

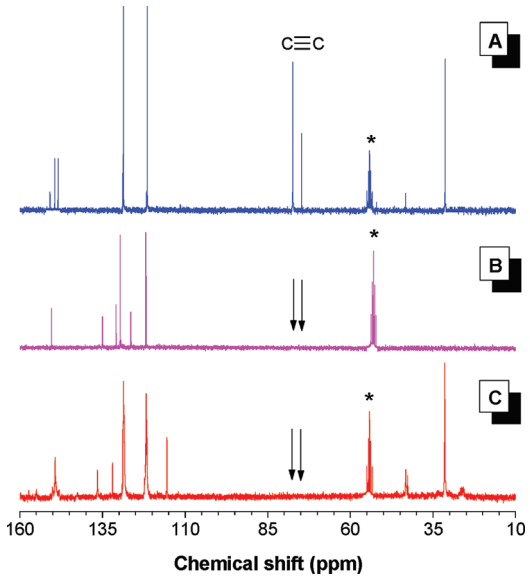
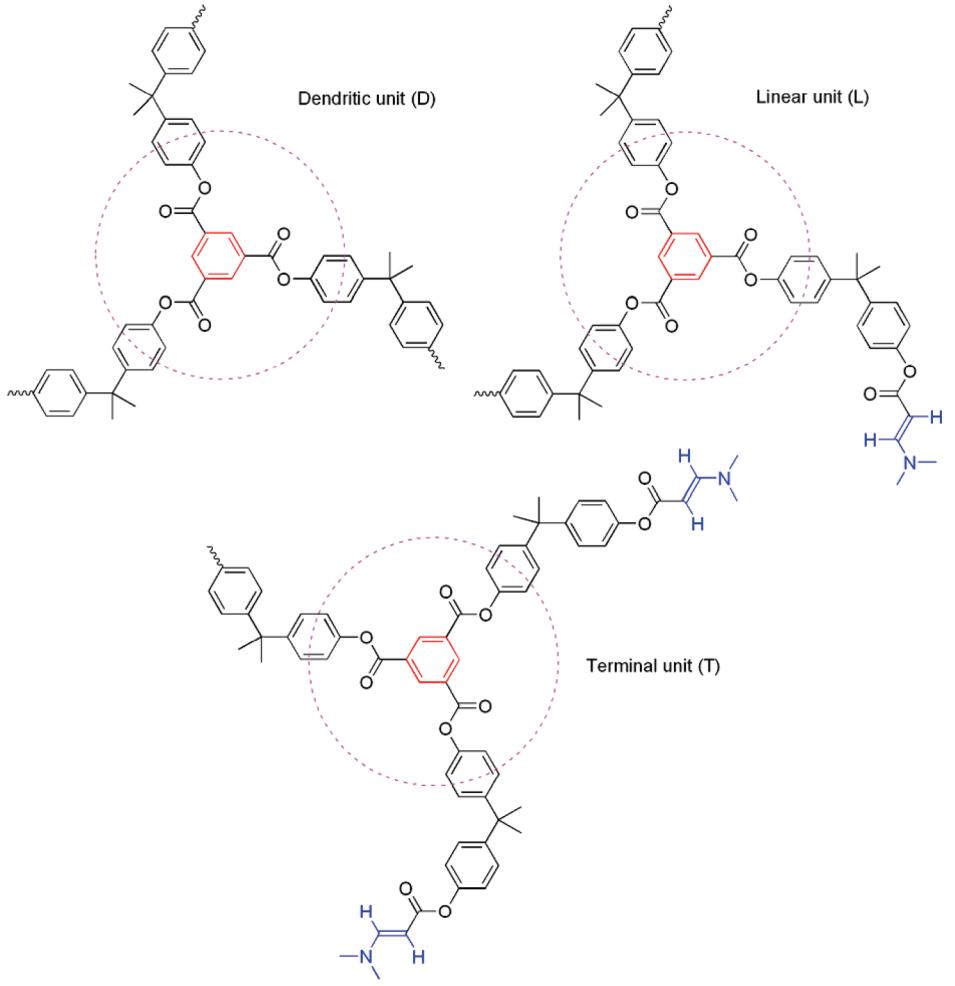


Figure 3. ^{13}C NMR of (A) monomer **1**, (B) model compound **10** (sample from Table 1, run 4), and (C) polymer *hb*-P**1** (Table 2, run 2) in DCM-d_2. The solvent peaks are marked with asterisks.

Light Refractivity. The *hb*-PTACPs are comprised of polarizable aromatic rings and ester groups and may show high refractive indices. Indeed, as can be seen from Figure 6, *hb*-P**1** displays high RI values (n = 1.6255−1.6181) in a wide wavelength region (400−1700 nm). The RI spectrum is almost flat: the RI value changes little over a wavelength span as wide as 1300 nm, which is very unusual and truly remarkable (vide post). Polymer *hb*-P**2** shows similarly high RI values, although its spectrum is not as flat as that of *hb*-P**1**. The RI value of *hb*-P**4** changes dramatically: the polymer has high (1.7687) and low (1.5133) RI values at 400 and 1700 nm, respectively. These different behaviors of the *hb*-PTACPs manifest the manipulability of their light refractivities by changing their molecular structures or through molecular engineering endeavors.

Unfortunately, a good fit could not be obtained between the experimental data and the theoretical model for *hb*-P**3**. Its RI value was thus measured at a single wavelength (632.8 nm) using a Gaertner ellipsometer. The RI data for all the *hb*-PTACPs at this wavelength are summarized in Table 6. The RI values of *hb*-P**1**−*hb*-P**3** are ≥1.62, much

Chart 2



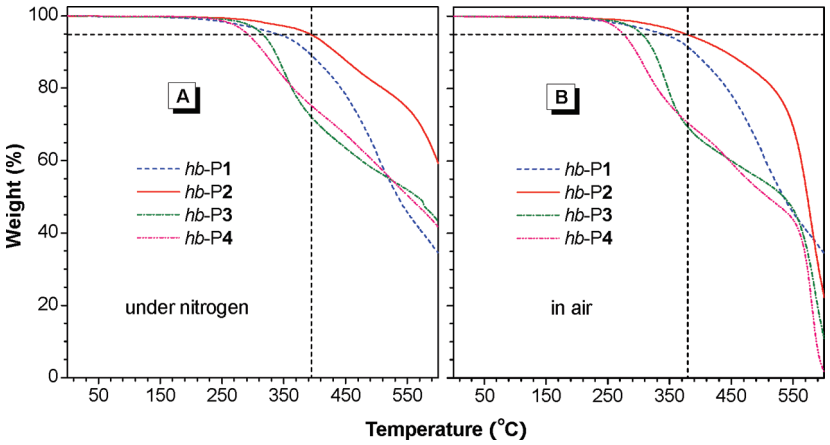


Figure 4. TGA thermograms of hyperbranched poly[1,3,5-tri(aroxycarbonyl)phenylene]s *hb*-**P1**−*hb*-**P4** recorded (A) under nitrogen and (B) in air at a heating rate of 10 °C/min.

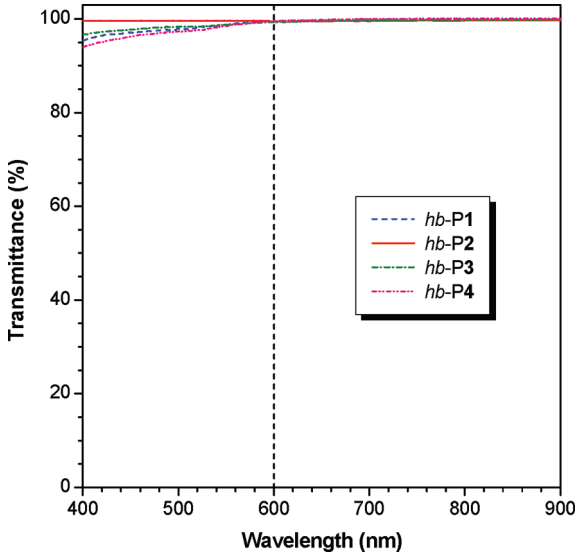


Figure 5. Light transmission spectra of THF solutions of *hb*-**P1**−*hb*-**P4**. Polymer concentration: 6.4 μg/mL (for *hb*-**P1**, *hb*-**P3**, and *hb*-**P4**) and 9.0 μg/mL (for *hb*-**P2**).

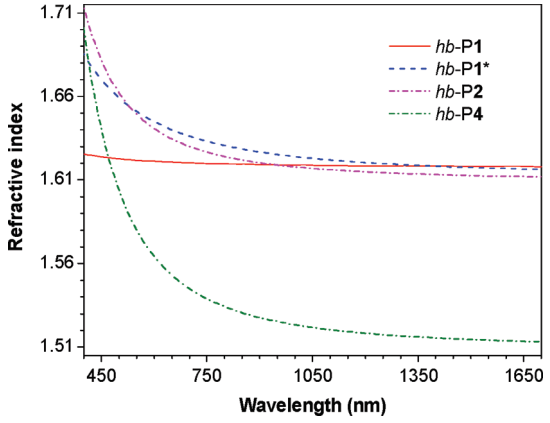


Figure 6. Wavelength dependence of refractive index of thin films of *hb*-**P1** (sample taken from Table 2, run 2), *hb*-**P2**, and *hb*-**P4**. Data for the thin film of *hb*-**P1** after UV irradiation under nitrogen for 30 min is denoted as *hb*-**P1***.

higher than those of the commercially important optical plastics (e.g., $n \sim 1.49$ for PMMA). While the light refractivity of *hb*-**P4** is relatively low ($n \sim 1.56$), it is still comparable to those of PET and PC (both $n \sim 1.58$). All the *hb*-PTACPs are thus highly refractive polymers. No or little birefringence is detected, implicative of the amorphous nature of their thin solid films.

Table 6. Refractive Indices and Chromatic Dispersions of *hb*-PTACPs[a]

film	$n_{632.8}$	ν_D	ν_D'	D	D'
hb-**P1**	1.6209	258.9	1030.7	0.0039	0.000 97
hb-**P1***[b]	1.6418	28.7	114.6	0.0348	0.008 73
hb-**P2**	1.6368	19.4	142.7	0.0516	0.007 01
hb-**P3**[c]	1.6200				
hb-**P4**	1.5571	9.3	72.7	0.1076	0.013 75

[a] All data taken from Figure 6, unless otherwise specified. Abbreviations: n = refractive index (at 632.8 nm), ν_D = Abbé number (calculated from eq 9), ν_D' = modified Abbé number (calculated from eq 10), and D' = chromatic dispersion (calculated from eq 11). [b] For the thin film of *hb*-**P1** after UV irradiation. [c] Single data point measured at 632.8 nm using an ellipsometer because a good fit could not be established for its RI spectrum.

The RI spectra of the thin solid films of *hb*-PTACPs can be tuned by UV irradiation. For example, upon exposure to a UV light of 365 nm under nitrogen for 30 min, the RI value of the thin film of *hb*-**P1** is greatly increased in the absorptive, short wavelength region. This is probably due to the structural change caused by polymer photolysis. It has been well-established that aromatic esters undergo photo-Fries rearrangement. The *hb*-PTACPs are poly(arylester)s and can therefore undergo the photo-Fries reaction (Scheme 5).[16] The C−O bond of the ester group in *hb*-**P1** is photocleaved, giving two polymer branches carrying radical terminals. Rearrangement and coupling of the radicals produce polymer **14** containing benzophenone units that give high RI values. Some carbonyl groups in polymer **14** may be further photolyzed, leading to the formation of polymer **16**, which will be discussed in the photo-cross-linking and photopatterning section below.

Figure 7 shows the UV absorption spectra of the thin solid film of *hb*-**P1** before and after the UV irradiation. The polymer absorbs only in the short wavelength region, in agreement with its high optical clarity in the visible spectral region. The peaks at 264 and 354 nm are due to the absorptions of its phenyl and triaroylphenyl groups, which are intensified by the photoirradiation, owing to the generation of the benzophenone units by the photo-Fries rearrangement. The high optical transparencies of the polymers in the long wavelength region, coupled with their high and tunable RI values, may allow them to find high-tech applications as coating materials in the advanced display systems such as microlens components for charge-coupled devices and high-performance CMOS image sensors.[17]

Chromatic Dispersion. For a material to be useful for practical applications, its optical aberrations should be small. The Abbé number (ν_D) of a material is a measure of the variation or dispersion in its RI value with wavelength, which is defined as

$$\nu_D = \frac{n_D - 1}{n_F - n_C} \quad (9)$$

where n_D, n_F, and n_C are the RI values at wavelengths of Fraunhofer D, F, and C spectral lines of 589.2, 486.1, and 656.3 nm, respectively. A modified Abbé number (ν_D') has been proposed to evaluate the application potential of an optical material, using its RI values at the nonabsorbing wavelengths of 1064, 1319, and 1550 nm.[18] The first two wavelengths are chosen in view of the practical interest of commercial laser wavelengths (Nd:YAG), while the last one is the wavelength for telecommunication. The modified Abbé number is defined as

$$\nu_D' = \frac{n_{1319} - 1}{n_{1064} - n_{1559}} \quad (10)$$

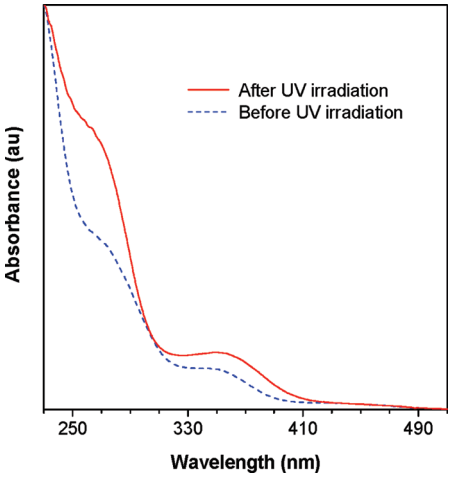


Figure 7. UV absorption spectra of a thin film of *hb*-**P1** (sample taken from Table 2, run 2) before and after UV irradiation under nitrogen for 30 min.

where n_{1319}, n_{1064}, and n_{1550} are the RI values at 1319, 1064, and 1550 nm, respectively. The chromatic dispersion (D') is the constringence of the Abbé number (ν_D'):

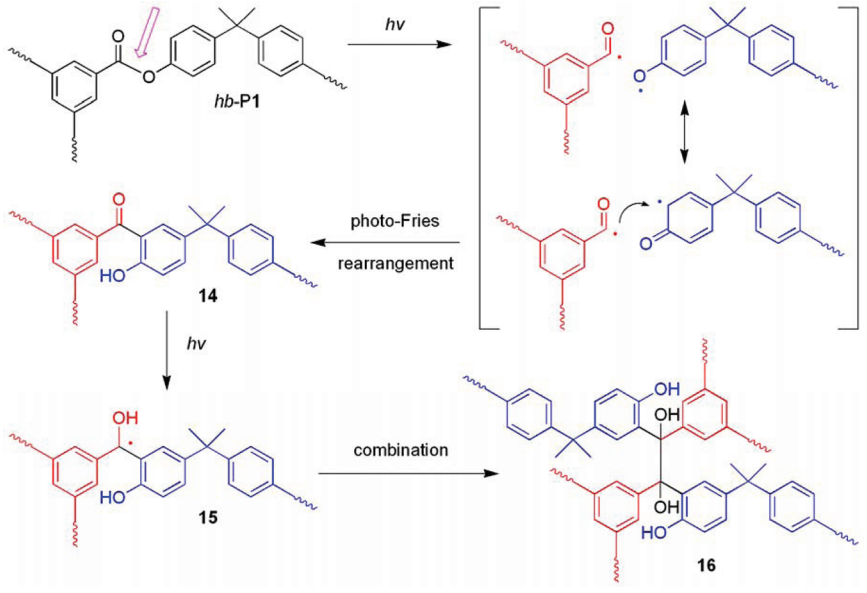
$$D' = \frac{1}{\nu_D'} \quad (11)$$

The ν_D and ν_D' values for *hb*-**P1** are as high as 258.9 and 1030.7, corresponding to D and D' values as low as 3.86×10^{-3} and 0.97×10^{-3}, respectively (Table 6). The chromatic dispersions of the polymer are much lower than those of the commercially important "organic glasses" such as PC ($D = 29.7 \times 10^{-3}$) and PMMA ($D = 17.5 \times 10^{-3}$).[20] The D' value is also much lower than those of the poly(aroyltriazole)s recently synthesized by our research groups by the metal-free "click" polymerizations ($D' = 6.1 \times 10^{-3}$–3.66×10^{-3}).[19] Although the Abbé numbers of *hb*-**P1** are increased after the photolysis, their chromatic dispersions ($D = 34.8 \times 10^{-3}$, $D' = 8.73 \times 10^{-3}$) are still comparable to those of the commercial optical plastics[20] and the newly synthesized poly(aroyltriazole)s.[19]

Photo-Cross-Linking and Photopatterning. The hyperbranched poly(1,3,5-triaroylarylene)s (**PII**) synthesized in our previous work contain many benzophenone units, which have enabled the polymers to be readily cross-linked by UV irradiation and to be used as sensitive photoresist materials.[9,21] As discussed above, the photoirradiation of the film of *hb*-**P1** generates benzophenone units in **14** through photo-Fries rearrangement (cf. Scheme 5), which should allow the polymer to be used as a photoresist. Indeed, UV irradiation of a thin film of *hb*-**P1** spin-coated on a silicon wafer in air through a copper photomask results in cross-linking of the exposed region and creates a negative photoresist pattern after development in 1,2-dichloroethane (Figure 8).

Figure 9 shows the dose effect on the gel formation in *hb*-**P1** films by UV irradiation. The polymer shows a moderate sensitivity ($D_{0.5} \sim 1.8$ J/cm^2). The mechanism for the photo-cross-linking reaction in *hb*-**P1** is probably similar to that for **PII**.[9] Some fractions of the photosensitive benzophenone units in **14** are photolyzed to generate hydroxydiphenylmethyl radicals in **15** (cf. Scheme 5). Combination of the radicals in different polymers results in the formation cross-linked gel. The photosensitivity of *hb*-**P1** is

Scheme 5



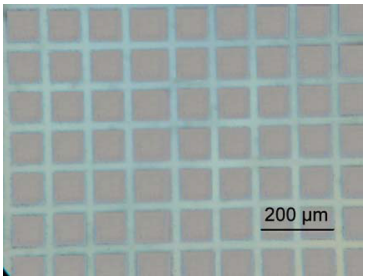


Figure 8. Negative photoresist pattern generated by photolithography of *hb*-**P1** (sample taken from Table 2, run 2).

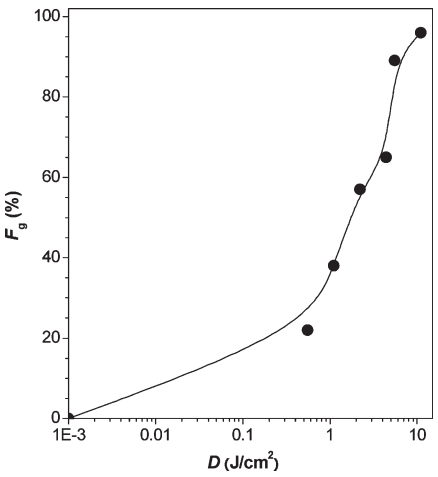


Figure 9. Plot of gel fraction (F_g) in *hb*-**P1** film versus exposure dose (D).

inferior to that of **PII**, which is reasonable, because photo-Fries rearrangement in polyester is not a very efficient process.

Conclusion

In this work, we have developed a facile synthetic route to regioregular hyperbranched polymers. The polycyclotrimerizations of arylene bipropiolate monomers **1**−**4** proceed in refluxing DMF in the absence of externally added catalysts, furnishing soluble *hb*-**P1**−*hb*-**P4** with high MWs and DBs in high yields. The monomers are easy to access from commercially available starting materials, and the polyaddition is strictly 1,3,5-regioselective and highly tolerant to functional groups, air, and moisture. The resultant *hb*-PTACPs are completely soluble, film-forming, thermally stable and optically transparent. The polymers show high light refractivities with unprecedented low chromatic aberrations, both being readily tunable by photoirradiation. The polymers are also photoresponsive and can be readily photo-cross-linked to generate photoresist patterns. These unique attributes make the polymers promising photonic materials for high-tech applications.

Acknowledgment. The work reported in this paper was partially supported by the Research Grants Council of Hong Kong (603008, 601608, 602707, and CUHK2/CRF/08), the National Natural Science Foundation of China (20634020 and 50703033), the Ministry of Science and Technology of China (2009CB623605), and the Nissan Chemical Industries, Ltd. We thank Drs. Borong Shi and Fanny L. Y. Shek of our University, Profs. Chi Wu and To Ngai of The Chinese University of Hong Kong, and Prof. Yuping Dong of Beijing Institute of Technology for their technical assistance and helpful discussions. B.Z.T. thanks the support from the Cao Guangbiao Foundation of Zhejiang University.

References and Notes

(1) (a) Gao, C.; Yan, D. *Prog. Polym. Sci.* **2004**, *29*, 183. (b) Tomalia, D. A.; Frechet, J. M. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2719. (c) Jikei, M.; Kakimoto, M. *Prog. Polym. Sci.* **2001**, *26*, 1233. (d) Kim, Y. H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685. (e) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901. (f) Häussler, M.; Sun, Q.; Xu, K.; Lam, J. W. Y.; Dong, H.; Tang, B. Z. *J. Inorg. Organomet. Polym. Mater.* **2005**, *15*, 67. (g) Xie, Z.; Peng, H.; Lam, J. W. Y.; Chen, J.; Zheng, Y.; Qiu, C.; Kwok, H. S.; Tang, B. Z. *Macromol. Symp.* **2003**, *195*, 179. (h) Lam, J. W. Y.; Luo, J.; Peng, H.; Xie, Z.; Xu, K.; Dong, Y.; Cheng, L.; Qiu, C.; Kwok, H. S.; Tang, B. Z. *Chin. J. Polym. Sci.* **2001**, *19*, 585. (i) Häussler, M.; Zheng, R.; Lam, J. W. Y.; Tong, H.; Dong, H.; Tang, B. Z. *J. Phys. Chem. B* **2004**, *108*, 10645. (j) Sun, Q.; Xu, K.; Peng, H.; Zheng, R.; Häuβler, M.; Tang, B. Z. *Macromolecules* **2003**, *36*, 2309. (k) Sun, Q.; Lam, J. W. Y.; Xu, K.; Xu, H.; Cha, J. A. K.; Wong, P. C. L.; Wen, G.; Zhang, X.; Jing, X.; Wang, F.; Tang, B. Z. *Chem. Mater.* **2000**, *12*, 2617.

(2) (a) Voit, B. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 2679. (b) Yates, C. R.; Hayes, W. *Eur. Polym. J.* **2004**, *40*, 1257.

(3) (a) Frechet, J. M. J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B. *Science* **1995**, *269*, 1080. (b) Hawker, C. J.; Frechet, J. M. J.; Grubbs, R. B.; Dao, J. *J. Am. Chem. Soc.* **1995**, *117*, 10763. (c) Gaynor, S. G.; Edelman, S.; Matyjaszewski, K. *Macromolecules* **1996**, *29*, 1079. (d) Dworak, A.; Walach, W.; Trzebicka, B. *Macromol. Chem. Phys.* **1995**, *196*, 1963. (e) Suzuki, M.; Yobbshida, S.; Shiraga, K.; Saegusa, T. *Macromolecules* **1998**, *31*, 1716. (f) Magnusson, H.; Malmstrom, E.; Hult, A. *Macromol. Rapid Commun.* **1999**, *20*, 453. (g) Sunder, A.; Hanselmann, R.; Frey, H.; Muelhaupt, R. *Macromolecules* **1999**, *32*, 4240.

(4) (a) Simon, P. F. W.; Radke, W.; Muller, A. H. E. *Macromol. Rapid Commun.* **1997**, *18*, 865. (b) Sakamoto, K.; Aimiya, T.; Kira, M. *Chem. Lett.* **1997**, 1245. (c) Matyjaszewski, K.; Gaynor, S. G.; Kulfan, A.; Podwika, M. *Macromolecules* **1997**, *30*, 5192. (d) Yan, D.; Zhou, Z.; Mueller, A. H. E. *Macromolecules* **1999**, *32*, 245. (e) Baskaran, D. *Polymer* **2003**, *44*, 2213. (f) Cheng, C.; Wooley, K. L.; Khoshdel, E. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4754.

(5) (a) Tang, B. Z. *Macromol. Chem. Phys.* **2008**, *209*, 1303. (b) Häussler, M.; Qin, A.; Tang, B. Z. *Polymer* **2007**, *48*, 6181. (c) Häussler, M.; Tang, B. Z. *Adv. Polym. Sci.* **2007**, *209*, 1.

(6) (a) Kim, Y. H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685. (b) Hult, A.; Johansson, M.; Malmstrom, E. *Adv. Polym. Sci.* **1999**, *143*, 1. (c) Hawker, C. J. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 117. (d) Inoue, K. *Prog. Polym. Sci.* **2000**, *25*, 453. (e) Voit, B. I. *J. Polym. Sci., Polym. Chem.* **2000**, *38*, 2505. (f) Grayson, S. M.; Frechet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819. (g) Tomalia, D. A.; Frechet, J. M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2002** ***40*, 2719.**

(7) (a) Häussler, M.; Tang, B. Z. *Acc. Chem. Res.* **2005**, *38*, 745. (b) Lam, J. W. Y.; Tang, B. Z. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2607. (c) Cheuk, K. K. L.; Li, B.; Tang, B. Z. *Curr. Trends Polym. Sci.* **2002**, *7*, 41. (d) Liu, J.; Zheng, R.; Tang, Y.; Häussler, M.; Lam, J. W. Y.; Qin, A.; Ye, M.; Hong, Y.; Gao, P.; Tang, B. Z. *Macromolecules* **2007**, *40*, 7473. (e) Häussler, M.; Lam, J. W. Y.; Qin, A.; Tse, K. K. C.; Li, M. K. S.; Liu, J.; Jim, C. K. W.; Gao, P.; Tang, B. Z. *Chem. Commun.* **2007**, 2584. (f) Häussler, M.; Liu, J.; Zheng, R.; Lam, J. W. Y.; Qin, A.; Tang, B. Z. *Macromolecules* **2007**, *40*, 1914. (g) Zheng, R.; Häussler, M.; Dong, H.; Lam, J. W. Y.; Tang, B. Z. *Macromolecules* **2006**, *39*, 7973. (h) Li, Z.; Lam, J. W. Y.; Dong, Y. Q.; Dong, Y. P.; Sung, H. H. Y.; Williams, I. D.; Tang, B. Z. *Macromolecules* **2006**, *39*, 6458. (i) Li, Z.; Qin, A.; Lam, J. W. Y.; Dong, Y. Q.; Dong, Y.; Ye, C.; Williams, I. D.; Tang, B. Z. *Macromolecules* **2006**, *39*, 1436.

(8) (a) Häussler, M.; Lam, J. W. Y.; Zheng, R.; Peng, H.; Tang, B. Z. *C. R. Chim.* **2003**, *6*, 833. (b) Lam, J. W. Y.; Chen, J.; Law, C. C. W.; Peng, H.; Xie, Z.; Cheuk, K. K. L.; Kwok, H. S.; Tang, B. Z. *Macromol. Symp.* **2003**, *196*, 289. (c) Lam, J. W. Y.; Peng, H.; Häussler, M.; Zheng, R.; Tang, B. Z. *Mol. Cryst. Liq. Cryst.* **2004**, *415*, 43. (d) Peng, H.; Dong, Y.; Jia, D.; Tang, B. Z. *Chin. Sci. Bull.* **2004**, *49*, 2637. (e) Peng, H.; Dong, H.; Dong, Y.; Jia, D.; Tang, B. Z. *Chin. J. Polym. Sci.* **2004**, *22*, 501. (f) Peng, H.; Lam, J. W. Y.; Tang, B. Z. *Macromol. Rapid Commun.* **2005**, *26*, 673. (g) Peng, H.; Zheng, R.; Dong, H.; Jia, D.; Tang, B. Z. *Chin. J. Polym. Sci.* **2005**, *23*, 1.

(9) (a) Qin, A.; Lam, J. W. Y.; Dong, H.; Lu, W.; Jim, C. K. W.; Dong, Y. Q.; Häussler, M.; Sung, H. H. Y.; Williams, I. D.; Wong, G. K.

L.; Tang, B. Z. *Macromolecules* **2007**, *40*, 4879. (b) Dong, H.; Zheng, R.; Lam, J. W. Y.; Häussler, M.; Tang, B. Z. *Macromolecules* **2005**, *38*, 6382. (c) Tang, B. Z.; Dong, H. C.; Qin, A. J. US Patent Pub No. US2006/ 0247410 A1, **2006**.

(10) Tang, B. Z.; Jim, C. K. W.; Qin, A.; Häussler, M.; Lam, J. W. Y. US Patent Pub. No. US60/933,884, **2007**.

(11) (a) Balasubramanian, K. K.; Selvaraj, S.; Venkataramani, P. S. *Synthesis* **1980**, 29. (b) Matsuda, K.; Nakamura, N.; Takahashi, K.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1995**, *117*, 5550. (c) Pigge, F. C.; Ghasedi, F.; Rath, N. P. *J. Org. Chem.* **2002**, *67*, 4547.

(12) (a) Muchtar, Z.; Schappacher, M.; Deffieux, A. *Macromolecules* **2001**, *34*, 7595. (b) Uhrich, K. E.; Hawker, C. J.; Frechet, J. M. J.; Turner, S. R. *Macromolecules* **1992**, *25*, 4583.

(13) (a) Zheng, R. H.; Dong, H. C.; Peng, H.; Lam, J. W. Y.; Tang, B. Z. *Macromolecules* **2004**, *37*, 5196. (b) Peng, H.; Cheng, L.; Luo, J.; Xu, K.; Sun, Q.; Dong, Y.; Salhi, F.; Lee, P. P. S.; Chen, J.; Tang, B. Z. *Macromolecules* **2002**, *35*, 5349.

(14) (a) Hawker, C. J.; Lee, R.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583. (b) Frey, H.; Hoelter, D. *Acta Polym.* **1999**, *50*, 67.

(15) (a) Otsuka, E.; Kurumada, K.; Suzuki, A.; Matsuzawa, S.; Takeuchi, K. *J. Sol.-Gel Sci. Technol.* **2008**, *46*, 71. (b) Chu, J. B.; Huang, S. M.; Zhu, H. B.; Xu, X. B.; Sun, Z.; Chen, Y. W.; Huang, F. Q. *J. Non-Cryst. Solids* **2008**, *354*, 5480.

(16) (a) Daschiel, U.; Hoefler, T.; Jakopic, G.; Schmidt, V.; Kern, W. *Macromol. Chem. Phys.* **2007**, *208*, 1190. (b) Anderson, J. C.; Reese, C. B. *Proc. Chem. Soc.* **1960**, 217. (c) Lochbrunner, S.; Zissler, M.; Piel, J.; Riedle, E.; Spiegel, A.; Bach, T. *J. Chem. Phys.* **2004**, *120*, 11634. (d) Li, S. K. L.; Guillet, J. E. *Macromolecules* **1977**, *10*, 840. (e) Finnegan, R. A.; Knutson, D. *Tetrahedron Lett.* **1968**, 3429. (f) Gu, W.; Abdallah, D. J.; Weiss, R. G. *J. Photochem. Photobiol. A: Chem.* **2001**, *139*, 79.(g) Miranda, M. A.; Galindo, F. In *CRC Handbook of Organic Photochemistry and Photobiology*, 2nd ed.; Horspool, W. M., Ed.; CRC Press: Boca Raton, FL, 2004.

(17) (a) Nakamura, T.; Tsutsumi, N.; Juni, N.; Fujii, H. *J. Appl. Phys.* **2005**, *97*, 054505. (b) Mikami, A.; Koshiyama, T.; Tsubokawa, T. *Jpn. J. Appl. Phys.* **2005**, *44*, 608. (c) Ochi, M.; Maeda, Y.; Wakao, K. *Nettowaku Porima* **2006**, *27*, 30. (d) Ju, Y. G.; Almuneau, G.; Kim, T. H.; Lee, B. W. *Jpn. J. Appl. Phys.* **2006**, *45*, 2546. (e) Krogman, K. C.; Druffel, T.; Sunkara, M. K. *Nanotechnology* **2005**, *16*, 338.(f) Nakai, J.; Aoki, T. U.S. Patent 7,087,945, **2006**. (g) Flaim, T. D.; Wang, Y.; Mercado, R. *SPIE Proc.* **2004**, *5250*, 423. (h) Su, W. F.; Fu, Y. C.; Pan, W. P. *Thermochim. Acta* **2002**, *392−393*, 385. (i) Lue, C.; Cui, Z.; Wang, Y.; Yang, B.; Shen, J. *J. Appl. Polym. Sci.* **2003**, *89*, 2426. (j) Lue, C.; Cui, Z.; Li, Z.; Yang, B.; Shen, J. *J. Mater. Chem.* **2003**, *13*, 526. (k) Minns, R. A.; Gaudiana, R. A. *J. Macromol. Sci., Pure Appl. Chem.* **1992**, *A29*, 19. (l) Terui, Y.; Ando, S. *J. Photopolym. Sci. Technol.* **2005** ***18*, 337.**

(18) (a) Yang, C. J.; Jenekhe, S. A. *Chem. Mater.* **1995**, *7*, 1276. (b) Yang, C. J.; Jenekhe, S. A. *Chem. Mater.* **1994**, *6*, 196.

(19) Qin, A.; Tang, L.; Lam, J. W. Y.; Jim, C. K. W.; Yu, Y.; Zhao, H.; Sun, J.; Tang, B. Z. *Adv. Funct. Mater.* **2009**, 19.

(20) (a) Seferis, J. C. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1989; pp VI/451−461. (b) Mills, N. J. In *Concise Encyclopedia of Polymer Science and Engineering*; Kroschwitz, J. I., Ed.; Wiley: New York, 1990; pp 683−687.

(21) (a) Luo, Y.; Leszyk, J.; Qian, Y.; Gergely, J.; Tao, T. *Biochemistry* **1999**, *38*, 6678. (b) Hasegawa, M.; Horie, K. *Prog. Polym. Sci.* **2001**, *26*, 259.