Incorporating Pendent Fullerenes with High Refractive Index Backbones: A Conjunction Effect Method for High Refractive Index Polymers

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Supporting Information

ABSTRACT: To achieve high refractive index polymers (HRIPs), we report here the design and synthesis of four fullerene polyesters (P1–P4), based on the conjunction effect from the high refractive index polyester backbones and pendent fullerene side chains. At sodium D line (589 nm), the refractive indices of the fullerene polyesters are all higher than 1.80, the used believed upper limitation of intrinsic organic polymers. To achieve precise pendent fullerene structure, these polyesters were synthesized via condensation polymerization by a fullerene dio with different aromatic diared chlorides where the diared chlorides with high redep



diacyl chlorides, where the diacyl chlorides with high molar refraction increment value moiety were selected by molecular tailoring according to Lorentz–Lorenz equation. The fullerene polyesters are characterized by gel permeation chromatography (GPC), ultraviolet–visible (UV–vis) spectroscopy, and the molecular weights are obtained by a quantitative NMR technique with end-group estimation. The formation of fullerene polyesters is also proved by the ¹H DOSY NMR results. These fullerene polyesters have good solubility in some common organic solvents, good thermal stability up to 320 °C, and film forming ability. All these films have good adhesion to glass sheets with relatively good hardness. Among them, the thiophene-containing fullerene polyesters (P1) has the best optical properties, with the highest refractive index value (1.86 at 589 nm), one of the highest value for intrinsic organic polymers, and the highest Abbe number (27.9).

■ INTRODUCTION

Traditional polymers exhibit relatively low refractive indices, often in the range of 1.30-1.70.¹ Those with refractive index higher than 1.70 are called high refractive index polymers (HRIPs) and have attracted great attention due to their weight reduction and fracture resistance compared to inorganic materials, with the applications in optical and optoelectronic devices, such as plastic lenses, prisms, encapsulants for organic light-emitting diodes, and antireflective coatings.^{2–8} To enhance the refractive index value of conventional polymers and fabricate HIRPs, two major types of methods have been developed.

The first approach uses the substituents with high molar refraction and low molar volume as building blocks in the polymer. Usually, groups with high π -electron density, heavy halogens, phosphorus, sulfur, and metallic elements are introduced to achieve high refractive index.^{9–15} For example, Allcock et al. discovered the high refractive index properties from polyphosphazenes, with the typical value ranging from

1.60 to 1.75.¹⁰ Ueda et al. carried out excellent works on the synthesis of sulfur-containing polymers and found they showed high refractive index properties.^{16–20} The polymers with high sulfur content usually displayed large refractive index, with the best about 1.77. However, the refractive index of the polymers designed by this method can rarely exceed 1.80.

The second approach utilizes a hybrid method, where polymers and high refractive index inorganic nanoparticles are used to form an organic–inorganic composites.^{21–24} This method can produce polymer composites with refractive index exceeding 2.0, yet its poor stability and processability limit their application. The problems can be solved partially by an improved sol–gel synthesis method, where the polymers form chemical bonds with the inorganic nanoparticles.^{25–29}

Received: August 12, 2015 Revised: November 10, 2015 Scheme 1. Synthetic Route of Fullerene Diol Monomer (4) and Polyesters P1-P4^a



^{*a*}Conditions: (i) 10-undecyn-1-ol, *p*-toluenesulfonic acid, 4-(dimethylamino)pyridine, *N*,*N*-diisopropylcarbodiimide, 1,2-dichlorobenzene, rt, 1 h (75%); (ii) CuSO₄·5H₂O, sodium ascorbate, chloroform, 30 °C, 72 h (56%); (iii) 1,2-dichlorobenzene, *N*,*N*-dimethylacetamide, pyridine, 80 °C, 48 h.

Fullerenes are all-carbon caged materials with excellent electrical and optical properties and can be modified with polymers, dendrimers, liquid crystals, etc., to incorporate corresponding properties.³⁰⁻³⁹ However, it is hard to synthesize fullerene polymers with controlled structure via radical or anionic polymerization due to the multiple addition of free radicals and nucleophiles on fullerenes, which results in star or branched structure.^{30,40} Recently, we reported a new route to achieve polyesters with pendant fullerenes via a condensation polymerization process from fullerene diol and diacyl chlorides.⁴¹ With the introduction of long flexible spacers between pendent fullerenes and polymer backbone, the stiffness of the mainchain is softened. As a result, the fullerene polyesters showed good solubility in common organic solvents like chloroform and chlorobenzene and good thermal stability and film forming ability. Because of the high π -electron density of fullerenes, these fullerene polyesters are HRIPs with the highest value reaching 1.79 (sodium D line, 589 nm).

This method can be ascribed to the hybrid method if fullerenes are considered as nanoparticles. For polymer/ nanoparticle hybrid system, the refractive index of the material can be approximately calculated by eq $1:^{42}$

$$n_{\rm comp} = \varphi_{\rm p} n_{\rm p} + \varphi_{\rm org} n_{\rm org} \tag{1}$$

where $n_{\rm comp}$, $n_{\rm p}$, and $n_{\rm org}$ represent the refractive index of composite, nanoparticle, and organic matrix, while $\varphi_{\rm p}$ and $\varphi_{\rm org}$ represent the volume fraction of nanoparticle and organic matrix, respectively. To increase the refractive index of the fullerene polymers, one can choose to either increase the volume fraction of fullerenes or increase the refractive index of organic part (e.g., polymer backbones). Since it is challenging to achieve stable, uniformly dispersed polymer composite with high volume fraction of the nanoparticles, increasing the

refractive index of polymer backbone would be a promising approach for HIRP design.

In this work, we focus on the design and synthesis of fullerene polyesters with very high refractive indices, i.e., higher than 1.80, which is used to be believed as the upper limitation of intrinsic organic polymers. The approach utilizes the conjugation method by incorporating pendent fullerenes (side chains) with high refractive index polymer backbones (main chains) based on previous analysis and the Lorentz-Lorenz equation.^{1,43,44} The polyesters with pendant fullerenes were synthesized via condensation polymerization of a fullerene diol and different diacyl chlorides with high molar refraction aromatic building blocks, as shown in Scheme 1. These fullerene polymers were characterized by gel permeation chromatography (GPC), NMR, thermogravimetric analysis (TGA), and ultraviolet-visible (UV-vis) spectroscopy. The refractive indices of these polyesters were measured to verify our hypothesis of conjunction approach.

EXPERIMENTAL SECTION

Materials. 4-(Dimethylamino)pyridine (DMAP, 98%), *p*-toluenesulfonic acid (PTSA, 99%), and *N*,*N*-diisopropylcarbodiimide (DIPC, 99%) were purchased from J&K. 1,4-Naphthalenedicarboxylic acid (98%) was purchased from Jiu Ding Chemistry (Shanghai) Co., Ltd. 2,5-Dibromoterephthalic acid (97%) and 1,4-thiophenedicarboxylic acid (98%) were purchased from Energy Chemical. [60]Fullerene (99.9%) was purchased from Puyang Yongxin Fullerene Technology Co., Ltd. 10-Undecyn-1-ol (96%) was purchased from Alfa Aesar. All the chemicals mentioned above were used as received without further purification. Terephthaloyl chloride (97%) was purchased from Aladdin and purified by recrystallization from hexane before use. All solvents were obtained from Sinopharm Group Chemical Reagent Co., Ltd. (China). Tetrahydrofuran (THF, AR) was distilled from calcium hydride under nitrogen immediately before use. 1,2-Dichlorobenzene (*o*-DCB, 99%), *N*,*N*-dimethylacetamide (DMAc, AR), and pyridine (Py, AR) were predried over calcium hydride and distilled under reduced pressure.

The fullerene diol monomer 4 was synthesized according to the synthetic route in Scheme 1. [60]Fullerenoacetic acid 1 and 3,5bis(hydroxymethyl)phenyl 6-azide hexyl ether 3 were synthesized using the same procedure as our previous work.⁴¹

Synthesis of 10-Undecyn-1-yl [60]Fullerenoacetate (2). [60]-Fullerenoacetic acid 1 (0.498 g, 0.640 mmol) was dissolved in the mixed solvent of o-DCB (20 mL) and DMF (1 mL). Then PTSA (0.122 g, 0.640 mmol), DMAP (0.078 g, 0.64 mmol), DIPC (0.121 g, 0.96 mmol), and 10-undecyn-1-ol (0.108 g, 0.640 mmol) were added into the solution. The mixture was stirred for 1 h at room temperature. Afterward, the mixture was filtered, and the filtrate was washed with distilled water (50 mL \times 3). The organic phase was dried over anhydrous sodium sulfate, and the crude product was purified by silica gel column chromatography using carbon disulfide as eluent. The product was precipitated in methanol, filtered, and dried in a vacuum oven to yield a brown solid 2 (0.45 g, 75%). $^1\!\mathrm{H}$ NMR (600 MHz, $CDCl_3$), δ (ppm): 4.79 (s, 1H, H at the bridging C), 4.46 (t, 2H, COOCH₂), 2.19 (m, 2H, COOCH₂CH₂), 1.94 (t, 1H, $-C \equiv CH$), 1.87 (m, 2H, CH₂C=CH), 1.52 (m, 4H, COOCH₂CH₂CH₂ and $CH_2CH_2C\equiv CH$), 1.35 (m, 8H, $CH_2CH_2CH_2CH_2CH_2C\equiv CH$).

Synthesis of 9-(1-(6-(3,5-Bis(hydroxymethyl)phenoxy)-1-hexyl)-1H-1,2,3-triazol-4-yl)-1-nonyl [60]Fullerenoacetate (Fullerene Diol Monomer 4). Into a 250 mL two-necked round-bottom flask, 2 (0.965 g, 1.04 mmol), 3 (0.291 g, 1.04 mmol), and chloroform (80 mL) were added and stirred for 10 min. A solution of CuSO₄·5H₂O (0.030 g, 0.12 mmol) in 20 mL of distilled water was added into the flask, followed by the adding of sodium ascorbate (0.063 g, 0.32 mmol) under a nitrogen atmosphere. The mixture was stirred for 3 days at room temperature under a nitrogen atmosphere. The organic phase was washed with distilled water (100 mL \times 3) and dried over anhydrous sodium sulfate. After filtration, the crude product was purified by column chromatography using carbon disulfide/ethyl acetate (1/1, v/v) as eluent, and the purified sample was obtained by being dissolved in chloroform and precipitated in hexane. After filtered and dried in a vacuum oven, a brown solid (0.71 g, 56%) was obtained. ¹H NMR (600 MHz, CDCl₃), δ (ppm): 7.24 (s, 1H, H at the triazole ring), 6.92 (s, 1H, phenyl H-4), 6.85 (s, 2H, phenyl H-2), 4.80 (s, 1H, H at the bridging C), 4.67 (s, 4H, CH₂OH), 4.46 (t, 2H, COOCH₂), 4.33 (t, 2H, CH₂O-Ar), 3.97 (t, 2H, CH₂ linked to N in the triazole ring), 2.69 (t, 2H, CH_2 linked to C in the triazole ring), 1.92 (m, 2H, COOCH₂CH₂), 1.86 (m, 2H, CH₂CH₂O-Ar), 1.77 (m, 2H, CH₂CH₂) linked to N in the triazole ring), 1.66 (m, 2H, CH2CH2 linked to C in the triazole ring), 1.52-1.38 (m, 14H, COOCH₂CH₂CH₂CH₂CH₂-CH₂CH₂CH₂ and CH₂CH₂CH₂CH₂CH₂O-Ar). ¹³C NMR (600 MHz, $CDCl_3$), δ (ppm): 166.48 (C=O), 159.53 (phenyl carbon adjacent to oxygen), 148.31, 145.86, 145.59, 145.26, 145.22, 145.18, 145.09, 145.08, 144.73, 144.69, 144.67, 144.60, 144.58, 144.41, 143.95, 143.73, 143.26, 143.09, 143.02, 142.98, 142.86, 142.82, 142.43, 142.20, 142.09, 141.13, 140.92, 140.47, 136.38, 120.50, 117.46, 112.22, 70.64 (sp³ carbons of fullerene), 67.67, 66.63, 65,16, 50.10 (CH₂N), 39.18 (bridging methene carbon to fullerene), 30.13, 29.45, 29.42, 29.28, 29.25, 28.77, 28.70, 26.07, 26.02, 25.59, 25.48. The 28 resonances from 140.47 to 149.31 ppm belong to the carbons from fullerene plus one for the carbons in the phenyl group linked with hydroxymethylene group. The resonances at 136.38 and 120.50 ppm are from triazole carbons, while at 117.46 and 112.22 ppm are from the methene carbons of benzene. The resonances at 67.67, 66.63, and 65.16 ppm are from methylene carbons connected with oxygen, while the other 11 resonances from 30.13 to 25.48 ppm belong to the 11 methylene carbons with adjacent methylene groups.

Synthesis of Dicarbonyl Chlorides. 2,5-Thiophenedicarbonyl chloride, 1,4-naphthalenedicarbonyl chloride, and 2,5-dibromoterephthaloyl chloride were synthesized from their corresponding diacids. A typical procedure is described in the following: excess of thionyl chloride (20 mL) was added to a flask containing corresponding diacid (1.5 g), and then a drop of DMF was added. The reaction mixture was refluxed for 6 h. The excess thionyl chloride was removed by rotation evaporation under reduced pressure. The pure samples were obtained by recrystallization of the crude product in hexane three times.

Synthesis of Fullerene Polyesters. All the polymerization reactions were conducted under nitrogen. A typical experimental procedure for the synthesis of polyesters is given below: into a 10 mL Schlenk tube equipped with a magnetic stirrer were placed fullerene diol monomer 4 (315 mg, 0.261 mmol), dicarbonyl chloride (0.261 mmol), and pyridine (49.6 mg, 0.627 mmol) in the mixed solvent of *o*-DCB (3.2 mL) and DMAc (0.8 mL) at room temperature. The reaction mixture was allowed to slowly warm up to 80 °C and was stirred at this temperature for 48 h. The polyesters were obtained by precipitating in methanol and purified by being dissolved in 1,2-dichlorobenzene and precipitated in THF to obtain dark red solid. Yield: P1, 63%; P2, 78%; P3, 58%; P4, 51%.

Instrumentation. ¹H NMR, ¹³C NMR, and ¹H DOSY NMR experiments were conducted on Agilent Technologies 600 MHz DD2 spectrometer with PFG ¹H/¹⁹F/X probe at 25 °C, using *d*-chloroform as the solvent and tetramethylsilane (TMS) as an internal standard. For measurements of the self-diffusion coefficient, the solution concentration was 1.0 mg/mL, and a DBPPSTE_CC (DOSY Bipolar Pulse Pair Stimulated Echo with Convection Compensation) sequence was used. Diffusion attenuation curves were obtained at a sequential 15-step linear increase of the amplitude of the magnetic field gradient pulse in the range from 2.07 to 51.7 G/cm at fixed values of diffusion time Δ , δ_{pulse} gradient pulse duration (2.0 ms), and relaxation time d_1 (1 s). DOSY spectra were processed by Agilent's VnmrJ 3.2 software.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum was acquired on a Bruker Ultraflex-Treme TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd:YAG laser (355 nm). trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, Aldrich, >99%) was served as matrix and prepared in CHCl₃ at a concentration of 20 mg/mL. Sodium trifluoroacetate (CF₂COONa) was served as cationizing agent and was prepared in ethanol at 10 mg/ mL. The sample was dissolved in $CHCl_3$ at a concentration of 10 mg/ mL. The matrix and CF₃COONa were mixed with the ratio of 10/1(v/v). The sample preparation involved depositing 0.5 μ L of matrix and salt mixture on the wells of a 384-well ground-steel plate, allowing the spots to dry, depositing 0.5 μ L of the sample on a spot of dry matrix, and adding another 0.5 μ L of matrix and salt mixture on top of the dry sample. After evaporation of the solvent, the plate was inserted into the MALDI source. The mass scale was calibrated externally using the peaks obtained from peptide standard at the molecular weight range under consideration. Data analysis was conducted with Bruker's flexAnalysis software.

GPC was conducted on a Waters GPC systems equipped with a Waters 1515 isocratic HPLC pump, a Waters 2489 UV-vis detector, and a set of Waters Styragel columns (HR3, HR4, and HR5 with molecular weight range of $5 \times 10^2 - 4 \times 10^6$ Da). The monomer and polymer solutions were freshly prepared by dissolving in chloroform (0.5 mg/mL) and then filtering through 0.45 μm PTFE syringe-type filters before being injected into the GPC system. Chloroform was served as the mobile phase at a flow rate of 1.0 mL/min at 35 °C. TGA was carried on a SDT-2960TG/DTA TA Instruments at a heating rate of 10 °C min⁻¹ from room temperature to 800 °C under a continuous nitrogen flow of 50 mL/min. The differential scanning calorimetry (DSC) was performed on a TA Instruments DSC 2010 over a temperature range of 0-280 °C at a scanning rate of 10 °C/min. UVvis spectra were recorded on a Hitachi U-3900 spectrophotometer at room temperature. For Fourier transform infrared spectroscopy (FTIR) measurements, samples were dispersed in potassium bromide and compressed into pellets, and spectra in the range of 400-4000 cm⁻¹ were recorded with the Nicolet 6700 FT-IR Instrument. Atomic force microscopy (AFM) image was carried out on a MultiMode 8 atomic force microscope (Bruker Veeco) in Peak Force QNM mode in air, and a SNL-10 cantilever (spring constant: 0.35 N/m; resonance frequency: 50-80 kHz) was used for measurement.

For refractive index measurements, a spectroscopic ellipsometer (M2000, J.A. Woollam Co.) was used to measure the ellipsometric data Psi (Ψ) and Delta (Δ) of the polymer films. All measurements

were performed between 370 and 1000 nm at an angle of incidence Φ_0 of 70 °C, and all data were acquired and analyzed using Complete EASE software version 4.46. Typically, samples were spin-coated on the silica wafer from chloroform solution (10 mg/mL) at the rotating speed of 1000 rpm. The films were regarded as a homogeneous material with the thickness fitted by Cauchy dispersion relation in the limited wavelength range from 720 to 1000 nm, where no light was absorbed by the material according to the UV-vis results. After the film thickness was determined and fixed, the experimental data were fitted by the B-Spline layer combined with the Wavelength Range Expansion (WVL-EXPAND) Fit. Subsequently, in order to guarantee the results physical, the initial B-Spline layer optical constant was parametrized by the Gen-Osc layer, in which Gaussian oscillators were used to match the optical constant curve shapes.^{45,46} Finally, the optical constant data, including refractive indices (n), were obtained in the Gen-Osc layer.

For hardness and adhesion measurements, a polymer solution (10 mg/mL in chloroform) was brush coated onto a piece of clean glass slide. Curing for 48 h, a thin film with the thickness of approximate 50 μ m was ready for the hardness and adhesion test. The corresponding pencil hardness was measured by a hardness pencil tester PPH-1 (Shanghai Meiyu Equimpment Co. Ltd.) according to GB/T 6739-2006, while the adhesion of the coatings to glass sheet was evaluated using GB/T 9286-1998 crosshatch adhesion method by an adhesion cross-cut tester QFH (Shanghai Meiyu Equipment Co. Ltd.).

RESULTS AND DISCUSSION

Synthesis and Characterization of Monomers and Polymers. For condensation polymerization, the purity of the monomer is critical for achieving high molecular weights polymers. Based on this, the dicarbonyl chloride monomers were all crystallized three times, and pure crystals were obtained with narrow melting point range (2,5-thiophenedicarbonyl chloride, 42–43 °C; 1,4-naphthalenedicarbonyl chloride, 97–98 °C; 2,5-dibromoterephthaloyl chloride, 84–85 °C; terephthaloyl chloride, 80–81 °C), which are in accordance with the literature reported value.^{47–50}

The synthetic route of fullerene diol monomer is illustrated in Scheme 1. The chemical structure of fullerenediol monomer is changed in this work compared to our previous reported work⁴¹ due to the following two merits: (1) the flexible spacer between triazol to fullerene is shortened to increase the content of fullerene; (2) the synthetic steps are reduced. Figure 1a is the ¹H NMR spectrum of fullerene diol monomer 4 in dchloroform, with the assignment of each peak to corresponding chemical structure listed above. The integration value ratio of each peak fitted well with the desired structure and no contamination of impurity was found. In ¹³C NMR spectrum (Figure S1), the intense resonances from 140 to 146 ppm are characteristic peaks for [60]fullerene. In addition, the structure of fullerene diol was confirmed by the MALDI-TOF mass spectrum (Figure 1b), where the observed strong peak was assigned to $[M + Na]^+$ (calculated: 1230.29; found: 1230.37).

Condensation polymerization of fullerene diol 4 with different dicarbonyl chlorides gave corresponding fullerene polyesters **P1–P4**. These fullerene polyesters showed good solubility in chloroform and chlorobenzene but insoluble in THF and DMF. As the monomers and oligomers can be dissolved in THF, the obtained polyesters were purified by precipitating in THF. Figure 2 is the GPC curves of the four fullerene polyesters, using chloroform as the eluent. Clearly, the retention volumes decreased after polymerization compared to monomer, indicating the formation of polymers. The molecular weights of the fullerene polyesters obtained from GPC, relative to polystyrene (PS) standards, were much smaller than



Figure 1. (a) ¹H NMR spectrum of fullerene diol monomer 4 in *d*chloroform (s: solvent). (b) MALDI-TOF mass spectra of monomer 4 (inserted is the enlarged figure of corresponding peak).



Figure 2. GPC curves of fullerene diol monomer 4 and fullerene polyesters P1–P4. Eluent: chloroform; flow rate: 1.0 mL/min.

expected. This is due to the difference of hydrodynamic volume of fullerene polyesters to PS, and the interaction of fullerenes with PS stationary phase, which is also observed in other fullerene polymers.^{32,41,51-53} This is supported by the observation that the molecular weights of fullerene diol monomer 4 obtained from GPC (210 g/mol) are much smaller than its theoretical one (1208 g/mol). The poly-dispersity index (PDI) obtained for these fullerene polyesters is smaller than theoretical value for traditional condensation polymerization (~2.0). This is due to the purification process after polymerization, where the polyesters were precipitated in THF to remove the monomer and oligomers. The data are summarized in Table 1.

Typically, in dilute concentrations where the chain entanglements between macromolecules can be neglected, macromolecules with higher molecular weights have larger

Table 1. Molecular Weights, Diffusion Coefficients, and Deduced Hydrodynamic Diameters of Monomer 4 and Fullerene Polymers P1–P4

sample	$\frac{M_n^a}{(g/mol)}$	M_n^b (g/mol)	PDI ^b	$D (10^{-10} m^2/s)$	$\begin{array}{c} D_{ m h} \ ({ m nm}) \end{array}$
monomer 4	1208 ^c	210	1.12	5.1	1.5
P1	6800	1500	1.36	2.3	3.5
P2	16800	1700	1.23	3.0	2.7
Р3	8400	1400	1.31	2.2	3.7
P4	10400	1500	1.59	2.1	3.8

^{*a*}Determined by ¹H NMR in CDCl₃. ^{*b*}Determined by GPC using CHCl₃ as eluent and PS as standard. ^{*c*}The molar molecular weight of fullerene diol monomer **4**.

hydrodynamic volume and lower diffusion coefficient if the topological structure is similar. Based on this, ¹H DOSY NMR experiments for the fullerene monomer and polymers were carried to confirm the formation of fullerene polyesters, and the spectra are shown in Figure 3 and the Supporting Information



Figure 3. ¹H DOSY NMR spectra of fullerene diol monomer 4 (a) and polyester P1 (b).

(Figures S2–S4). For comparison, the same experimental conditions were used for all the samples. The concentration of the solution was quite low (1.0 mg/mL); thus, the chain entanglements can be neglected.

Figure 3a is the ¹H DOSY NMR spectrum of fullerene monomer 4. The diffusion coefficient (*D*) measured was 5.1×10^{-10} m²/s. Based on the Stokes–Einstein equation, the corresponding hydrodynamic radius (*R*_h) can be deduced by⁵⁴

$$R_{\rm h} = \frac{kT}{6\pi\eta D} \tag{2}$$

where k, T, and η are the Boltzmann constant, the absolute temperature, and the solution viscosity, respectively. Since the concentrations used here were relatively low (1.0 mg/mL), the solvent's viscosity could be used instead of the solutions. From eq 2, the calculated hydrodynamic radius for monomer was

0.76 nm, corresponding to a sphere with diameter of 1.5 nm. This value is slightly larger than the diameter of [60]fullerene (1.0 nm with π electrons) and is quite reasonable by taking into account of the substitution groups on fullerene, indicating the measured diffusion coefficient is valid.

Figure 3b is the ¹H DOSY NMR spectrum of fullerene polyester P1, while Figures S2, S3, and S4 are for P2, P3, and P4, respectively. The measured diffusion coefficient was 2.3×10^{-10} m²/s for P1, 3.0×10^{-10} m²/s for P2, 2.2×10^{-10} m²/s for P3, and 2.1×10^{-10} m²/s for P4, with the corresponding deduced hydrodynamic diameter of 3.5, 2.7, 3.7, and 3.8 nm, respectively, as listed in Table 1. The smaller diffusion coefficients and larger hydrodynamic diameters of the polyesters than that of the monomer confirm the formation of polymers.

Quantitative ¹H NMR experiments were conducted to obtain the absolute molecular weights of these fullerene polyesters, based on a method we previous established.^{41,55} Figure 4 is the



Figure 4. Quantitative ¹H NMR spectrum of fullerene polyester **P1** in *d*-chloroform (s: solvent).

quantitative ¹H NMR spectrum of P1, with the corresponding resonance assignments shown on the top, while Figures S5–S7 are for P2, P3, and P4, respectively. Compared to the spectrum of monomer (Figure 1a), the new resonance at 5.29 ppm (k') is from the methylene groups adjacent to the ester bonds, while the remaining much weaker resonance at 4.67 ppm is from chain-ends. By the functional group and chain-ends estimation, the molecular weights of the fullerene polyesters can be obtained. Detailed analysis is listed in the Supporting Information. The calculated number-average molecular weights are 6800 g/mol for P1, 16 800 g/mol for P2, 8400 g/mol for P3, and 10 400 g/mol for P4. The results are listed in Table 1.

It should be noted that though P2 sample has the highest molecular weights; interestingly, it has the highest diffusion coefficient and smallest hydrodynamic diameter among the four polyesters. This suggests that P2 polymer chains are less swollen and more compact in the solution, which can be

attributed to the naphthalene structure in the polymer backbone that increases the chain stiffness. This is supported by Figure S8, where the diffusion coefficients of fullerene polyesters vs their corresponding molecular weights are plotted. Clearly, P1, P3, and P4 polymers can be viewed as following a linear extrapolation line, which means they may have similar relationship of diffusion coefficient vs molecular weights. This coincides well with the chemical structure of these polyesters, where only the central aromatic ring in the backbone is slightly different.

FTIR spectra of fullerene polyesters P1–P4 are presented in Figure 5. All four samples showed the characteristic absorption



Figure 5. FTIR spectra of fullerene polyesters P1-P4. The dotted lines indicate the characteristic absorption bands for fullerene (526, 574, 1183, and 1427 cm⁻¹).

bands at 526, 574, 1183, and 1427 cm⁻¹, which can be attributed to the strong intramolecular modes of C_{60} .⁵⁶ The absorption bands at 2920 and 2850 cm⁻¹ are corresponding to the C–H stretching of methylene groups, while the strong absorption at 1720 cm⁻¹ belongs to the carbonyl groups. The absorption at 1598 cm⁻¹ is ascribed to the carbon–carbon stretching vibrations in the aromatic ring, while at 1460 cm⁻¹ to the bending vibrations of CH₂ in the long alkyl chain.

Figure 6 is the TGA curves of these fullerene polyesters, where they show good thermal stability. The degradation temperatures for P1–P4 (5% weight loss) under nitrogen were 335, 373, 320, and 385 °C, respectively. At 800 °C, the residual weight ratio of all the fullerene polymers exceeded 60%, in agreement with the high fullerene content in these polyesters. DSC measurements of the fullerene polyesters were carried out,



Figure 6. TGA curves of P1, P2, P3, and P4 under nitrogen with a heating rate of 10 $^{\circ}$ C/min.

and the curves are provided in the Supporting Information (Figure S9). No glass transition was observed for all fullerene polyesters, which may due to the bulky fullerenes in side chains that limit the movements of main-chain segments in the bulk state.

The UV–vis absorption spectra of the monomer and P1–P4 polyesters in chloroform solution (Figure 7a) and as a thin film (Figure 7b) at room temperature were measured and shown in Figure 7. In Figure 7a, the strong peaks at 258 and 326 nm are the characteristic peaks for [60]fullerenes.⁵⁷ The weak peaks at 427 and 690 nm are the characteristic peaks in the spectra of methano[60]fullerenes,^{58,59} which can be better viewed in Figure S10 measured at much higher concentrations. In thin solid film, the characteristic peaks of [60]fullerenes were observed at 265 and 333 nm, as presented in Figure 7b. The red-shift of absorption peaks from solution to solid is typical in conjugated polymers and fullerenes, which is attributed to the π – π stacking between molecules in the film.^{60,61}

High Refractive Index Properties. The refractive indices of the polymers were determined using a variable angle spectroscopic ellipsometer. Thin films of P1-P4 polyesters were prepared by spin-coating the corresponding chloroform solution (10 mg/mL) onto silicon wafers. The obtained refractive index of the fullerene polyesters as a function of wavelength is presented in Figure 8. Clearly, all polymers show refractive index higher than 1.78 at measured wavelength region, and the refractive index decreases monotonically with increasing incident wavelength. The refractive indices of P1-P4 at sodium D line (589 nm) were 1.864, 1.847, 1.854, and 1.830, respectively, much higher than traditional polymers, which are among the intrinsic polymers with highest refractive index. These refractive indices are higher than our previous reported fullerene polyester (1.75-1.79),⁴¹ indicating that our approach of designing HRIPs by the conjunction effect of high refractive index side chains and backbones works here. As a result, the refractive indices of fullerene polyesters in this work are all higher than 1.80 (589 nm), which is used to be considered as the upper limitation of organic polymers.⁶² With such high refractive indices, these fullerene polyesters should have good applications in optoelectronic devices.

The measured refractive indices at sodium D line (589 nm) agree well with the calculated refractive indices by Lorentz–Lorenz equation, as listed in Table 2, proving the reliability of our data. The molar refraction of repeating units increases with the introduction of high molar refraction aromatic moieties in the polyester backbone, without diminishing their solubility and film forming properties. In addition, those aromatic groups also lead to higher density of the fullerene polyesters (1.46–1.57 g/cm³) compared to fullerene polyesters with aliphatic backbones (1.40–1.42 g/cm³).⁴¹ They should also be the reason for the much higher refractive index value of fullerene polyesters synthesized in this work than the previous reported fullerene polyesters with aliphatic backbones (1.75–1.77).

It should be noted that though P4 has the highest fullerene content, it does not have the highest refractive index among these polyesters. The density and molar refraction of the repeating units also play important roles here. As a result, P1, which contains thiophene moiety in the backbone, showed the highest refractive index at wavelengths higher than 500 nm. At short wavelength region, P2, with the naphthalene moiety in the backbone, showed the highest refractive index. For P3, despite the fullerene content is less than 50%, it showed



Figure 7. UV-vis spectra of monomer 4 and P1-P4 polyesters: (a) in chloroform solution (C_{60} concentration normalized to 0.02 mg/mL); (b) thin films on fused silica substrate by spin-coating from the corresponding chloroform solution.



Figure 8. Refractive indices of fullerene polyesters P1-P4 at different wavelengths determined by ellipsometry.

comparable high refractive index due to its much higher density than others, for the dibromobenzene moieties in the backbone.

The Abbe number of the four polyesters was calculated, and the results are listed in Table 2. Normally, materials with high Abbe number show better optical properties since their refractive indices are less sensitive to the change of incident light wavelength. As a result, the optical dispersion will be smaller. In our polymers, **P1** showed the largest Abbe number. This is due to the thiophene groups in the polymer backbone, where the sulfur-containing materials usually show larger Abbe number.^{6,19,20,63} Combined with the highest refractive indices from this polymer at wavelength region higher than 500 nm, **P1** displays the best optical properties among our fullerene polyesters.

Traditionally, the absorption coefficients (α) obtained from ellipsometry are compared with UV–vis spectroscopy to verify whether the refractive indices obtained from ellipsometry are reliable.^{64,65} For the calculation of absorption coefficient from UV–vis spectroscopy, the film thickness needs to be measured.

Figure S11 is the AFM image of P1 film, where it shows a flat smooth surface on silica substrate, with average thickness of about 42 nm. Figure 9 is the measured absorption coefficient of



Figure 9. Absorption spectra of P1 film derived from ellipsometry data and directly measured from a spectrophotometer.

P1 from UV–vis spectroscopy and ellipsometry. The two curves are similar, decrease with increment of wavelength, and agree well with each other. The absorption coefficients from UV–vis spectroscopy are slightly larger than those calculated from ellipsometry, which is due to the reflection losses at the film/air and film/substrate interfaces.⁶⁶ Apart from the reflection losses, the result gives a good agreement between spectrophotometry and ellipsometry data, indicating the fitting method used in analyzing the ellipsometry data is reasonable and the measured refractive indices are reliable.

The hardness of the films and their adhesion to glass sheets were measured, and the results are listed in Table 2. P1, P2, and P3 have relatively good hardness of 2H, 3H, and 4H, respectively, while P4 has the relatively low hardness of <H. The results show that the film hardness can be improved by

Table 2. Fullerene Content, Molar Refraction, Density, Refractive Index, Abbe Number (v_D) , Hardness, and Adhesion to Glass Slides of Fullerene Polyesters P1–P4

sample	C_{60}^{a} (wt %)	$R_{\rm L}^{\ b} ({\rm cm}^3/{\rm mol})$	$ ho^c (g/cm^3)$	n ^d	n ^e	$v_{\rm D}$	hardness	adhesion
P1	53.6	402.5	1.504	1.864	1.860	27.9	2H	0
P2	51.9	421.9	1.463	1.847	1.845	13.0	3H	0
P3	48.1	421.0	1.572	1.854	1.839	19.4	4H	0
P4	53.8	404.2	1.476	1.830	1.848	15.4	< H	0

^{*a*}Fullerene content calculated by the mass fraction of fullerene in the repeating units of corresponding fullerene polyesters. ^{*b*}Molar refraction calculated from polymer repeating units based on the substructures listed in Table S1. ^{*c*}Measured density. ^{*d*}Measured refractive index by ellipsometry at the sodium D line (589 nm). ^{*e*}Calculated refractive index by the Lorentz–Lorenz equation.

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introducing rigid moieties like naphthalene or dibromobenzene groups in the main chain. All these fullerene polyesters showed excellent affinity to glass sheets, with the value of 0 indicating no detachment of any piece was observed after cross-hatching.

CONCLUSION

In summary, we have designed and successfully synthesized a new series of polyesters with pendent fullerenes. Through condensation polymerization, we are able to incorporate high molar refractive index aromatic moieties and fullerenes in the polymer backbones and side chain, respectively. The structure of these resultant fullerene polyesters has been fully characterized by GPC, ¹H NMR, UV-vis spectroscopy, FTIR, and TGA. The introduction of aromatic moiety in the polymer backbone leads to high refractive index polyesters, in conjunction with the high refractive index fullerenes, while not affecting the solubility and film forming properties. These fullerene polyesters have high refractive indices of more than 1.80 at sodium D line (589 nm), which exceeds most high refractive index polymers reported in the literatures. Among them, the polyesters with thiophene as building blocks in the backbone (P1) has the best optical properties, with the highest refractive index (1.86 at 589 nm) and highest Abbe number (27.9). These fullerene polyester films showed relatively high hardness and excellent adhesion to glass sheets. The design method here by conjunction effect of polymer backbones and side chains provides a new way to HRIPs.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.5b01791.

¹³C NMR of the fullerene diol monomer **4**, quantitative ¹H NMR of polyesters and deduction of the calculation of polymer molecular weights, DOSY NMR figures of polyesters, DSC curves, and AFM figure of **P1** film to measure the film thickness (PDF)

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Notes

The authors declare no competing financial interest.

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