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Side-chain fullerene polyesters: a new class of high refractive index polymers†

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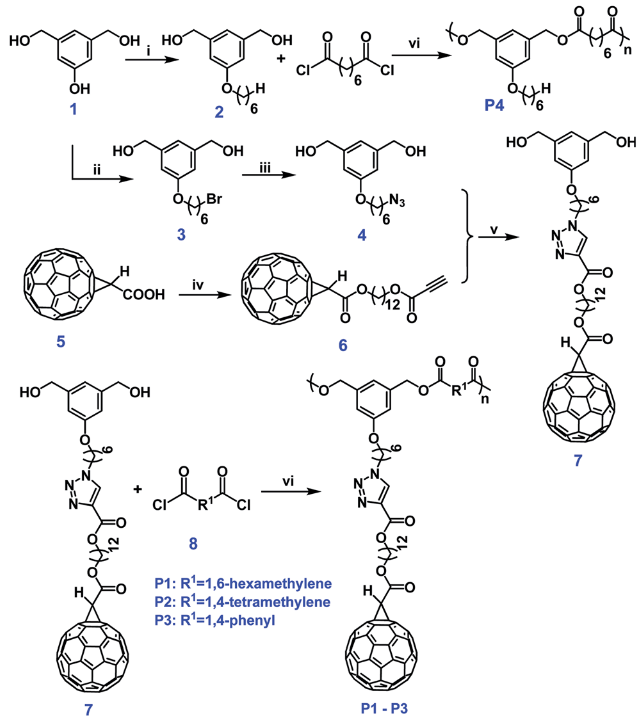
By introducing flexible spacers between pendant fullerenes and the backbone, side-chain fullerene polyesters with high fullerene content and good solubility were synthesized by condensation polymerization. These polyesters are a new class of soluble high refractive index polymers (HRIPs) with the highest value of 1.79 at the sodium D line (589 nm).

Fullerene-based polymers have attracted great interest as they incorporate the good processability of polymeric materials with fullerene's special electronic and optical properties.[1–12] Because of the multiple additions of free radicals and nucleophiles onto fullerenes, polymerization of fullerene monomers by free radical, anionic or metal-catalyzed polymerization usually produces star, branched or crosslinked polymers with uncontrolled structures.[13–28] Though a clear structure is important for understanding the structure–property relationships of fullerene polymers, due to the synthetic problems stated above, there are only a few reports about the synthesis of fullerene polymer with clear structure, which mainly used the condensation polymerization method.[7–12] This method can produce fullerene polymers with well-defined structure, yet the poor solubility problem of the obtained polymers limits their applications due to the high stiffness ofthe polymer backbones from the repulsion between fullerenes.[7–9] Recently, Nierengarten *et al.* reported the synthesis of fullerene polyesters with good solubility by introducing long alkyl chains.[10–12] However, the application of these fullerene polymers in all-polymer solar cells failed due to the low fullerene content in the polymers (~30%).[11] How to synthesize well-defined fullerene polymers with high fullerene content (for outstanding fullerene properties) and good solubility in organic solvents (for good processability) is still a big challenge for polymer chemists.



Scheme 1 Synthetic route to fullerene monomer and polymers. *Conditions*: (i) K_2CO_3, 1-bromohexane, acetone, 60 °C, 6 h (80%); (ii) K_2CO_3, 1,6-dibromohexane, acetone, 60 °C, 6 h (66%); (iii) NaN_3, DMF, 60 °C, 48 h (85%); (iv) 12-hydroxydodecyl propiolate, *p*-toluenesulfonic acid, 4-dimethylaminopyridine, *N*,*N*-diisopropylcarbodiimide, *o*-dichlorobenzene, rt, 1 h (80%); (v) $CuSO_4 \cdot 5H_2O$, sodium ascorbate, CH_2Cl_2, 30 °C (50%); (vi) pyridine, anisole, 60 °C, 24 h.

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We report here the design and synthesis of fullerene polyesters **P1–P3** with clear structure as shown in Scheme 1. By utilizing liquid crystalline polymers' Finkelmann's decoupling effect method,[29] we introduce flexible long spacer groups between the pendent fullerene and polymer backbone to minimize the fullerene's influence on chain stiffness, and obtain polyesters with high fullerene content (>50 wt%) and good solubility. The fullerenoacetic acid was used to synthesize monomer 7, since methanofullerene derivatives are stable and widely used in the opto-electronics field.[30–32] Condensation polymerization of this monomer with three different diacyl chlorides at mild temperature afforded three polyesters **P1–P3**. The detailed synthesis and characterization of the monomer and polymers are described in ESI (Fig. S1–S7†). These polyesters have good solubility in organic solvents (chloroform, dichloromethane, anisole, *etc.*) at room temperature. In particular, the high solubility of 20 mg mL^{-1} in chloroform and the good film-forming properties make them useful for applications.

Fig. 1 is the ^{1}H NMR spectra of monomer 7 and polyester **P2**. The diminished peak k ($\delta = 4.67$ ppm) and the emerging peak k′ ($\delta = 5.05$ ppm) clearly indicate the formation of ester bonds in the polymer. By the end-group estimation, the number-average molecular weights of the polymers were calculated by ^{1}H NMR. Detailed calculation can be found in ESI.† The molecular weights calculated from NMR for polyesters are listed in Table 1.

Analysis of the polyesters by gel permeation chromatography (GPC) (Fig. 2) revealed a single peak of the polymers, suggesting there should be no detectable side reactions. The measured molecular weight of the monomer 7 ($M_n = 670$ g mol^{-1}) using polystyrene (PS) as standard is much lower than the theoretical value (1293 g mol^{-1}). This is due to the difference in hydrodynamic volume of the monomer compared to linear polystyrene standards, and the interaction of fullerenes with the phenyl groups of PS stationary phase, which leads to the increase of elution time with the corresponding decrease of the molecular weights.[11,33–36] Nevertheless, the apparent number-average molecular weights obtained by GPC for **P1–P3** are between 3000 g mol^{-1} and 4000 g mol^{-1}, suggesting the successful synthesis of the polymers. The polydispersity index (M_w/M_n) values (1.2–1.4) are smaller than traditional condensation polymerization. This comes from the postpolymerization treatment by precipitating the obtained material into tetrahydrofuran (THF), where monomer and oligomers are washed out.

Table 1 Molecular weights, polydispersity values and decomposition temperatures of the polyesters

Sample	M_n^{a} (g mol^{-1})	M_n^{b} (g mol^{-1})	PDI^b	T_d^{d} (°C)
P1	9720	3900	1.29	361
P2	14 800	3200	1.35	346
P3	7440	3100	1.20	360
P4	6840	7700^c	1.47^c	378

[a] Determined by ^{1}H NMR in *d*-CHCl$_3$. [b] Determined by GPC using CHCl$_3$ as eluent and PS as standard. [c] Determined by GPC using THF as eluent and PS as standard. [d] Temperature at 5% weight loss by a heating rate of 10 °C min^{-1} under nitrogen.

The fullerene polymers were further characterized by UV-Vis spectroscopy (see Fig. S4 and S5†), thermogravimetric analysis (TGA, Fig. S6†) and Fourier transform Infrared (FTIR) spectroscopy (Fig. S7†). The sharp peaks at 428 nm and small peaks at 690 nm in Fig. S4† are characteristic features in the spectra of methano[60]fullerenes.[37,38] The similar absorption spectra and peaks in solution and in film form indicate the chemical structure of the fullerene polymers is the same in solution and in film. In Fig. S6,† all polymers exhibit high thermal stability with the 5% weight loss temperatures (T_d) higher than 340 °C. It should be noted that even at 600 °C, there is more than 60% weight remaining for all the polymers, indicating the high fullerene content of the polyesters. The fullerene polymers' structure is further proved by the FTIR spectra (Fig. S7†), where the peaks at 526 cm^{-1}, 574 cm^{-1}, 1183 cm^{-1}, and 1427 cm^{-1} are the characteristic peaks of C$_{60}$ corresponding to its intramolecular vibration modes.[39]

Thin films of **P1–P3** polymers were prepared by spin coating the corresponding chloroform solution onto silicon wafers. The refractive indices as a function of wavelength for the polymer

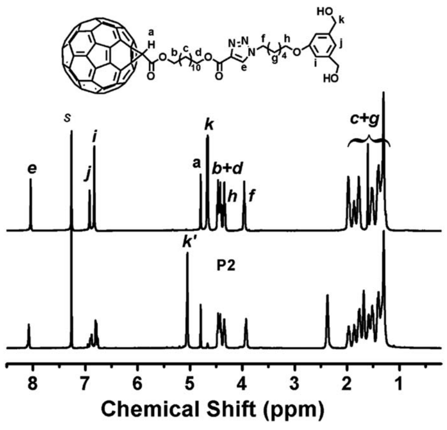

Fig. 1 ^{1}H NMR spectra of monomer 7 (upper part) and fullerene polyester **P2** (lower part) in *d*-chloroform. s: solvent peak.

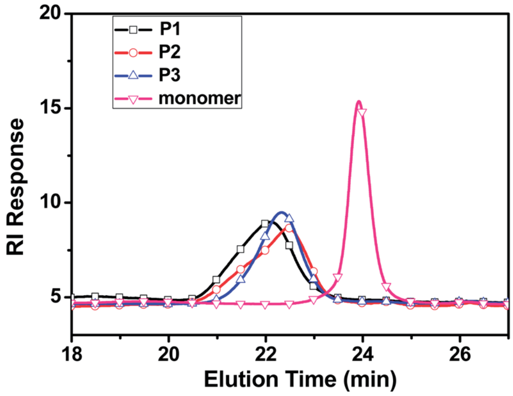

Fig. 2 GPC analysis of monomer 7 and fullerene polyesters **P1–P3**. Eluent: chloroform; flow rate: 1.0 mL min^{-1}. Concentration normalized to 1.0 mg mL^{-1}.

films were determined using a variable angle spectroscopic ellipsometer, and the results are presented in Fig. 3. Detailed fitting method and data can be found in ESI (Fig. S8 and S9†). All the fullerene polymers exhibit refractive indices higher than 1.70 in the measured wavelength range from 500 to 900 nm, with the value decreasing slightly with increasing wavelength. As we know, these are the first reported high refractive index polymers (HRIPs) by incorporating fullerenes in the polymers.[40–43] The refractive index at the sodium D line (589 nm) for **P3** ($n = 1.79$) is so high that it exceeds most of the polymers which normally exhibit values between 1.30 and 1.70.[40] This value is comparable to the refractive indices of well-known HRIPs (~1.80), which mainly consist of two types of material: conjugated polymers and polymer/inorganic material hybrids.[41,44–48] Due to the stability and processability problems for polymer hybrid systems, conjugated polymers have attracted much interest recently. In these polymers, the high refractive indices are due to the highly polarizable π-conjugated functionalities. Since [60]fullerene is a buckyball-like molecule surrounded by conjugated π-electrons and has a high refractive index, we believe this is the origin of the high refractive index for our fullerene polyesters.

To see if the high refractive indices of these polyesters are from the incorporation of side-chain fullerenes, controlled experiments were carried where a similar polyester without pendent fullerenes (**P4**, Scheme 1) was synthesized. This polymer has good solubility in common organic solvents, with a refractive index around 1.52 at the measured wavelength (Fig. 3), similar to typical polyesters. This result clearly indicates that the pendent fullerenes are the key for the high index of refraction.

To explain the high refractive indices of the fullerene polymers, the Lorentz–Lorenz equation (1) is introduced, which is commonly used to predict a polymer's refractive index:[40,49]

$$\frac{n^2-1}{n^2+2}=\frac{R}{M}\rho \tag{1}$$

where n is the refractive index, R is the molar refraction (cm^3 mol^{-1}), M is the molecular weight of repeating units (g mol^{-1}), and ρ is the density (g cm^{-3}). Detailed calculation of molar refraction can be found in ESI,† and the results for eqn (1) are listed in Table 2.

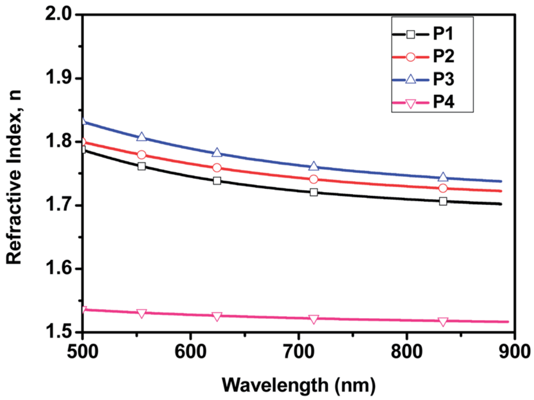

Fig. 3 Refractive indices of polymers at different wavelengths.

Table 2 Fullerene contents, density values, measured and calculated refractive indices of fullerene polyesters

Sample	C_{60} (%)	Molar refraction (cm^3 mol^{-1})	ρ (g cm^{-3})	n^a	n^b
P1	50.3	425.8	1.404	1.748	1.775
P2	51.3	416.8	1.418	1.771	1.783
P3	50.6	424.1	1.430	1.793	1.795

[a] Measured refractive index by ellipsometry. [b] Calculated refractive index by Lorentz–Lorenz equation at sodium D line (589 nm).

The calculated refractive indices agree well with the measured refractive indices, indicating the good reliability of our measured data. According to eqn (1), the high refractive index of these fullerene polymers can be attributed to the high molar refraction of fullerene and the high density of the polymers. On the other hand, the refractive index of the polymers has the trend of **P3** > **P2** > **P1** at the same measured wavelength, despite the fact that the fullerene content in the polymers is **P2** > **P3** > **P1**. This is due to the highest density of **P3** (1.430 g cm^{-3}) among the fullerene polyesters (1.418 g cm^{-3} for **P2**, and 1.404 g cm^{-3} for **P1**).

Since HRIPs have many applications in advanced optical fields to improve the performance of optoelectronic devices,[41–47] our results provide a new method to design HRIPs by the incorporation of fullerenes. On the other hand, since fullerene derivatives are widely used in organic solar cells as acceptor materials,[50,51] the potential application of our fullerene polymers in these field is under current investigation.

In summary, we have successfully synthesized a series of side-chain high fullerene content polyesters by condensation polymerization. The polyesters have high refractive indices (above 1.70) due to the incorporation of pendent fullerenes. Among them, polymer **P3** has the highest refractive index (1.79 at 589 nm) due to its high density, and is among the highest values reported for HRIPs with good solubility and without metal elements. With the semiconducting behaviour from the fullerene moieties, these polymers can be viewed as molecular wires with the insulating polyester backbone as the core and semiconducting fullerenes outside, and have potential applications in optoelectronics devices.

Acknowledgements

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