Metallized hyperbranched polydiyne: a photonic material with a large refractive index tunability and a spin-coatable catalyst for facile fabrication of carbon nanotubes†

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A cobalt-containing hyperbranched polydiyne shows refractive indexes (n) as high as 1.713–1.813 in the long wavelength region, which can be tuned to a large extent (Δn up to $\sim$0.048) by UV irradiation; the polymer can also function as a spin-coatable catalyst for the growth of carbon nanotubes.

Organometallic polymers are molecular hybrids of organic and metallic species that exhibit useful catalytic, photonic, electrical, optical and magnetic properties as well as excellent macroscopic processability, which are often inaccessible by their pure organic and inorganic counterparts.[1–3] Polymers containing lead and iron atoms in the polymer backbones, for example, exhibit refractive index (RI) values higher than those of their organic cousins.[4,5] Development of new, processable materials with high RI values is fascinating yet rather challenging. To find practical applications in optoelectronic devices such as optical waveguides, memories, and photochromatic and holographic image recording systems, the highly refractive materials should ideally undergo large changes in their refractivities when stimulated by an external perturbation.[6]

Our group has been interested in the design and synthesis of hyperbranched conjugated polymers.[7] We have succeeded in the preparation of completely soluble hyperbranched polydiynes (*hb*-PDYs) with high molecular weights. The internally triple-bonded scaffolds of the *hb*-PDYs function as excellent macroligands for complexation with metallic species such as cobalt carbonyls. The cobalt-containing *hb*-PDYs have been transformed into advanced ceramics, which exhibit outstanding soft ferromagnetism with very high magnetizability (M_s up to $\sim$120 emu g^{-1}) and extremely low hysteresis losses (H_c and M_r approaching zero).[8,9] In this short communication, using a cobalt-metallized, triphenylamine-cored *hb*-PDY as an example, we show that the organometallic *hb*-PDYs possess high RIs in the long wavelength region, which can be modulated to a large extent by photolysis. We also demonstrate that spin-coated thin films of the metal–polymer hybrids can serve as catalyst seeds for the fabrication of carbon nanotubes (CNTs).

The *hb*-PDY used in this study is poly[tris(4-ethynylphenyl)-amine] (*hb*-PTEPA), which is readily metallized, through its facile complexation with octacarbonyldicobalt, to give *hb*-PTEPA(Co) (Scheme 1).[8,9] Spin-coating toluene solutions of *hb*-PTEPA(Co) onto silicon wafers or glass substrates gives thin films of good quality with thickness of $\sim$1 μm, as determined by ellipsometry measurement. The films of *hb*-PTEPA(Co) are stable and can be stored without any special protection under ambient conditions for more than six months. UV irradiation (λ = 360–400 nm), however, can induce a visible photochromic response, readily bleaching the brownish films.

The color change may stem from photoinduced decomplexation of the organocobalt polymer. Fig. S1 shows the IR spectra of the films of *hb*-PTEPA(Co) before and after UV irradiation. Whereas *hb*-PTEPA(Co) shows strong, typical cobalt-carbonyl absorptions at 2090, 2055 and 2025 cm^{-1},[10] these bands are greatly weakened by UV irradiation. The bands at 569, 515 and 494 cm^{-1}, associated with cobalt–carbon vibrations and cobalt-carbonyl deformations,[11] almost completely disappear after the photolysis. On the other hand, a broad shoulder emerges in the C=C stretching region at 1700–1600 cm^{-1}, suggesting that diene, triene and/or higher conjugated double-bond structures have resulted from the photoinduced polymerization of the diyne moieties after metal decomplexation of *hb*-PTEPA(Co). Other absorption bands remain more or less the same, further confirming that the photobleaching originates from the decomplexation of the organometallic moieties.

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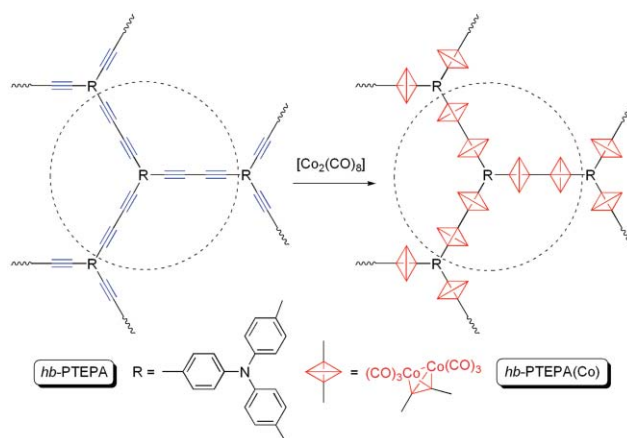[b]*Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China*
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Scheme 1 Preparation of cobalt-containing polymer *hb*-PTEPA(Co) *via* metallization of hyperbranched polydiyne *hb*-PTEPA.

We utilized the visible photochromic change to fabricate micro-structured films. Photopatterns are readily generated by simply irradiating a thin film of *hb*-PTEPA(Co) with UV light for 30 min through a Cu-negative mask, without going through a wet or dry development step. Fig. 1A shows an optical micrograph of the photopatterned film, with the bleached areas being those exposed to the UV light. Fig. 1B shows a magnified image where sharp edges between the exposed and unexposed regions are clearly seen, while Fig. 1C illustrates the excellent patternability of the polymer film. The feature size of the photonic pattern is basically determined by the photomask used. We believe that smaller feature sizes should be achievable by employing alternative patterning techniques such as electron-beam lithography and multi-beam interference holography.[12]

Wavelength-dependent RI measurements of the unexposed and exposed films of *hb*-PTEPA(Co) reveal interesting results. Like its nonmetallated parent (*hb*-PTEPA),[8] the metallated polymer exhibits very high RIs (n = 1.813–1.713) in the spectral region of 600–1700 nm (Fig. 2). Its RIs drop dramatically after the UV irradiation (n = 1.777–1.665), possibly due to the large structural changes induced by the photolysis of the organometallic complex. The difference in the RI (Δn) at the telecommunication-important wavelength (λ = 1550 nm) is as large as 0.047 (Table 1).

For a material to be useful for technological applications, its optical dispersion, which is a measure of the change in its RI with wavelength, should be small. For a conventional optical material working in the visible spectral region, its optical dispersion is expressed by the Abbé number (v_D), which is calculated from equation 1:

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

where n_D, n_F and n_C are the respective RIs at 589, 486 and 656 nm. Generally, an organic polymer with a high RI also displays a high dispersion (or low v_D) and *vice versa*. Thus, poly(vinylcarbazole), for example, shows a high RI (1.675) and a low v_D (19), whereas Teflon or poly(tetrafluoroethylene) shows a low RI (1.345) and a high v_D (83).[13] Evidently, development of polymeric materials with both high RI and v_D values (hence low optical dispersions) is a much sought after research goal.

Thanks to their highly polarizable π-electrons, *hb*-PTEPA(Co) and *hb*-PTEPA(Co)-UV both fulfil the requirement of exhibiting
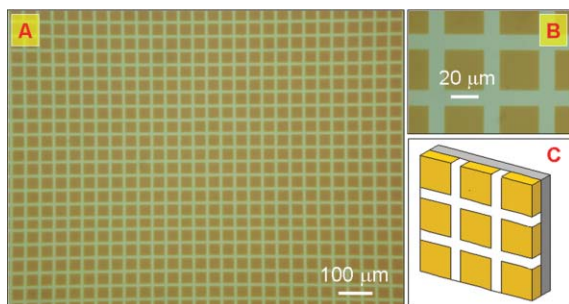
Fig. 1 (A) Optical micrograph of a two-dimensional photonic pattern generated by UV irradiation of *hb*-PTEPA(Co) through a Cu-negative mask, (B) image with a high magnification, and (C) model of the photopattern, with brown and white colors denoting unexposed and exposed areas, respectively.
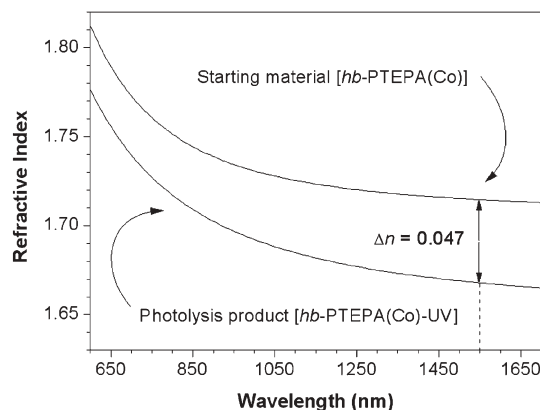
Fig. 2 Refractive indexes of thin films of the cobalt-containing polymer before [*hb*-PTEPA(Co)] and after photolysis [*hb*-PTEPA(Co)-UV].

Table 1 Refractive indexes (n) and revised Abbé numbers (v_D') of films of the cobalt-containing hyperbranched polymer before [*hb*-PTEPA(Co)] and after photolysis [*hb*-PTEPA(Co)-UV]

Polymer	n_{1064}	n_{1319}	n_{1550}	v_D'
hb-PTEPA(Co)	1.727	1.718	1.715	59.8
hb-PTEPA(Co)-UV	1.687	1.674	1.668	35.5

high RI values. Both of the polymers, like other conjugated polymers,[14] absorb in the visible spectral region, showing higher RI values in the shorter wavelength regions. This interference not only complicates the RI measurements below 700 nm but also makes the associated low v_D values meaningless as they are derived from the resonance-enhanced, highly dispersive RI values.

To explore the real potential of optical applications of the polymers, it has been suggested to use a revised Abbé number (v'), utilizing their RI values at nonabsorbing wavelengths at 1064, 1319 and 2500 nm.[14] The first two wavelengths are chosen in view of the practical interest of commercial laser lines (Nd:YAG lasers),[14a,15] while the last wavelength represents the longest measurable non-resonant line. The value at 2500 nm may well reflect the real optical dispersion but for more common and convenient usage, we suggest employing the RI value at 1550 nm to calculate v_D' values for conjugated polymers.[16c] The v_D' is thus now defined by equation 2:

$$v'_D = \frac{n_{1319} - 1}{n_{1064} - n_{1550}} \quad (2)$$

where n_{1319}, n_{1064} and n_{1550} are the RI values at 1319, 1064 and 1550 nm, respectively.

The v_D' value for *hb*-PTEPA(Co) is as high as 60, while its photolyzed product of *hb*-PTEPA(Co)-UV exhibits a v_D' value of 36 (Table 1). Previously reported v_D' values for other conjugated polymers with absorptivity in the visible region have been from 9 to 38, with the majority of the data in the range of 10–20.[14a] The v_D' values of our polymers are significantly higher, indicative of their lower optical dispersions and hence lower chromatic aberrations. Together with their very high RI values, our polymers are promising candidate materials for applications in the construction of photonic and holographic devices such as read-only memories in the near-IR region.[16]

Metallic species such as iron, nickel and cobalt nanoclusters are known to catalyze CNT growth in the chemical vapor deposition
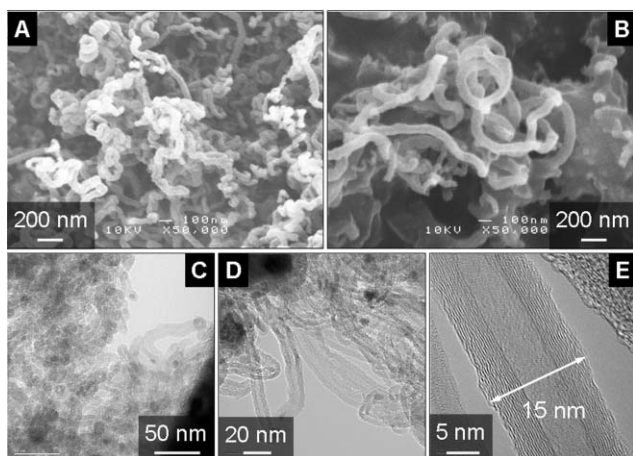
Fig. 3 (A and B) SEM and (C–E) TEM microphotographs of the carbon nanotubes prepared by a CVD process at 700 °C on silicon wafers spin-coated with thin films of *hb*-PTEPA(Co).
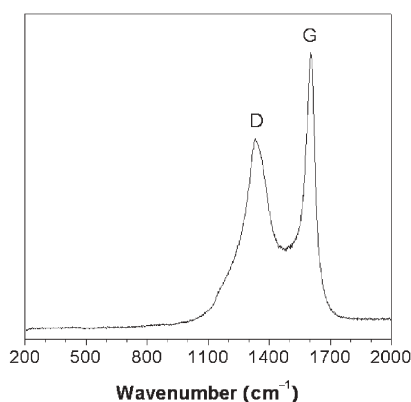
Fig. 4 Raman spectra of multiwalled carbon nanotubes fabricated by the CVD process catalyzed by the cobalt nanoclusters generated *in-situ* from pyrolysis of the *hb*-PTEPA(Co) film.

(CVD) process.[17] Because of the ready thermal curability of the *hb*-PDYs,[8] spin-coated films of *hb*-PTEPA(Co) are expected to restrict the agglomeration of the cobalt nanoclusters formed *in situ* in the CVD process and hence to provide nanoscopic catalyst seeds for the CNT growth. This proves to be the case. Uniform bundles of CNTs are grown by the CVD process at 700 °C with acetylene gas as the carbon source (Fig. 3). As expected from a CNT growing temperature below 800 °C,[18] the formed CNTs are multiwalled in nature. Thanks to the homogeneous organometallic thin films, the CNTs have a narrow size distribution or a small dispersity, with the diameters of their external walls being as small as 15 nm (Fig. 3E).

Raman spectra of the CNTs (Fig. 4) reveal two characteristic peaks: a sharp G band at ~ 1600 cm^{-1}, which corresponds to a first-order Raman process involving an in-plane oscillation of the carbon atoms in the graphene sheet, and a relatively broad D band at ~ 1340 cm^{-1}, which relates to the second-order defect-induced Raman mode involving a one phonon elastic scattering process. The appearance of these two Raman bands is in good agreement with the multiwalled nature of the CNTs, as proved by TEM analysis.

In conclusion, the cobalt-complexed *hb*-PDY possesses a good film formability and shows a high optical transparency in the long wavelength region. UV irradiation of the brownish *hb*-PTEPA(Co) film induces photobleaching, accompanied by large changes in its RI values. The organocobalt polymer and its UV-cured product exhibit large v_D' values hence low optical dispersions in the near-IR region. The thin film of *hb*-PTEPA(Co) can efficiently catalyze the growth of CNTs in the CVD process, making it a versatile material for an array of high-tech applications.

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