An Axially Grafted Charm Bracelet Type Indium Phthalocyanine Copolymer

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As one of the most investigated classes of functional organic materials, phthalocyanines (Pc's) exhibit outstanding optoelectronic effects, nonlinear optical (including optical limiting) properties, and biological activities.[1,2] Like [60]fullerene, phthalocyanine has also been incorporated covalently into polymers[3] by a variety of reactions as part of the main chain,[4] at the end of side chains,[5] as end groups,[6] as branch points of star,[7] and as junctions of networks.[8] In most phthalocyanine polymers cofacial association predominates, as it does in low molar mass derivatives, and only axial substitution of the central ion is successful for its prevention.[3] Much less work, however, has been done on the axial polymeric modification of metallophthalocyanines so far.

For a practical nonlinear optical device, strong intermolecular interactions are generally undesirable since they usually add relaxation pathways, shorten the excited-state lifetime, and reduce the effective nonlinear absorption.[2,9,10] In recent years, we have systematically studied the effect of axial substitution on the optical properties of indium and gallium phthalocyanine compounds.[9,10] The results showed that axial ligands did not apparently affect the linear optical properties of Pc's but resulted in the considerable enhancement in optical limiting response.[9,10] The reason for this is associated with the fact that there is a permanent dipole moment perpendicular to the macrocycle in these axially substituted Pc's. We report here for the first time the synthesis of indium phthalocyanine axially grafted polystyrene polymer (**4**, $t\mathrm{Bu_4PcIn{-}PS}$ copolymer, $M_n = 3.8 \times 10^4$, $M_w/M_n = 1.65$, RI detector, linear polystyrene as reference standard) and its nonlinear optical properties in solution.

As shown in Scheme 1, polymer **4** was obtained by the reaction of $t\mathrm{Bu_4PcInCl}$ (**3**, $\mathrm{C_{48}H_{48}ClInN_8}$, 887.2 g/mol) with freshly prepared $\mathrm{PS(MgBr)}_n$ (**2**) in room temperature. To a suspension of magnesium turning, previously activated by means of an ultrasonic bath, in dry THF was added dropwise a solution of poly(*p*-bromostyrene) (**1**, Aldrich product, $M_n = 3.6 \times 10^4$, $M_w/M_n = 1.75$, RI detector) in anhydrous THF over a period of 1 h under ultrasonic irradiation. After addition was completed, ultrasonic irradiation was continued for 2−3 h at room temperature. After most of the magnesium had been consumed, the solution was filtered to remove any insoluble byproducts (if any) and excess solid magnesium. A dilute solution of **3** in dry THF was added dropwise into a stirred solution of **2** under argon at ambient temperature. The resultant polymer **4** was precipitated with methanol, washed, redissolved in THF, filtered to remove any insoluble impurity, and then reprecipitated with methanol to give a light blue solid powder (this procedure was repeated at least 4−5 times). To further remove a trace of possible trapped $t\mathrm{Bu_4PcInCl}$, which is slightly soluble in methanol, the above polymer was subjected to Soxhlet extraction with methanol for 72 h before characterization. Solvent residues were removed by freeze-drying under vacuum for 10 h.

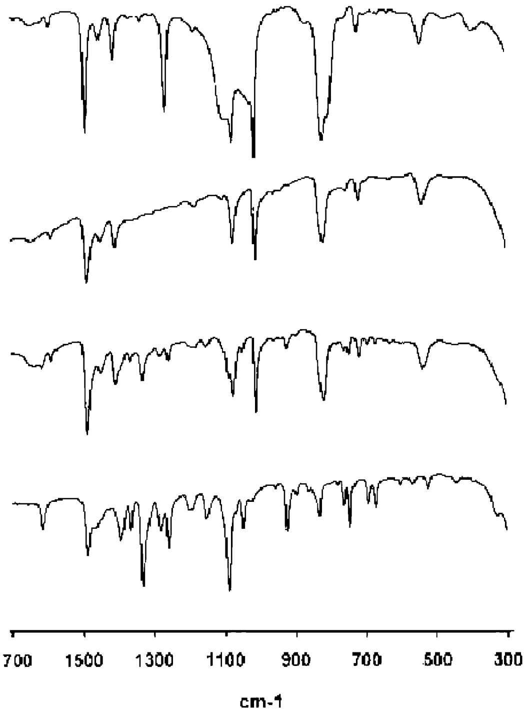

Figure 1. IR spectra of (a) $t\mathrm{Bu_4PcInCl}$, (b) a mixture of $t\mathrm{Bu_4PcInCl}$ and poly(*p*-bromostyrene), (c) poly(*p*-bromostyrene), and (d) $t\mathrm{Bu_4PcIn{-}PS}$ polymer (from bottom to top: a, b, c, and d).

The confirmation of the structure of **4** and its photophysical properties have been carried out by a variety of techniques such as UV/vis, IR, NMR, GPC, DSC, and transient absorption spectroscopy. Like the axially aryl-substituted indium phthalocyanine monomers,[9,10] the effect of axial polymeric modification on the linear optical properties of Pc's is also very small. The observed red shifts of the Q- and B-bands in the UV/vis spectrum of **4** in $\mathrm{CHCl_3}$ are only of the order of 1−3 nm relative to **3**. In the UV region, the strong absorption bands at 262, 270, and 278 nm of **4** are in general agreement with poly(*p*-bromostyrene), but their relatively intensities are very different. The UV/vis absorption bands of pure polystyrene appear at 254, 261, and 269 nm under the same experimental conditions. A comparison of the UV/vis absorption spectra of thin film and dilute solutions

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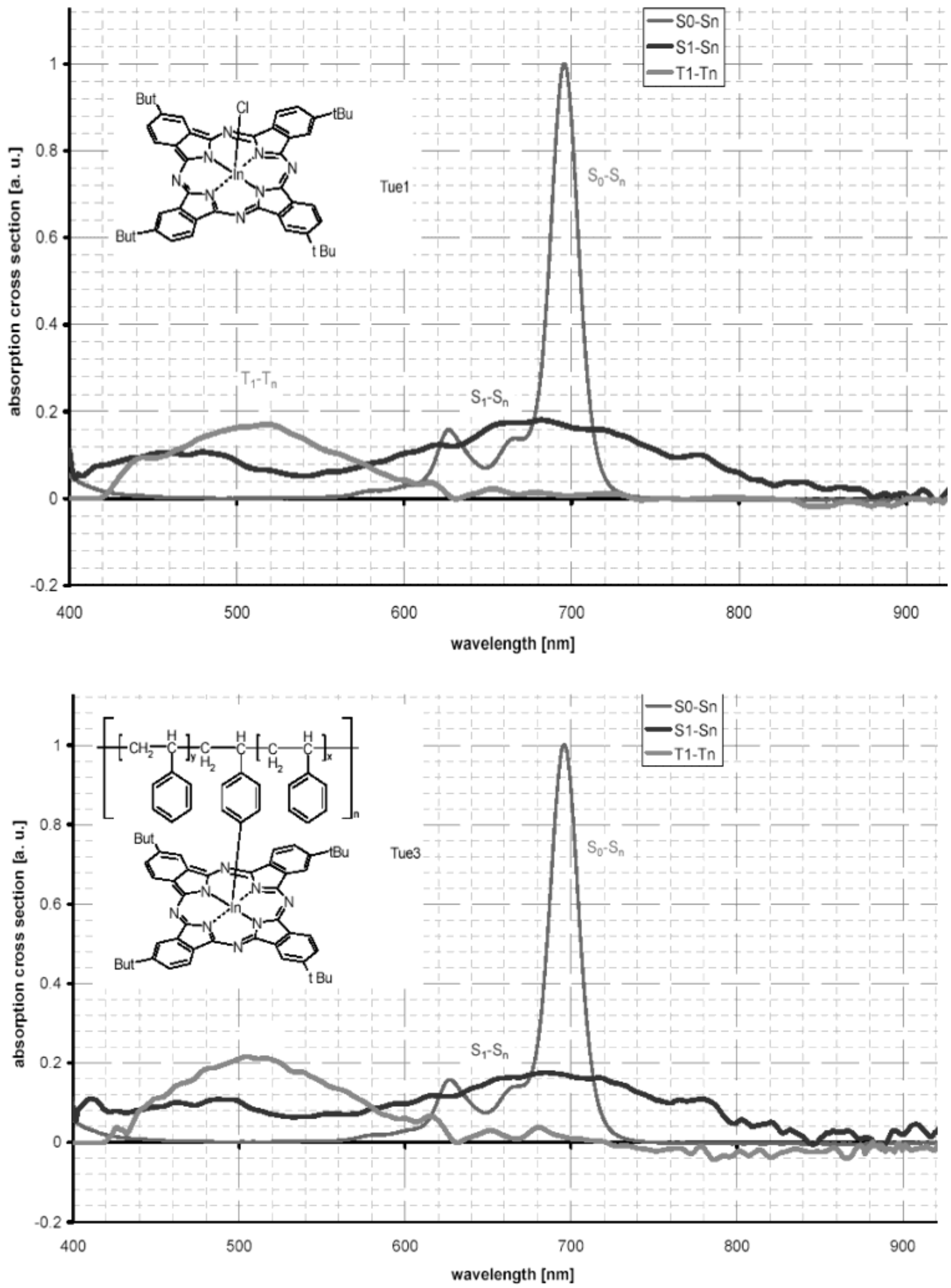
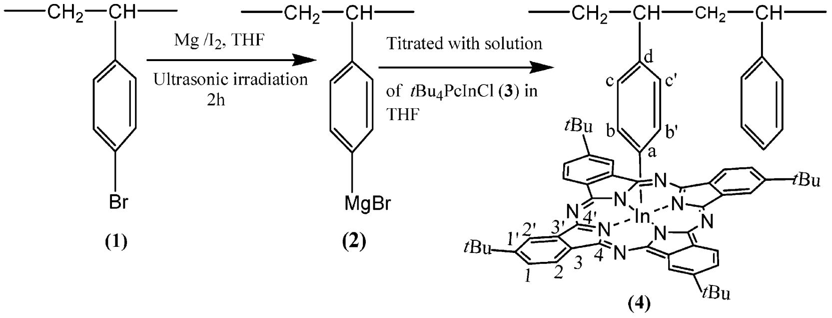


Figure 2. Absorption cross sections of *t*Bu_4PcInCl (top) and *t*Bu_4PcIn−PS polymer (bottom). The cross sections of the excited single and triplet state are shown in comparison with the ground-state absorption.

Scheme 1



of **3** and **4** in $CHCl_3$ shows that the absorption spectra of thin films of **3** and **4** are marginally broader. Upon comparing the thin film and dilute solution UV/vis spectrum of **3**, it is observed that position of the Q-band maximum is shifted slightly toward longer wavelength. In the case of **4**, the same comparison shows that the position of the Q-band maximum is almost unchanged. This result is suggestive of only weak aggregation of **4** in solution. Similarly, as we have reported earlier,[9,10] the introduction of axial aryl ligands into indium or gallium Pc's also cause a considerable decrease in intermolecular interactions between neighboring molecules.

Like polystyrene and poly(*p*-bromostyrene), the DSC thermogram of **4** shows only a single glass transition temperature, indicating that phase separation is not occurring in **4**. Also, the values for glass transition temperatures were found to increase from 114.6 °C (**1**) to 145.9 °C (**4**). The bulky indium phthalocyanine units grafted to polystyrene should hinder the linear styrene segments to fold properly and result in an increase in the glass transition temperatures. Similar results are also observed in the pendant charm bracelet-type C_{60}−PVK, C_{60}−PBS, and C_{60}−PS copolymers.[11] From Figure 1, it can be seen that the IR spectrum of the tBu$_4$PcInCl-doped poly(*p*-bromostyrene) (i.e., a simple blends of **1** and **3**) seems to be a simple superposition of two spectra corresponding to **1** and **3**, whereas the IR spectrum of **4** is apparently different from those of **1**, **3**, and their mixture. As expected, the weak absorption band of the In−Cl stretching mode at 336 cm^{-1} of tBu$_4$PcInCl is absent in the IR spectrum of **4**. The absorption band of the C−Br stretching mode at 650 cm^{-1} of poly(*p*-bromostyrene) was not apparently detected in polymer **4**. Some new strong absorption peaks at 802, 1025, and 1100 cm^{-1} are observed, being associated with the covalent attachment of tBu$_4$PcIn units onto the polystyrene backbone.

The ^{1}H NMR results further confirmed the covalent attachment of tBu$_4$PcIn units onto the polystyrene backbone. In the ^{1}H NMR spectra (in CDCl$_3$) of **3** and **4,** the aromatic protons of tBu$_4$PcInCl (**3**) appear at $\delta =$ 8.27−8.33 (m, 1-H, see Scheme 1), 9.27−9.33 (m, 2-H), and 9.42−9.47 (m, 2′-H) ppm, whereas the corresponding aromatic protons of **4** are located at 8.36−8.39 (m), 9.44−9.51 (m), and 9.60 ppm (m), respectively. In comparison with **3**, a downfield shift of $\Delta\delta \approx 0.08$, 0.18, and 0.16 ppm is found for the 1-H, 2-H, and the 2′-H protons in **4**, respectively. The axially aryl-substituted indium phthalocyanine monomers[9] also exhibited similar results compared to the chloroindium phthalocyanine. In contrast, the aromatic proton signals of the axial polystyrene segments directly attached to indium phthalocyanine are considerably shielded by the influence of the large diamagnetic ring current of phthalocyanine rings on the protons of their axial ligands and appear at $\delta = 3.36-3.41$ (m, c,c′-H), and 2.35−2.41 (m, b,b′-H). As comparison, the proton chemical shifts of axial phenyl group of phenylindium(III) 2,3-octapentylphthalocyanine [2,3-$(C_5H_{11})_8$PcIn(C_6H_5)][9b] are also very similar to that of the former.

As shown in Figure 2, both indium phthalocyanine monomer (**3**) and its polymeric derivative (**4**) are suitable for optical limiting in the spectra range 450−550 nm for nanosecond laser pulses. For the picosecond laser pulses the optical limiting properties are not as good as for nanosecond laser pulses due to the smaller S_1-S_n cross section. However, it should still work. The NLO properties of **3** and **4** in solution were studied using the open aperture Z-scan method.[12] All experiments described in this study were performed using 6 ns pulses from a Q-switched frequency-doubled Nd:YAG laser (532 nm), focused with a 9 cm focal length lens. Open aperture Z-scan spectra in toluene were collected with pulses of various energies for each sample, and all scans performed exhibit a decrease of transmittance about the focus typical of an induced positive nonlinear absorption of incident light. The theory presented by Sheik-Bahae et al.[13] was fitted to the open aperture spectra, and the effective imaginary third-order susceptibilities (Im$\{\chi^{(3)}_{\text{eff}}\}$) were calculated from the fits. The values of Im$\{\chi^{(3)}_{\text{eff}}\}$ at 532 nm for **3** and **4** were determined to be about 1.56×10^{-11} and 0.62×10^{-11} esu, respectively. The corresponding effective second-order hyperpolarizability (γ_{eff}) values for these compounds are approximately 1.15×10^{-32} and 0.26×10^{-32} esu, respectively. The ratio of the excited to ground-state absorption cross sections κ ($\kappa = \sigma_{\text{ex}}/\sigma_0$, where σ_{ex} and σ_0 represent the excited- and ground-state absorption cross sections, respectively) differs significantly with the monomer exhibiting a κ coefficient ($\kappa \approx 27.4 \pm 0.6$) just in excess of 2 times that of the polymerized sample which exhibited $\kappa \approx 13.2 \pm 0.7$.

Polystyrene and poly(*p*-bromostyrene) exhibited no NLO response under the same experimental conditions. Studies of the NLO properties of solid thin film of the resultant polymer **4** are currently in progress.

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