Conducting Polymer Composite Films with Core−Shell-like Nanostructure Prepared from Terthiophene-Terminated Starburst Poly(*n*-butyl acrylate)

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Since the discovery of electrically conductive polyacetylene in 1977, conducting polymers have attracted considerable attention in academic fields and industrial sectors due to their novel optoelectronic properties and apparent potential use in organic electronic devices.[1] An important characteristic of a conducting polymer is its conjugated π-system along its backbone, making it typically both fragile and rigid. The most common method for solving this problem is to blend thermoplastics or elastomers into conducting polymers to produce polymer composite. Potential applications of these materials have been found in various fields,[2] such as electromagnetic shielding, anticorrosion, and antistatic coating. In recent years, several routes for preparing conductive polymer blends have been described, including in-situ polymerization, solution blending, colloidal dispersion, emulsion, and electrochemical polymerization.[3] Another interesting route is the electrochemical polymerization of a precursor polymer that contains a covalently bound pendant electroactive monomer in an electrolyte solution to generate a thin cross-linked film with an interpenetrating network of conductive polymer.[4] The main advantages of this technique include the easy of control of the film thickness and the excellent processability. However, the total surface area of the working electrode severely limits the size of the polymer film, which is generally very small. The conductive film can be prepared only on a conductive substrate, and the viscous precursor solution may also reduce the rate of polymerization.

Recent studies have demonstrated that polymer composite particles with nonconjugated cores and conducting polymeric shells can have a very low conductivity percolation threshold—normally only 5−20% of conjugated polymers by mass[5]—enabling the mechanical and optical properties of the core material to be optimized, such that they can be used practically in the coating industry. These core−shell particles are generally prepared by coating sterically stabilized latex, such as polystyrene, poly(methyl methacrylate), and polyurethane, with a thin overlayer of conducting polymers via in-situ oxidative polymerization.[6] This work elucidates a facile route for synthesizing conductive core−shell-like polymer film by the solid-state oxidation polymerization of terthiophene-terminated starburst poly(*n*-butyl acrylate). This approach is easy to implement and rapidly produces a large uniform conducting film on almost any substrate.

Scheme 1 illustrates the route for synthesizing conductive core−shell-like polymer films. The dodecabromo-functionalized initiator was used as a core molecule to build 12-armed poly(*n*-butyl acrylate) via atom transfer radical polymerization (ATRP)[7] in the presence of the CuBr/PMDETA complex. The feeding molar ratios of the catalytic complex and monomer to dodecabromo-functionalized initiator were set to 12 and 6000, respectively, to ensure sufficient activity of catalyst on each chain end of the polyfunctional initiator and to prevent star−star coupling. The GPC trace of as-prepared 12-PBA exhibits a single symmetric peak and a narrow molecular weight distribution (PDI = 1.09), indicating the well-controlled growth of poly(*n*-butyl acrylate) chains during polymerization. Both GPC and ^{1}H NMR techniques were adopted to determine the number-average molecular weight (M_n) of 12-PBA. The average degree of polymerization (X_n) per polymer arm on the star was calculated from the ratio of the areas under the peak of the methylene protons ($\delta = 4.05$ ppm, 2H) on *n*-butyl ester side chain of the polymer backbone to that under the peak of the peripheral methyl protons ($\delta = 1.10$ ppm, 6H) on the core initiator and was found to be around 35, which is equivalent to a M_n of 56 600. However, a much smaller M_n (40 700) was obtained using the GPC technique, in which linear polystyrene samples were used as standards to establish the calibration curve. Several investigations have reported that the GPC method frequently underestimates the molecular weight of hyperbranched polymers because branched polymers in solution have a more globular conformation than linear polymers, leading to a smaller molecular size of the branched polymer than of the linear polymer for the same molecular weight.

The ω-bromo ends of the 12-PBA were modified to generate the same number of hydroxyl groups by nucleophilic substitution using excess ethanolamine as a nucleophile and base. The complete substitution with ethanolamine was verified by the total disappearance of the signal at $\delta = 4.05$ ppm, corresponding to the proton in the terminal −CHBr− groups, and the appearance of two new signals at $\delta = 3.1$ and 3.3 ppm in the ^{1}H NMR spectrum, corresponding to the methylene proton on ethanolamine. Interestingly, the GPC-determined M_n of 12-armed star decreased drastically from 40 700 to 25 500 as their arm ends were simply transformed from −Br to −OH moieties, perhaps because the strong intramolecular H-bonding between −NH and −OH groups in 12 PBA-OH limits the extension of polymer chains into solvent and thus reduces molecular size. A similar observation has been made of the OH-terminated 3-armed polystyrene system.[8] 12-PBA-OH was then esterified with (2,2′:5′,2″-terthiophene)-3-acetic acid in CH_2Cl_2 with DCC and DPTS as the dehydration agent and the reaction promoter, respectively. The product (12 PBA-terTh) is very soluble in a wide range of organic solvents, including acetone, chloroform, dichloromethane, and THF. Similarly, the extent of terthiophene functionalization on 12 PBA-OH was estimated from the ratio of the area under the peak of the methine proton ($\delta = 7.31$ ppm, 1H, **a**) on terthiophene in the ^{1}H NMR spectrum to that of the peripheral methyl protons ($\delta = 1.10$ ppm, 6H, **b**) on the core initiators, as displayed in Figure 1. The **a**:**b** ratio was determined to be 1:5.95, revealing a terthiophene grafting efficiency of almost 100%. Table 1 presents the molecular weight characteristics of these starburst polymers determined by both GPC and NMR methods.

After a precursor film on glass substrate had been prepared from 1 wt % 12-PBA-terTh solution in chloroform by spin-

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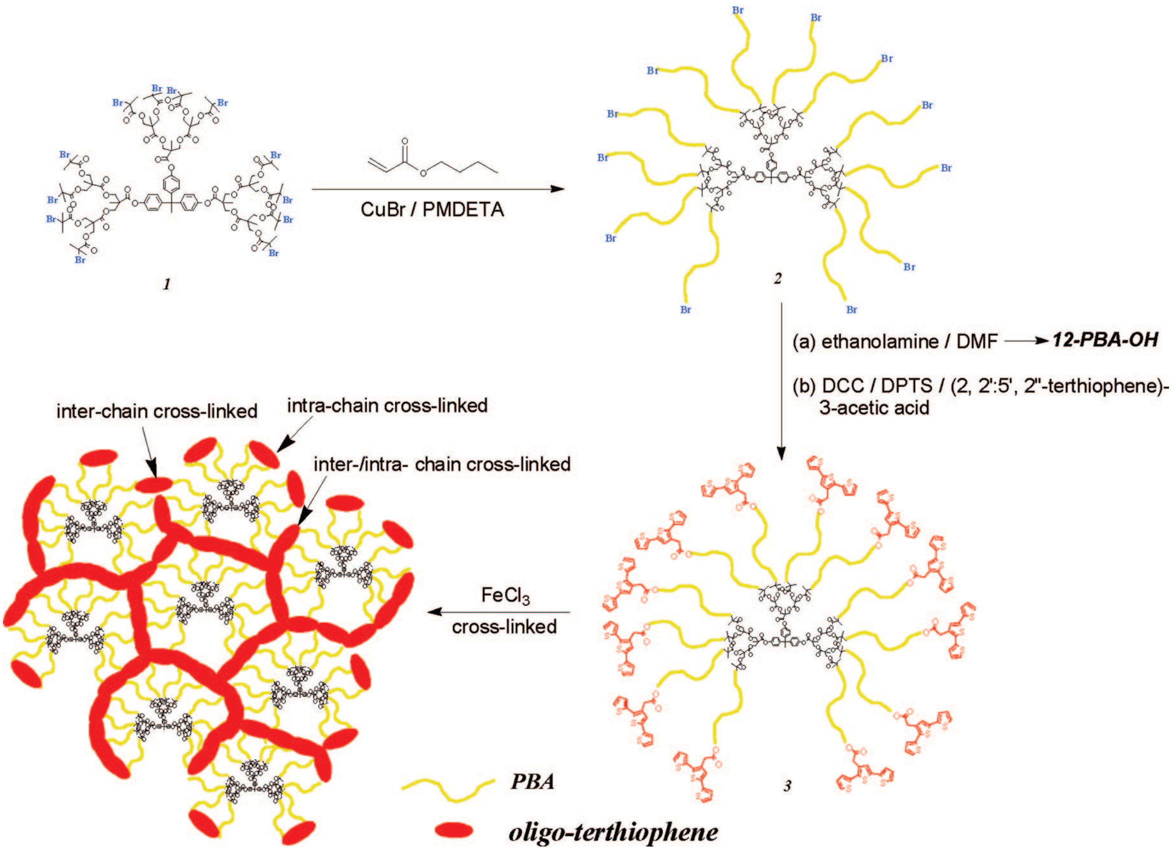
Scheme 1. Synthetic Scheme for Cross-Linked 12-Armed Terthiophene-Terminated Poly(*n*-butyl acrylate) Film



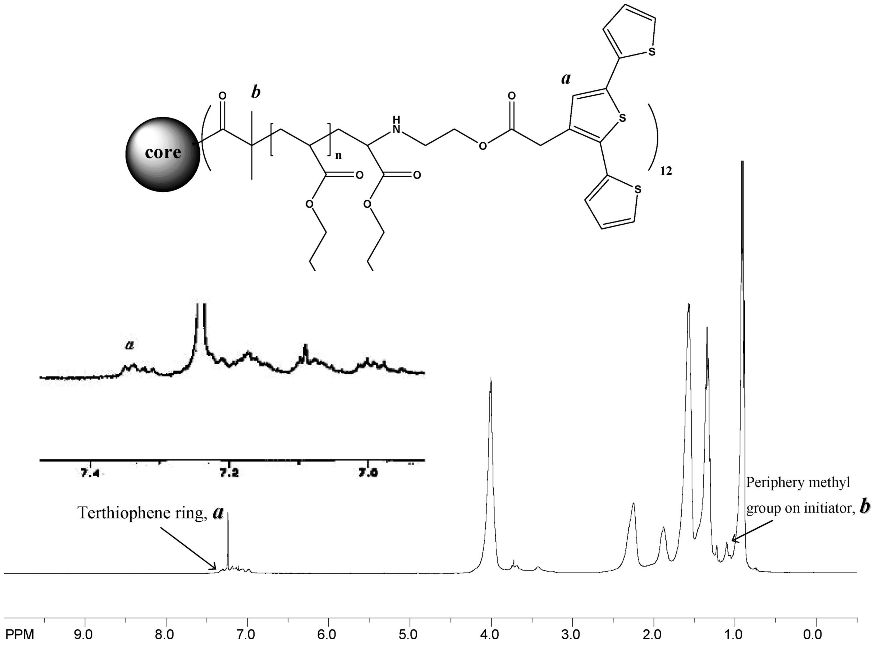


Figure 1. ^{1}H NMR of terthiophene-terminated 12-armed poly(*n*-butyl acrylate) in $CDCl_3$ at 25 °C.

casting, iron(III) chloride solution (3 M) was spread on top of the precursor film to induce the oxidative cross-linking reaction among peripheral terthiophene units. Treatment with $FeCl_3$ immediately changed the color of the 12-PBA-terTh film from light-yellow to dark-brown. The resulting film was insoluble in organic solvents. The as-prepared film was then washed with methanol, acetone, hexane, and chloroform, and became red. Figure 2 presents both the UV−vis absorption and photoluminescence emission spectra of the 12-PBA-terTh film before and

Table 1. Molecular Weight Characteristics of 12-Armed Poly(*n*-butyl acrylate)s with Various End Groups

sample entry	$M_{n,GPC}$[a]	$M_{n,NMR}$[b]	PDI[a]
12-PBA-Br	40 700	56 600	1.09
12-PBA-OH	25 500	NA	1.21
12-PBA-terTh	28 800	60 800	1.32

[a] Determined via GPC analysis with RI detector. [b] The number-average molecular weight (M_n) was calculated from the average degree of polymerization (X_n) per polymer arm on the star determined by NMR analysis.

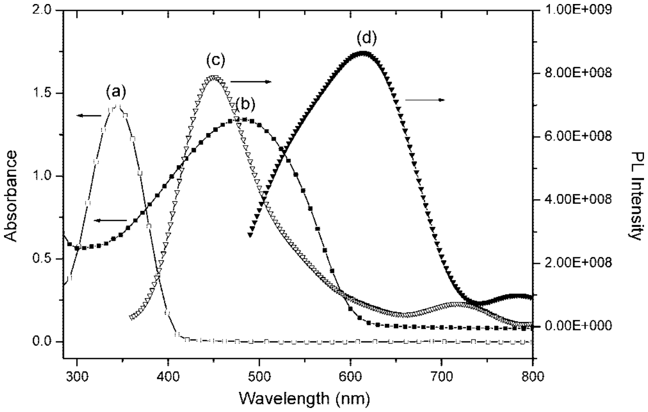


Figure 2. UV−vis absorption spectra of (a) terthiophene-terminated 12-armed poly(*n*-butyl acrylate) (12 PBA-terTh) and (b) cross-linked 12 PBA-terTh films and photoluminescence spectra of (c) 12 PBA-terTh ($\lambda_{ex} = 350$ nm) and (d) cross-linked 12 PBA-terTh films ($\lambda_{ex} = 480$ nm).

after oxidative polymerization. Comparing curves a and b demonstrates that the cross-linking reaction of the terthiophenes broadened the absorption spectrum and shifted the maximum wavelength of absorption from 345 to 480 nm. Similarly, the maximum emission wavelength was markedly shifted from 450 to 610 nm. These experimental findings clearly indicate the effective extension of the π-conjugated structure of the terthienyl moiety and thus prove the formation of oligoterthiophenes.

The surface morphology of cross-linked 12-PBA-terTh was examined using atomic force microscopy (AFM). The cross-linked 12-PBA-terTh formed a continuous and uniform thin film with a root-mean-square (rms) roughness of 1.13 nm upon being spin-cast on a glass slide and treated with iron(III) chloride (Figure SI-1 of the Supporting Information). Film thickness can be varied easily by controlling spin speed while coating the 12-PBA-terTh precursor onto the glass substrate. Experimental results from the alpha-step profilometer and AFM indicate that as the spin speed increased from 500 to 1500 to 3000 rpm, film thickness declined from 225 to 130 to 90 nm, respectively; however, all films remained uniform and continuous with similar degrees of roughness. Furthermore, the thermal stability of 12-armed PBAs and cross-linked 12 PBA-terTh was studied by thermal gravimetric analysis (TGA). All 12-armed PBAs gave similar TGA thermograms with a char yield of about 4% and a thermal degradation temperature (T_d) of ~350 °C for a weight loss of 5%. The structure of the terminal groups did not obviously affect the thermal stability of 12-armed PBAs. However, the cross-linked 12 PBA-terTh yielded a single-step thermogram and a slightly lower T_d (333 °C), but it did have a much higher char-yield (17%), again suggesting cross-linking among therthiophene moieties.

The cross-linked film of 12 PBA-terTh in its neutral state exhibited a strong absorption band from 300 to 600 nm with a peak at 480 nm, as shown in Figure 3. After it had been treated with 0.1 M iron(III) perchlorate in acetonitrile, the doped film exhibited two additional absorption peaks at 760 and 1440 nm, corresponding to the polaron and bipolaron transitions, respectively. The conductivity of the iron(III) perchlorate-doped cross-linked 12 PBA-terTh was measured using the standard four-point probe method. Very interestingly, although the weight content of terthiophene in 12 PBA-terTh is only around 5%, the electrical conductivity of the film was determined to be 0.62 mS/cm, which is comparable to that of cross-linked poly[(2-terthiophenyl)norbornene] with more than 60 wt % of terthiophene.[4b] To investigate the effects of dopant type on film conductivity, the cross-linked 12-PBA-terTh was also treated with gaseous iodine and an iron(III) chloride−acetonitrile solution. The conductivity of I_2- and $FeCl_3$-doped films was 0.69 and 0.75 mS/cm, respectively. However, the conductivity of I_2-doped film decreased dramatically when heated or stored in a vacuum. Conversely, the $FeCl_3$-doped film exhibited excellent thermal stability (Figure 4). Apparently, the core−shell structure substantially facilitates the development of a three-dimensional conducting network even at very low oligoterthiophene content, effectively increasing the conductivity of the cross-linked composite film. Moreover, the as-synthesized cross-linked 12 PBA-terTh film demonstrated notable flexibility and excellent adhesion to the substrate because of the large poly(*n*-butyl acrylate) content.

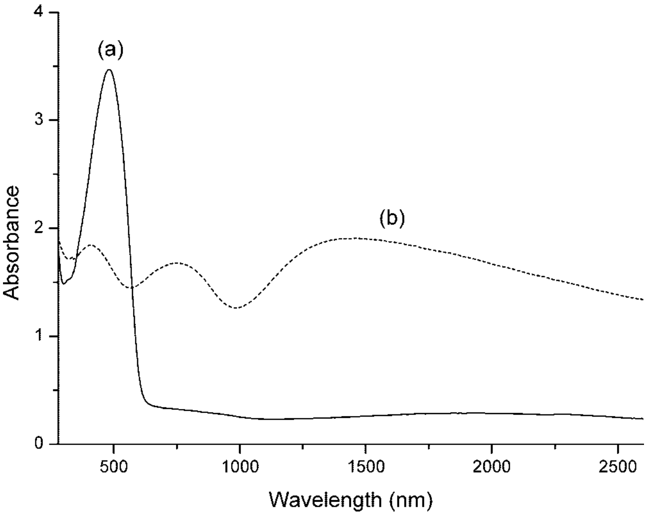


Figure 3. UV−vis spectra of cross-linked 12 PBA-terTh film in (a) neutralized state and (b) oxidized state using iron(III) perchlorate as dopant.

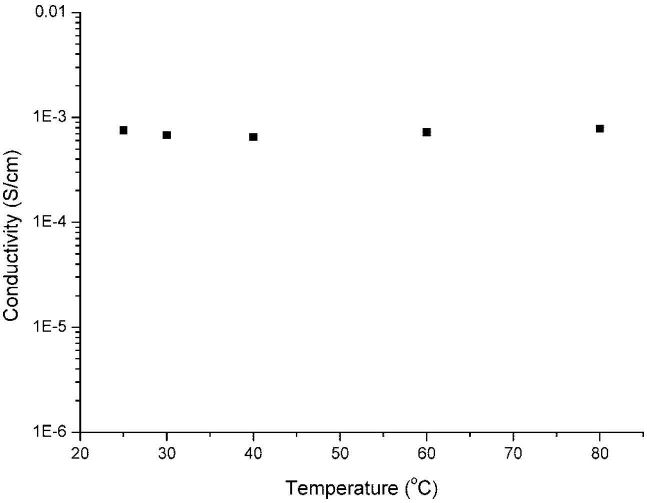


Figure 4. Temperature dependence of the conductivity of $FeCl_3$-doped cross-linked 12 PBA-terTh film.

In conclusion, novel conductive polymer composite with core−shell-like nanostructure was successfully synthesized using 12-armed terthiophene-terminated starburst poly(*n*-butyl acrylate) as precursor. Solid-state coupling among terthienyl groups on the chain ends of the star polymer can be effectively performed by simple oxidative polymerization using $FeCl_3$ as an oxidant to yield a three-dimensional network of oligoterthiophene. The unique core−shell-like structure enables the composite film to possess good conductivity at very low conjugated moiety content. Furthermore, the elastomeric PBA core allows the preparation of a uniform and large-area conductive thin film with notable flexibility and excellent adhesion to a wide variety of substrates.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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