

Synthesis and characterization of polypyrrole-graft-poly(ϵ -caprolactone) copolymers: new electrically conductive nanocomposites

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Abstract

A series of polypyrrole-graft-poly(ϵ -caprolactone) (PPy-g-PCL) copolymers have been synthesized via oxidative copolymerization of pyrrole and pyrrole-end functional macromonomers. Copolymerizations were carried out in tetrahydrofuran at 0 °C using FeCl₃ as the oxidizing and doping agent. Poly(ϵ -caprolactone) rich copolymers (>85 wt.%) were partly soluble in common organic solvents, whereas polypyrrole-rich copolymers were completely insoluble. The composition of the PPy-g-PCL copolymers was determined by Fourier transform infra-red (FTIR) spectroscopy and thermal gravimetric analysis (TGA). By controlling the monomer feed and molecular weight of the macromonomer, graft copolymers across a broad composition range were obtained. Both differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) show that the PPy-g-PCL copolymers phase separate into PPy and PCL rich domains. The electrical conductivity of the nanocomposites increases with the amount of polypyrrole in the copolymer between the value of pure PCL (10^{-12} S/cm) and that of polypyrrole (10 S/cm). Atomic force microscopy (AFM) confirmed the presence of nanophases (15–40 nm) and hence, the preparation of new nanomaterials. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Polypyrrole; Graft copolymers; Nanocomposite

1. Introduction

Electrically conductive copolymers have attracted much attention due to their electrical, electrochemical and optical properties. Among them, polypyrrole is one of the most frequently used in commercial applications due to the long-term stability of its conductivity. Unfortunately, polypyrrole is an amorphous, insoluble and powdery product, which needs to be modified in order to make it as processable as conventional thermoplastics. In this search of manufacturability, the preparation of composites by incorporating polypyrrole and other conducting polymers as a filler in thermoplastics has been extensively studied ([1] and references therein).

More recently the preparation of conductive nanocomposites or nanomaterials based on polypyrrole has been investigated [2]. Actually, conductive nanomaterials would be of great interest for applications in chemical sensors and

nanodevices. In the case of polypyrrole, conductive nanocomposites have been prepared by selective in situ polymerization of pyrrole inside the pores of different type of membranes as well as within the lamellar microdomains of a block copolymer [3,4]. Among the different ways of preparing nanomaterials, block and graft copolymers are a popular class due to their unique morphologies in the nanometer regime. Depending on different parameters such as composition, molecular weight, interaction parameter between blocks and polydispersity, the copolymer self-assembles into spherical, cylindrical or lamellar microdomains [5]. This intrinsic morphology can be used to design new nanocomposites. As an example, Hedrick and coworkers introduced the concept of low dielectric nanoporous materials by preparing nanoporous polyimides by selective thermal degradation of the second constituent of a phase separated polyimide block copolymer [6,7]. The use of block copolymers to prepare conductive nanocomposites is not new. For example, Meijer and coworkers, and Lazzarani and coworkers, have observed organized nanostructures on poly(*p*-phenylene) and poly(thiophene)-based block

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copolymers, respectively [8,9]. The purpose of this paper is to describe the synthesis of polypyrrole-graft-poly(ϵ -caprolactone) (PPy-g-PCL) copolymers and the characterization of these new electrically conductive nanocomposites. To our knowledge this is the first report on the direct observation of polypyrrole nanostructures from pure block or graft copolymers.

2. Experimental

2.1. Materials

The *N*-2-hydroxyethylpyrrole was prepared as reported elsewhere and dried by storing over molecular sieves [10]. The ϵ -caprolactone (99%) (Aldrich) was dried over CaH_2 and used freshly distilled. All other chemicals, pyrrole (98%), FeCl_3 (98%) were purchased from Aldrich and used as received.

2.1.1. Synthesis of α -pyrrole poly(ϵ -caprolactone) macromonomers

In a typical experiment, *N*-2-hydroxyethylpyrrole (0.33 g), ϵ -caprolactone (10 g) and tin octanoate (20 mg) were mixed under dry argon and reacted at 110 °C during 14 h. The polymer was purified by dissolving in toluene and precipitation in cold methanol (yield 90%).

2.1.2. Synthesis of polypyrrole-graft-poly(ϵ -caprolactone) copolymers

Graft copolymers of various compositions were prepared via chemical oxidative copolymerization of pyrrole and α -pyrrole PCL macromonomers using FeCl_3 as oxidizing/dopant and THF as a solvent. In a typical experiment, pyrrole (1.5 g) and macromonomer (1.4 g) were dissolved in 40 ml of THF. To this mixture, 16 g of FeCl_3 were added batch-wise under nitrogen at 0 °C. The reaction was stopped after 20 min by filtration of the product as a black precipitate which was washed three times with methanol and acetone. The product was finally dried under vacuum at room temperature (35% yield).

2.2. Characterization

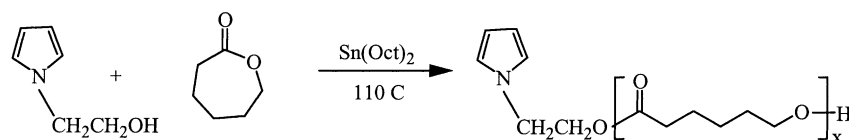
The ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker AM 250 (250 MHz) spectrometer. Size exclusion chromatography (SEC) was carried out on a Waters chromatograph connected to a Waters 410 differential refractometer, using polystyrene of known molecular weight as

the calibration standards. Four 5 μm Waters columns (300 mm \times 7.7 mm) connected in series in order of increasing pore size (100, 1000, 10^5 , and 10^6) were used with THF as elution solvent. Dynamic scanning calorimetry (DSC) was performed in a DSC 2920 MDSC apparatus from TA Instruments at a scan rate of 4 °C/min. Thermal gravimetric analysis were performed in a Perkin-Elmer TGS-2 apparatus at 10 °C/min rate under high purity nitrogen. Infra-red spectra were taken in a Nicolet Magma-IR spectrometer 550. Dynamic Mechanical Analysis were performed using a TA Instruments DMA 983 at 5 °C/min rate. Surface morphology of block copolymer film was obtained by atomic force microscopy, employing molecular imaging PicoSPM operated in non-contact (tapping) mode. Images were gathered at room temperature, in air and using nanosensors microfabricated silicon cantilevers (spring constant of 3 N/m). Scan speed was at one line per second and 512 data points per line. Multiple images were collected for the same area with no observable changes in surface morphology for these particular scanning parameters, indicating that little or no damages were done to polymer film surface. Electrical conductivity was measured by the four-point probe method at room temperature using conventional procedures.

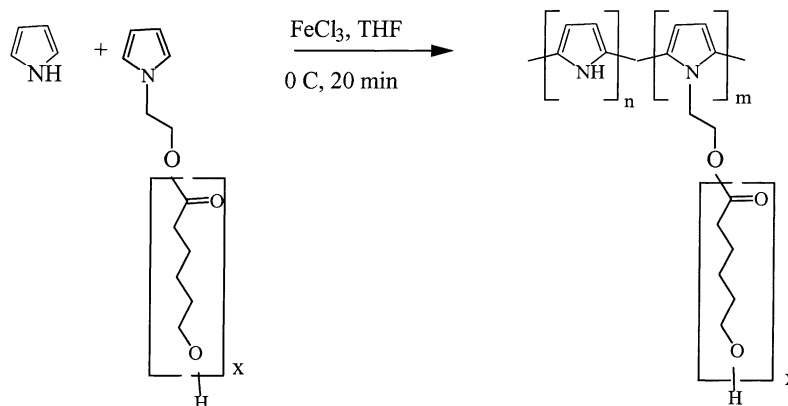
3. Results and discussion

The most versatile and common way of preparing graft copolymers is by copolymerization of small monomers with a macromolecular monomer or macromonomer. This method requires the previous synthesis of the macromonomer or end-functional polymer with the desired polymerizable end group. In this respect, we have recently reported the preparation of a new family of macromonomers functionalized with a *N*-substituted pyrrole end-group. A variety of macromonomers were prepared by the use of pyrrole functional initiators for ring opening (ROP) and atom transfer radical (ATRP) polymerizations from lactones, acrylic, methacrylic and styrenic monomers [11]. The macromonomers used in this study were prepared as shown in Scheme 1 by ring opening polymerization of ϵ -caprolactone as initiated by *N*-2-hydroxyethylpyrrole in the presence of stannous octanoate as catalyst at 110 °C (Scheme 1).

Several reports have described the synthesis of graft copolymers of polypyrrole and polythiophene using a “grafting onto” approach [12,13]. However, this method is limited to compositions very low in polypyrrole (PPy (wt.%) < 30). On the other hand, Toppare and coworkers



Scheme 1.



Scheme 2.

have recently reported the preparation of a variety of polypyrrole graft copolymers by electrochemical copolymerization of pyrrole with different macromonomers [14,15]. However, electrochemically the product is obtained as a thin copolymer film deposited on the electrode which avoids the preparation of materials in a gram scale. In this paper, we have investigated the chemical pathway towards PPy-g-PCL copolymers which allows to work at least in a gram scale and is known for being more versatile in terms of controlling the copolymer composition. Recently, Jérôme et al. reported the electrochemical and chemical synthesis of similar copolymers, but the chemical pathway was not investigated extensively [16]. In our case, graft copolymers were prepared via oxidative copolymerization of pyrrole and α -pyrrole poly(ϵ -caprolactone) macromonomers in THF at 0 °C using FeCl_3 as an oxidizing/doping agent (Scheme 2). The reactions were carried out for 20 min using 2.5 equivalents of FeCl_3 with respect to pyrrole using the conditions reported elsewhere [17]. Due to the cross-linked nature of the polypyrrole segments prepared by this method, the graft copolymers precipitated from solution. The reaction products were recovered by filtration as black–grey powdery materials and washed several times with tetrahydrofuran, water and methanol to remove homopolymer contamination. Because of its insoluble nature, the characterization of the graft copolymers was not possible by classic solution SEC and

NMR techniques. Therefore, FTIR spectroscopy was used as a tool to characterize the copolymers. Fig. 1 shows the FTIR spectra of PPy, PPy-g-PCL copolymer 2b and PCL. Qualitatively, the graft copolymer spectrum shows bands related to both homopolymers which confirms the validity of our synthetic approach toward PPy-g-PCL copolymers. In order to confirm the graft copolymer nature and the validity of our synthetic approach a similar reaction was performed using a non-functional PCL polymer. In this case, no peaks related to the PCL segments were detected in the IR spectrum of the product. This fact indicates the graft copolymer nature of our products.

Furthermore, FTIR can be used as a quantitative tool by using a calibration curve from homopolymer mixtures plotted from the peak areas of two separate bands (band at 1536 cm^{-1} for PPy (ring vibration) and band at 1724 cm^{-1} for PCL ($\text{C}=\text{O}$ vibration)). A series of reactions were carried out varying the pyrrole versus macromonomer ratio as well as the macromonomer molecular weight. The composition of the copolymers was then calculated and the results are shown in Table 1. As a first observation, the composition of the graft copolymers (W_{PCL}) is higher in polypyrrole than the composition in the initial reaction mixture (W_{PCL}). For instance, in order to get 10 wt.% PCL incorporation into the graft copolymer the reaction feed must be at least 50 wt.% in PCL (entry 1b). In this

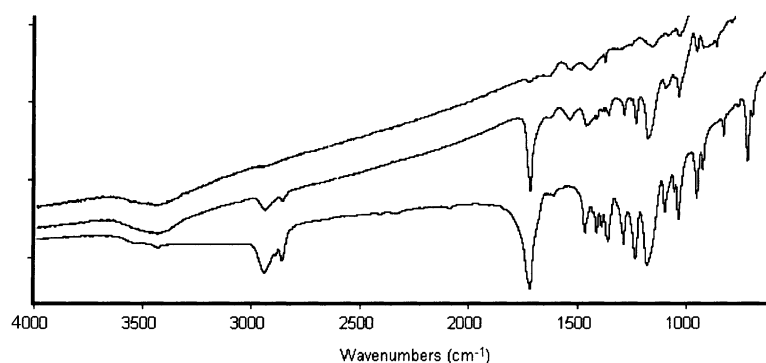


Fig. 1. FTIR spectra of PPy (upper spectrum), PPy-g-PCL 1c (middle) and PCL (lower spectrum).

Table 1
Copolymerization of pyrrole with PCL macromonomers in THF at 0 °C for 20 min^a

Code	Macro-monomer Mn (g/mol)	Yield (wt.%)	W_{PCL}^b	W_{PCL}^c
1a	2000	20	0.25	0.0
1b	2000	40	0.50	0.10
1c	2000	40	0.75	0.29
1d	4500	35	0.75	0.24
1e	20000	30	0.75	0.08
1f	2000	45	0.85	0.39
1g	2000	42	0.90	0.45
1h	2000	50	0.95	0.78

^a [Pyrrole] = 1 M, [FeCl₃]/[Pyrrole] = 2.5.

^b Weight fraction of PCL in the reaction feed.

^c Weight fraction of PCL in the products as measured by FTIR.

case, Entries 1c–e compares similar reaction conditions for macromonomers of different molecular weight. The products are richer in PCL when macromonomers with lower molecular weight are copolymerized, 8 wt.% for 20,000 g/mol, 24 wt.% for 4500 g/mol and 29 wt.% for 2000 g/mol. These two facts correlate with previous observations in the copolymerization of macromonomers, which usually have a disfavored and molecular weight dependent reactivity ratio versus small monomers [18]. Interestingly, graft copolymers across a broad composition range can be prepared by simply adjusting the experimental conditions (monomer feed). For instance, entries 1b, c, f, g and h in Table 1 show a series of graft copolymers prepared using the same macromonomer (Mn = 2000 g/mol) with increasing amounts of PCL, 10, 29, 39, 45 and 78 wt.%, respectively. This can be clearly seen in Fig. 2, which shows a comparison on the thermogravimetric analysis (TGA) of PPy, PPy-g-PCL copolymers 1b, 1c, 1f, 1h and PCL. While PPy shows a residue of 70% weight retention at 500 °C, PCL is completely degraded at that temperature. Accordingly, the graft copolymers show an intermediate behavior where the residue at 500 °C decreases with the increasing amount of PCL in the copolymer.

The electrical conductivity of the graft copolymers is shown in Fig. 3. As expected, the electrical conductivity

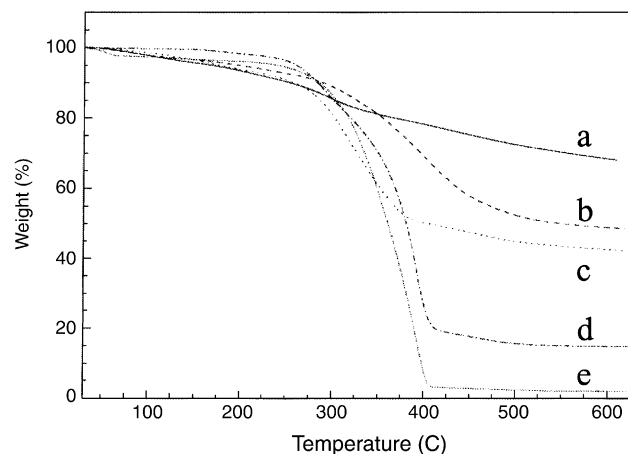


Fig. 2. Thermogravimetric analysis (TGA) curves obtained at 10 °C/min under nitrogen for (a) PPy, (b) PPy-g-PCL 1c, (c) 1f, (d) 1h and (e) PCL.

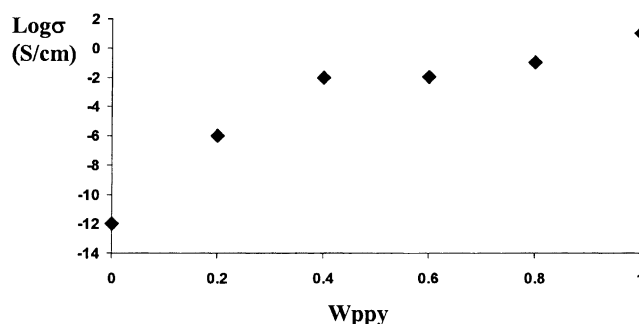


Fig. 3. Conductivity data of the PPy-g-PCL systems as a function of composition.

increases with the amount of PPy in the copolymer between the value of PCL (10^{-12} S/cm) and that of PPy prepared under similar conditions (10 S/cm). From these results, it is not evident the observation of a percolation threshold as observed in other conductive–insulating mixtures.

The phase separation of the graft copolymers was studied by DSC and DMA. Fig. 4 shows the DSC curves for

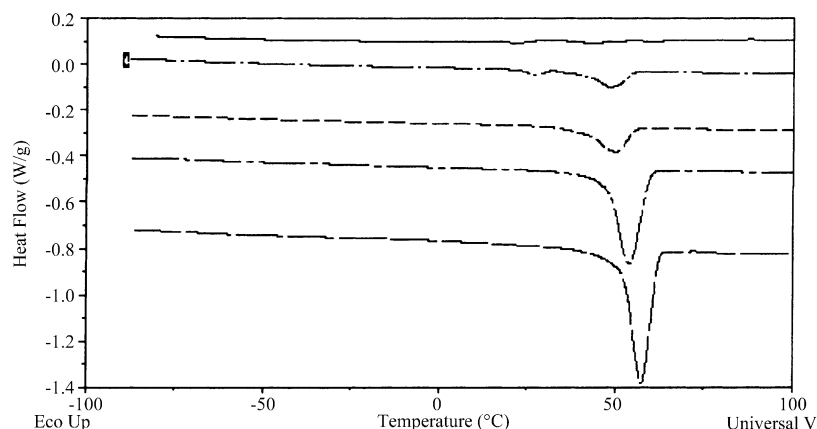


Fig. 4. From top to bottom, dynamic scanning calorimetry curves for PPy, PPy-g-PCL 1c, g, h and PCL.

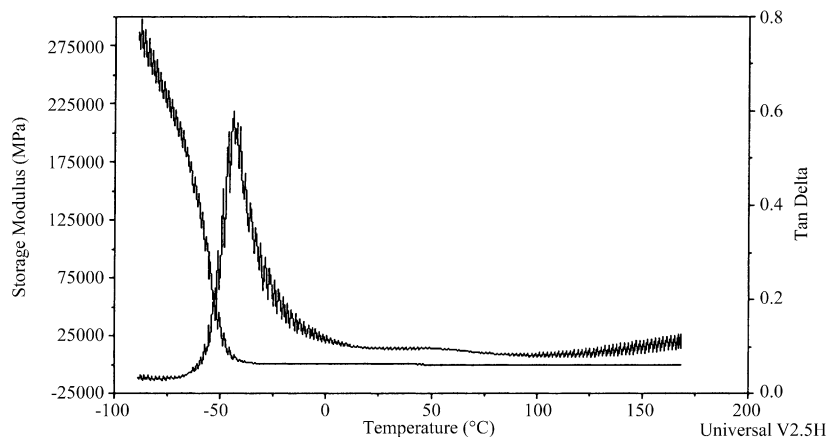


Fig. 5. Dynamic mechanical analysis (DMA) for PPy-g-PCL 1g.

PPy, PPy-g-PCL 1c, g, h and PCL powders. The copolymers show a melting endothermic associated with the crystallinity of the PCL segments. The enthalpy of melting as well as the melting temperature (T_m) decrease with decreasing amount of PCL in the copolymers indicating less crystallinity and perfection of the crystals, respectively. The melting temperature is 65 °C for pure PCL, T_m is 55 °C for copolymer 1h ($W_{PCL} = 0.78$), 50 °C for copolymer 1g ($W_{PCL} = 0.45$) and 48 °C for copolymer 1c ($W_{PCL} = 0.22$) and no T_m is observed for copolymer 1b. Unfortunately, any glass transition temperature is detected by DSC for these copolymers. Although normal for PPy that does not show a defined T_g , we expected to see a glass transition for the amorphous phase of the PCL rich domains, in order to confirm or deny the phase separation. Dynamic mechanical analysis (DMA), which is known as a more sensitive technique than DSC, were performed in the copolymers. As an example, Fig. 5 shows the DMA spectra for copolymer 1g ($W_{PCL} = 0.45$) where a clear transition is observed at -55 °C. This can be attributed to the glass transition of the PCL domains since the value is very close to the T_g of pure PCL (-60 °C). All in all, DSC and DMA results show that the graft copolymers phase separate into PCL and PPy rich domains in all the studied compositions. Inside the PCL domains both amorphous and crystalline phases coexists except at very low PCL contents ($W_{PCL} < 0.20$) where the copolymers are found to be essentially amorphous.

In order to confirm that the size of the domains is in the nanometer regime as expected for graft copolymers, PCL-rich copolymer films prepared by solvent casting of solution-suspensions were studied by AFM. The surface morphology of copolymer 1h ($W_{PCL} = 0.78$) was studied by AFM (Fig. 6). Both topography and tip amplitude images are shown (see horizontal cross-section data). The images showed phase separated microdomains of PCL which constitutes the bright matrix and PPy which constitute the dark elongated structure. The images of the surface show an ordered lamellae type structure. Phase images (data not shown) also exhibited 20 nanometer domains and moreover,

indicated little interaction between polymer and cantilever as evidenced by no phase shifting in the oscillation of the cantilever as compared with the phase of the exciting signal. Unfortunately, this copolymer was the only sample that we could use for AFM imaging due to the poor quality of the remaining films.

To conclude, a series of PPy-g-PCL copolymers have been synthesized via chemical oxidative copolymerization of pyrrole and pyrrole-end PCL macromonomers. The graft copolymers showed microphase separation between the polypyrrole and the polycaprolactone phases leading to the formation of a nanocomposite between electrically conductive PPy and insulating PCL. The electrical conductivity of the copolymers varies from 10^{-6} to 10 S/cm depending on the composition of the graft copolymer. Future work will pursue the preparation of soluble graft copolymers containing other different polymers as grafted materials. Interestingly, due to the increased interfacial area related

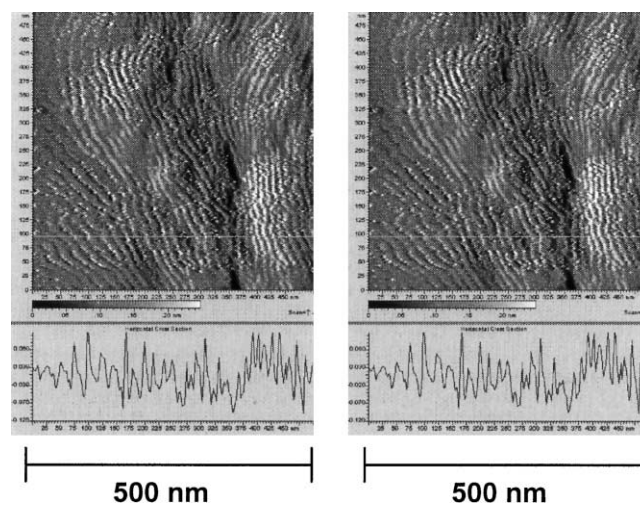


Fig. 6. Atomic force microscopy (AFM) (left image) topography and (right image) tip amplitude images for surface morphology of films of graft copolymer 1h.

with the nanocomposite, these materials are interesting as chemical sensors, interfacial agents and microelectronic applications.

Acknowledgements

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