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Synthesis of New (Pyrrole-g-ε-caprolactone) Copolymers

Christine Jérôme[1], Lucien Martinot[2], Pierre Louette[3], Robert Jérôme[1*]

[1]Center for Education and Research on Macromolecules (CERM),
University of Liège, B6 Sart-Tilman, B-4000 Liège, Belgium
[2]Radiochemistry, University of Liège, B16 Sart-Tilman, B-4000 Liège, Belgium
[3] Laboratoire LISE, Facultés Universitaires N-D de la Paix, B-5000 Namur, Belgium

SUMMARY: Poly-ε-caprolactone end-capped by a pyrrole moiety has been synthesized and successfully copolymerized with pyrrole with formation of new brush copolymers. Copolymerization has been achieved by electrochemical and chemical techniques. Formation of copolymer has been confirmed by various methods including XPS, DSC, TGA, and SEM. The effect of the PCL branches on conductivity, morphology and stability of PPy has been studied.

Introduction

The recent years have witnessed growing interest for conducting polymers because of a wide range of potential applications, e.g. in the design of biomedical sensors1) and drug delivery systems2). Polypyrrole (PPy) is one example of conducting polymer with high conductivity, environmental stability and ease of preparation. However, some deficient properties, such as poor mechanical properties and processability have considerably limited the common use of conducting polymers. Combination of conducting polymers with insulating ones (e.g. polyethylene3), polyimide4), polyvinylchloride5), polycarbonate6)) is an efficient way to alleviate this problem. This general strategy allows materials of improved mechanical properties to be prepared with limited loss in conductivity. Another possible approach of improving the properties of conducting polymers consists of the synthesis of block or graft-copolymers. For instance, pyrrole has been electropolymerized in the presence of poly [(methylmethacrylate)-co-(2N-pyrrolyl) (methacrylate)], and the grafted copolymer formed has the same conductivity as pure PPy with the benefit of a better thermal stability7).

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Poly-ε-caprolactone (PCL) is a synthetic biomaterial used in surgery and sustained drug delivery[8)] because of unique combination of biodegradability, biocompatibility and high mechanical strength. In order to impart these properties to conducting polymers, synthesis of grafted copolymers of pyrrole and ε-caprolactone (CL) has been considered in this paper. Polymerization of CL initiated by aluminum alkoxides is known to be living, and the coordination-insertion mechanism is such that the alkyl group of the initiator is systematically the ω-end group of the chains[9)]. As a result, any functional group (e.g. unsaturation, halogen or tertiary amine) attached to the alkoxide systematically caps one chain-end of the polymer. This characteristic feature has been used in this study to prepare PCL end-capped by a pyrrole unit, thus forming a macromonomer that could be copolymerized with pyrrole.

The availability of pyrrole containing Al alkoxide (**$Et_2Al\text{-}O\text{-}(CH_2)_{11}\text{-}Py$**) is the requirement for the synthesis of ω-pyrrole PCL macromonomer (Py-PCL). Under strictly anhydrous conditions, the ethyl aluminum bonds are inactive in the lactone polymerization, in contrast to the Al-alkoxide bond in which the CL is inserted as result of the acyl-oxygen cleavage of the ring. This mechanism maintains the growing PCL chain attached to Al through an alkoxide, the second end-group being an ester carrying the radical of the alkoxide initiator[10)] i.e. **$(CH_2)_{11}\text{-}Py$**. The final hydrolysis of the propagating species releases a hydroxyl end-group as shown in Figure 1.

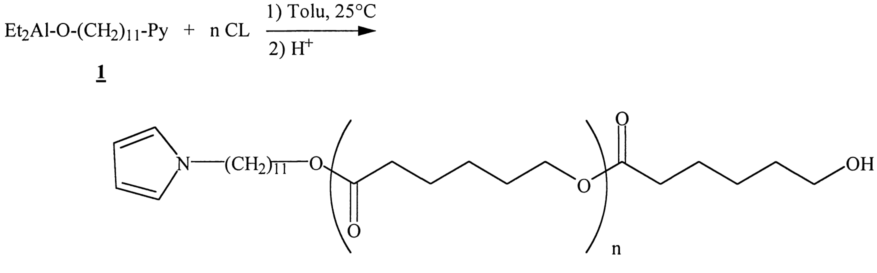


Fig.1: preparation of the macromonomer

The aim of this paper is to report on the macromonomer synthesis (Figure 1) and chemical and electrochemical copolymerization of this macromonomer with Py in order to form brush-like grafted copolymer. The main characteristics of the parent copolymers will be studied, mainly composition, electrochemical and thermal behavior, morphology and conductivity. Attention will be paid to the thermal stability of the copolymers and their stability towards acidic aqueous solutions.

Experimental

Materials

CL was dried over calcium hydride for 48 hours at room temperature and distilled under reduced pressure just before use. Triethylaluminum was dissolved in dry toluene and the solution concentration was determined by complexometric titration of Al by EDTA. Toluene was dried by refluxing over CaH_2. N-Pyrrole-11-undecanol was prepared by adding bromo-11-undecanol (Aldrich) to pyrrolyl potassium salt$^{11)}$. It was dried by repeated toluene azeotropic distillation just before use.
$FeCl_3$ and $LiClO_4$ were used as received. Tetrahydrofurane was refluxed over the purple benzophenone Na complex.

Initiator preparation

The diethyl aluminum alkoxide (**1**) was prepared by reaction of triethylaluminum with the N-pyrrol-11-undecanol. 4.28 mmol of alcohol in 40 ml toluene was slowly added into a carefully dried Pyrex flask containing an equimolar amount of $AlEt_3$ in 15 ml of toluene. The reaction proceeded under nitrogen and vigorous stirring at room temperature until the evolution of ethane stops.

Macromonomer synthesis

CL polymerization was carried out under stirring at room temperature for 4 hours in toluene solution in a flask previously dried and purged with nitrogen. The monomer / initiator molar ratio was fixed at 43, so targeting chains of Mn of 5000, since for living polymerization, the molecular weight is dictated by the monomer/initiator molar ratio ($Mn=[CL]_0.M_{CL}/[Al]$) at 100% conversion. The reaction was stopped by adding a tenfold molar excess of 2N HCl solution with respect to Al.

The catalyst residue was removed by repeated extraction with an aqueous EDTA solution (0.1M), and the polymer solution was washed with water up to neutral pH. Part of toluene was distilled off, and the polymer was recovered by precipitation into heptane with 80% of conversion. It was finally dried for 24 hours at room temperature under reduced pressure.

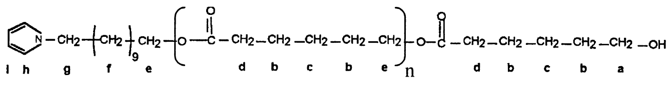
Characterization techniques

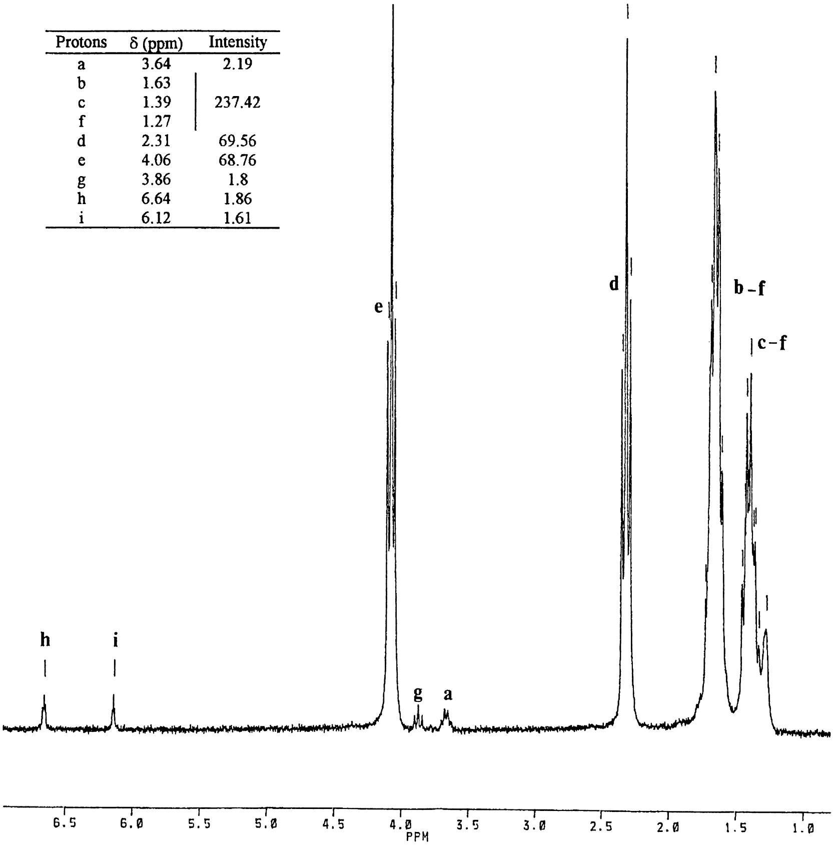
^{1}H-NMR spectra were recorded with a Brucker AM 250 apparatus in $CDCl_3$ as solvent and TMS was used as internal standard. Size Exclusion Chromatography (SEC) was performed in THF at 40°C using a Hewlett-Packard model 1090 liquid chromatograph equipped with columns HP PLgel 5μm being calibrated with polystyrene standards.
Differential scanning calorimetry (DSC) was carried out under nitrogen atmosphere at a heating rate of 10°C/min with a DSC Thermal analyst 2100 (TA Instrument Inc., New Castle, DE, USA). Thermal stability was analyzed by thermogravimetric analysis (TGA) (TA Instrument), under the same conditions as used for DSC. Scanning electron microscopy (SEM) was performed on an Explorer Scanning Electron Microscope. Electrochemical experiments were carried out with the EG&G PAR (M273A) potentiostat/galvanostat. X-ray Photoelectron Spectra (XPS) were recorded with a SSX-100 spectrometer (Surface Science Instrument). Resistance was measured with two probes separated one apart each other by 0.5 cm. The electrode contacts were improved by using Ag paint such that their contribution to the measurement could be neglected.

Results and discussion

Macromonomer characterization

^{1}H-NMR spectroscopy confirms the end-functionalization of PCL by the $(CH_2)_{11}$-Py group (Figure 2). The experimental molecular weight has been calculated from the relative intensity of the signals of protons **h** (6.64 ppm) and protons **e** (4.06 ppm). This calculated value (4000) is smaller than expected (5000) in agreement with the uncompleted monomer conversion. The same value is calculated in reference to the protons **a** characteristic of the hydroxyl end-group (3.64 ppm) and protons **e**. This agreement supports that PCL is capped by as many Py groups at one chain end as hydroxyl groups at the second chain extremity, consistently with the expected structure (Figure 1). Moreover, the molecular weight distribution is narrow (Mw/Mn=1.2), as measured by SEC calibrated by PSt standards.





Protons	δ (ppm)	Intensity
a	3.64	2.19
b	1.63	237.42
c	1.39	
f	1.27	
d	2.31	69.56
e	4.06	68.76
g	3.86	1.8
h	6.64	1.86
i	6.12	1.61

Fig. 2: ^{1}H-NMR spectrum of the Py-PCL macromonomer, analyzed after hydrolysis of the living polymer initiated by Py-$(CH_2)_{11}$-O-$AlEt_2$.

Electrochemical copolymerization.

Cyclic voltammetry onto Pt in THF containing 0.01M Py-PCL macromonomer and 0.1M $LiClO_4$ shows that Py-PCL does not (homo)polymerize under these conditions. Only the reaction of the solvent is observed. The same conclusion holds when the concentration of Py-PCL is two times increased (0.02M). When Py is added to the solution (0.1M), the electropolymerization starts at 0.6V/Pt (Figure 3). Thus the potential at which Py is polymerized is shifted by 0.15V in the presence of Py-PCL. Adsorption of Py-PCL onto the electrode upon polarization might delay the pyrrole diffusion to the electrode and thus the polymerization. Nucleation phenomenon, characteristic of the growth of conducting polymers is observed by the crossing-over of the curve during the first cycle of the potential (Figure 3), and the increase of the current intensity is observed during the second potential scanning. A bright black film is deposited onto the electrode surface as the result of electrolysis at E=0.8V/Pt for t= 6000s. The charge increases linearly with time, the slope being slightly smaller than for PPy synthesis.

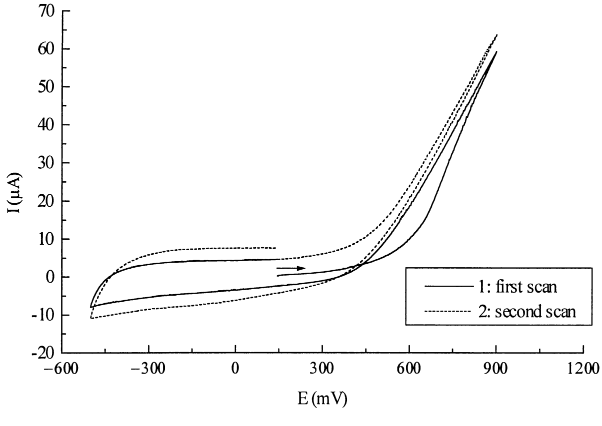


Fig 3: Cyclic voltammogram onto Pt in THF solution containing Py (0.1M), Py-PCL (0.01M) and $LiClO_4$ (0.1M), (v=50mV/s)

Various Py/Py-PCL molar ratios from 0.75/1 to 10/1 have been used in copolymerization experiments, leading to formation of conducting films. Only small change has been noted in the chronoamperogram, i.e. a small decrease in the current when the relative content of Py-PCL is increased. The Py-PCL macromonomer left unreacted in the electrolysis bath has been recovered by precipitation and analyzed by SEC and ^{1}H-NMR. Both the molecular weight and the molecular weight distribution are unchanged, and ^{1}H-NMR spectrum confirms the stability of the Py-PCL during the electrolysis.

After electrolysis (E=1V, t=2400s), films have been carefully rinsed with THF, dried and analyzed by XPS in order to confirm that macromonomer has been actually copolymerized with pyrrole (Table 1). Although the Py content of the comonomer feed is increased by a factor three in the bath, the content of the macromonomer in the film is increased by 1.5. One explanation for this unexpected observation could be the more important formation of soluble oligomers when the Py content is low in the reaction medium, which leads to a decrease in the PCL amount measured on the insoluble part of the copolymer remaining on the electrode surface.

Table 1: XPS analysis of Py-g-CL copolymers prepared by electrochemistry.

Electrolytic bath composition Py/Py-PCL mol ratio	Film composition Py/Py-PCL mol ratio	Film composition Py/CL Monomer unit ratio
3.6/1	1/0.08	1/3
7/1	1/0.11	1/4
10/1	1/0.13	1/4.5

The relative area of the C, N, and O peaks confirms that Py-g-CL copolymer has been formed. Figure 4 shows the C1s peak for two Py-g-CL copolymer films of increasing Py-PCL content. The peak at higher binding energy typical of the C atom of the carbonyl increases expectedly in parallel.

The morphology of the films is influenced by the PCL branches of the copolymer. Figure 5 compares the morphology for pure PPy and for Py-g-CL copolymer prepared under the same experimental conditions (E=1V, Qs=50mC, $LiClO_4$ 0.1M, Py 0.1M, THF). At low magnification, the surface of the Py-g-CL copolymer is smoother than PPy. This effect has also been observed when a polymeric counter-ion is inserted in PPy such as polystyrene sulfonate$^{12)}$.

Higher magnifications show a rather uniform distribution of PPy nodules on the surface of PPy accordingly with the classical nucleation and growth mechanism for the formation of this polymer leading to a cauliflower-like morphology.

In contrast, few large PPy nodules of various dimensions that might be agglomerates of smaller particles are observed on the copolymer. The insertion of the PCL component disturbs the growth of the nodular PPy making the PPy nodules more interdependent.

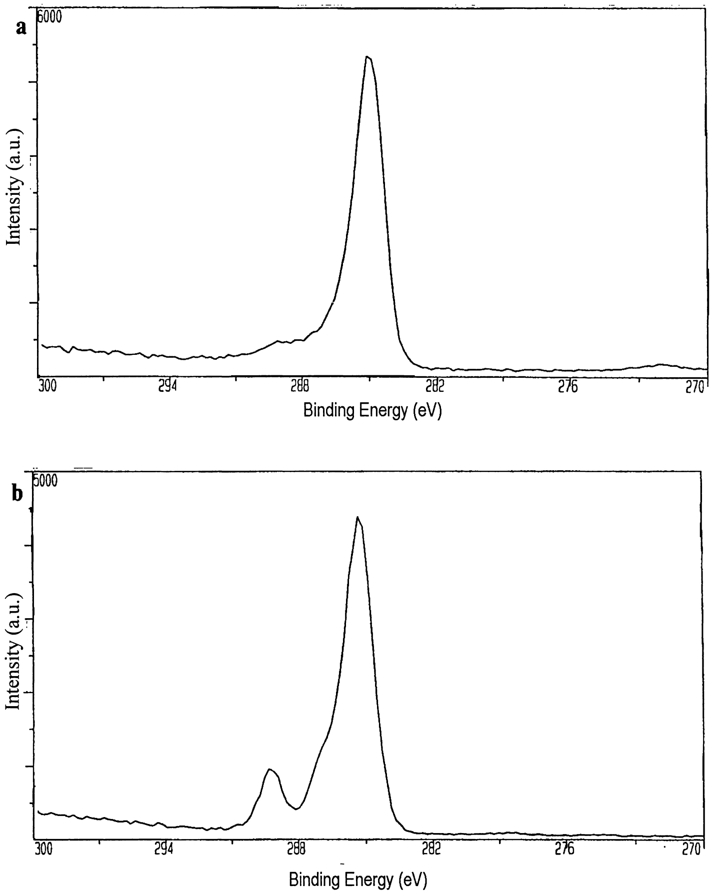


Fig. 4: C 1s XPS spectra for the electrochemically synthesized Py-g-CL copolymers of various compositions
a. Py/CL:1/2.5 b. Py/CL:1/4

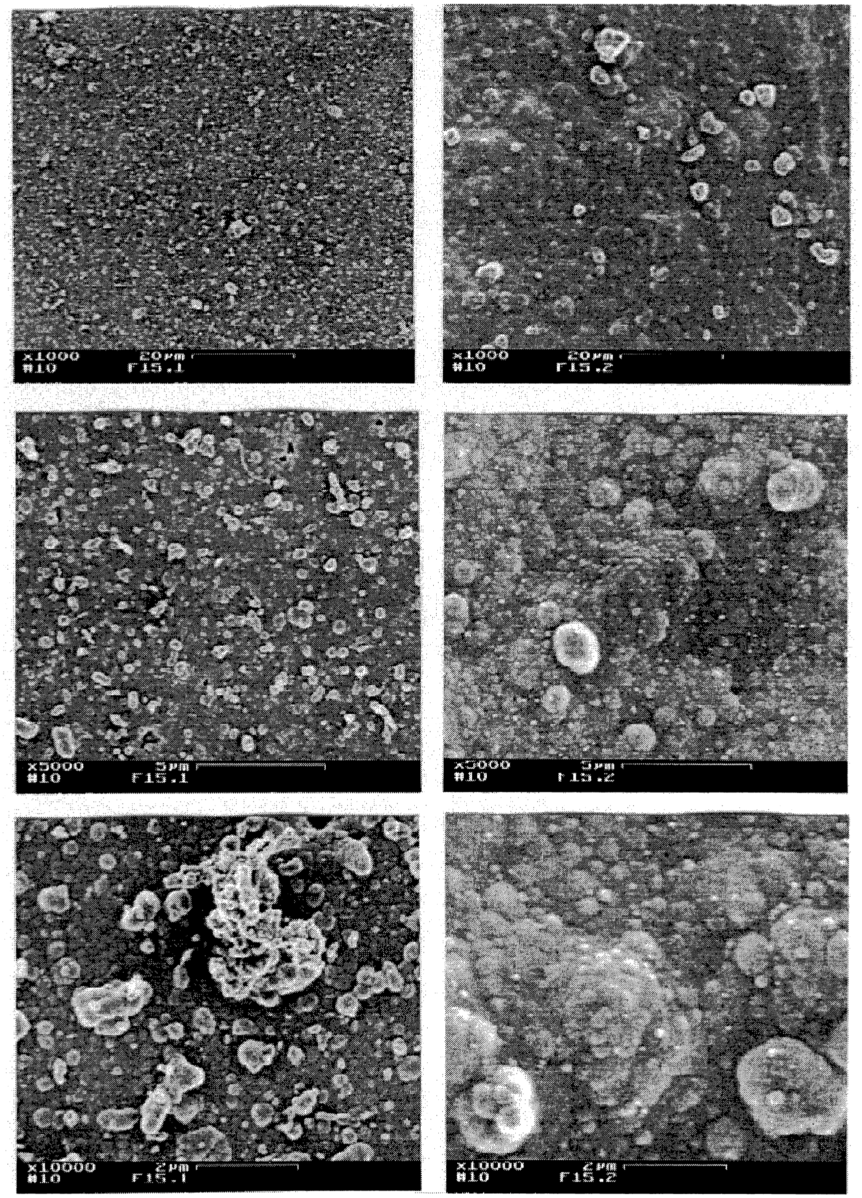


Fig. 5: SEM observation of the morphology of electrochemically synthesized films
Left. PPy Right. Py-g-CL copolymer

Resistance of peeled Py-g-CL copolymer films (l = 0.4 cm, L = 0.5 cm, Qs = 10C) has been measured in the range of 200 to 700Ω which is comparable to pure PPy films.

Chemical copolymerization

Copolymerization of Py and Py-PCL macromonomer has also been achieved by $FeCl_3$ in THF. A solution containing 1.25g Py-PCL (0.6 mmol) and 0.2 ml Py (3 mmol) in THF (100 ml) has been slowly added to 3.12g of $FeCl_3$ dissolved in THF (250 ml). The reaction mixture has been let to react for 4 hours at room temperature. The black powder formed has been separated by filtration and carefully washed with THF and $CHCl_3$, respectively, until these solvents remain non-colored. 1g of insoluble material has been collected after drying under vacuum at 40°C.

This insoluble black powder has been analyzed by XPS, the conclusion being that nitrogen, thus no PPy is detected. Similarly, the chlorine counter-ion of PPy is unobserved. The analysis of the C 1s peak shows a shift to higher energy compared to the electrochemically synthesized Py-g-CL copolymer films, indicating the absence of aromatic carbons. This C1s peak is thus essentially characteristic of PCL. The insolubility and the black color of the powder are the indirect signature of PPy. Therefore, we suppose that the PCL component of the copolymer migrates to the surface and is preferentially detected by the XPS in the surface layer of 5 to 10 nm, masking the underlying PPy component.

Elemental analysis has then been carried out on this sample. This technique allows the detection of the nitrogen from the PPy component leading to a copolymer composition of Py/CL=1/9. The chemical copolymerization leads thus to more important incorporation of the macromonomer compared with the electrochemical synthesis. This can be understood probably, by the better homogeneity of the medium used for the chemical synthesis. The electrochemical technique leads to the comonomers consumption at the electrode surface exclusively and the refeeding of the vicinity of the electrode by the comonomers depends on the diffusion rate of the two comonomers in the electrochemical bath. Since the macromonomer has a smaller diffusion coefficient than Py, which is not a polymer, the Py concentration at the electrode surface should be more favorable than the one of the macromonomer leading to a decrease in the macromonomer incorporation in the copolymer.

DSC profiles have been compared for pure PPy, for the Py-PCL macromonomer and for the Py-g-CL copolymer. While PPy does not show any specific transition between -50°C and 100°C, Py-PCL shows a well-defined melting peak at 57°C characteristic of PCL. The Py-g-CL copolymer also shows an endotherm, although shifted to lower temperature (36°C) and showing a shoulder on the high temperature side (Figure 6). This modification in the DSC profile of the copolymer more likely indicates that crystallization of PCL is perturbed by the PPy component resulting in less stable crystallites.

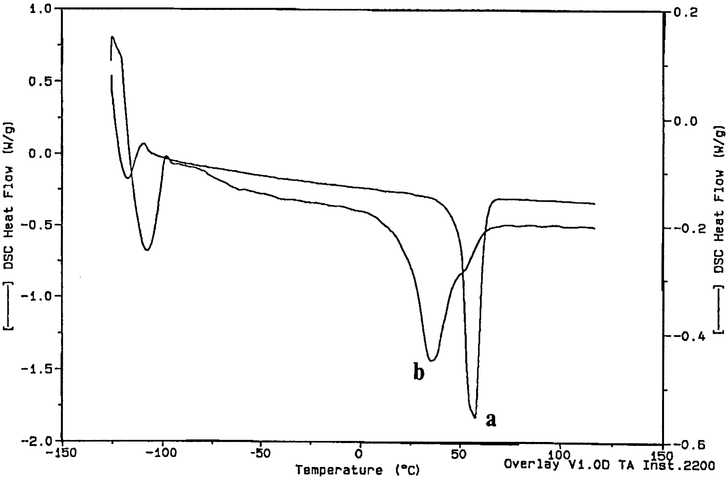


Fig. 6: DSC thermograms of the Py-PCL macromonomer (a) and the chemically prepared Py-g-CL copolymer (b)

TGA of the same samples has also been carried out under nitrogen. Pure PPy starts to degrade at 300°C, the major degradation being observed at 400°C. A residue of 35wt% is left at 700°C. The Py-PCL macromonomer shows quite a comparable profile except that no residue is observed at 700°C. The Py-g-CL copolymer is degraded at 420°C temperature at the peak maximum leading to a residue of 10wt% at 700°C (Figure 7). It is thus quite a problem to determine the Py/CL composition of the copolymers from the degradation profiles. The solid residue observed when the sample contains PPy is attributed to iron incorporated in the conducting polymer as part of the negatively charged counter-ion (complex with chloride). So the solid residue left at 700°C by the copolymer is additional (indirect) evidence that doped PPy is actually combined with PCL.

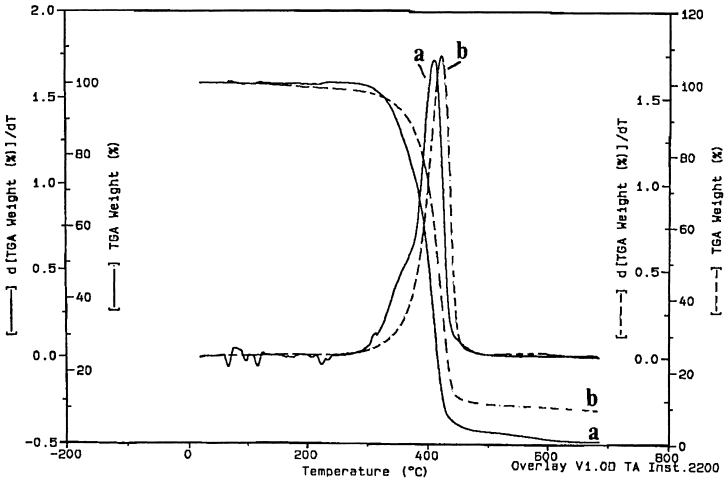


Fig. 7: TGA of the Py-PCL macromonomer (a) and the chemically prepared Py-g-CL copolymer (b)

In sharp contrast to the electrochemically-synthesized copolymer, the copolymer formed by $FeCl_3$ is insulating, in accordance with a higher amount of insulating PCL in the copolymer. Since the PCL is soluble in THF, we can imagine that kind of micelles with a PPy core and PCL shell are formed. After drying, if the PPy content is low, a continuous PPy phase is not achieved leading to an insulating copolymer.

Stability against hydrolysis

Both chemically and electrochemically prepared copolymers have been dipped in 1M HCl aqueous solution at 60°C for 15 days in order to hydrolyze the PCL component. After washing with water, the treated samples have been analyzed by SEM. In the case of the chemically synthesized Py-g-CL copolymer, the formation of pores is the clear signature of the PCL degradation. XPS measurements still detect only the PCL component, the PPy cores being probably removed simultaneously to the PCL degradation.

In the case of the electrochemically prepared film, the Py/CL monomer unit ratio is decreased by the HCl treatment from 4/1 to 2/1. Pores are also observed as result of the removal of PPy agglomerates.

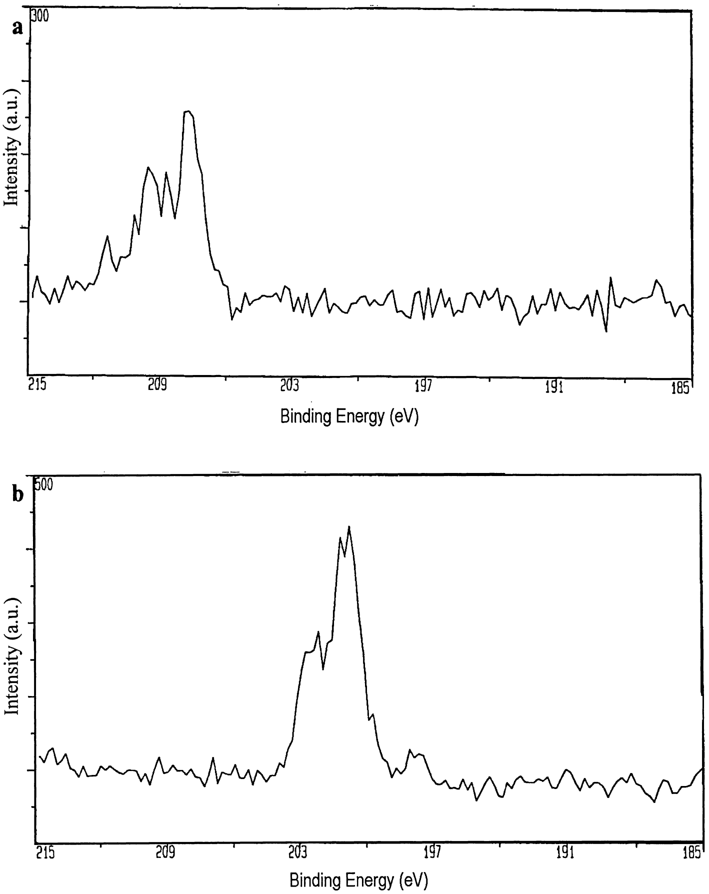


Fig. 8: Cl 2p XPS spectra of the electrochemically synthesized Py-g-CL copolymer film
a. After synthesis b. After dipping in HCl solution

It is worth noting that the Py-g-CL copolymer has been electropolymerized in $LiClO_4$, and accordingly contains ClO_4^- anions. The HCl treatment results in the complete extraction of the ClO_4^- anions, which are replaced by Cl^- anions. Indeed, the Cl 2p peak is observed at 208 eV (ClO_4^- anions) for the pristine Py-g-CL film and at 198 eV (Cl^- anions) after dipping in HCl (Figure 8).

The copolymer is thus permeable to ions and the counter-ion of the PPy component remains easily exchangeable. All these conclusions are valid in the limits of the XPS analysis, so that it is not granted that the anionic exchange occurs through the whole thickness of the film.

Conclusions

Synthesis of pyrrole N-substituted by a long chain alcohol is a suitable precursor to initiate the caprolactone polymerization, so leading to PCL end-capped by Py, i.e. a macromonomer for the synthesis of Py-g-CL copolymer.

Modification of PPy by the electrochemical grafting by PCL chains has no important effect on the conductivity. The film surface appears to be smoother, and the counter-ion of the PPy component can still be exchanged at least in the surface layer.

Chemical copolymerization (by $FeCl_3$) leads to insulating material due to higher PCL content. TGA analysis shows that the thermal stability of the copolymer remains comparable to that one of pure PPy. According to DSC, the PCL crystallization is perturbed by the PPy component. PCL grafts of higher molecular mass is expected to improve the crystallization.

The improvement of the mechanical properties that has been qualitatively shown by this preliminary study (the copolymer prepared electrochemically has good film forming properties compared to polypyrrole, and the chemically prepared copolymer is less friable than PPy) will be quantified in the future.

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