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Polypyrrole Dispersions on Poly(methyl methacrylate)-blok-Poly(acrylic acid) Core-shell Latex

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Abstract

Poly(methyl methacrylate)-blok-poly(acrylic acid) (PMMA-b-PAA) core-shell latex has been prepared by hydrolysis of poly(ethyl acrylate) blok in poly(methyl methacrylate) blok poly(ethyl acrylate) which was prepared using cupper mediated ATRP technique. Pyrrole was polymerized oxidatively on the PMMA-b-PAA core-shell latex forming polypyrrole nanoparticles. Presence of the carboxylate groups on the core-shell latex provides stable dispersions. Resulting polymers were characterized by spectroscopically, electrochemically and four point-probe conductivity.

Keywords: polypyrrole, nanoparticles, core-shell latex, oxidative polymerization

1. Introduction

Polypyrrole (PPy) is one of the most widely studied conducting polymer because of its ease of synthesis, stability in the oxidized state and useful electrical and optical properties for technological applications [1,2]. The most important problem with the applications of PPy is its solubility in the oxidized form. To overcome this problem, pyrrole has been polymerized oxidatively in the presence of anionic polymers [3,4,5].

In this respect, the new emerging technique core-shell latex polymers offer possibility of preparing a nano-size dispersions of insoluble PPy [6]. Efficiency of the core-shell latex particles has also been demonstrated in preparing fine metal dispersitions. This interesting methodology seems to be applicable for stabilization of some condensation polymers in future.

In this study, poly(methyl methacrylate)-blok-poly(acrylic acid) (PMMA-b-PAA) core-shell latex has been prepared by hydrolysis of poly(ethyl acrylate) blok in poly(methyl methacrylate) blok poly(ethyl acrylate) which was prepared using cupper mediated ATRP technique. Then, pyrrole was polymerized oxidatively on the PMMA-b-PAA core-shell latex forming polypyrrole nanoparticles in the solution. Presence of the carboxylate groups on the core-shell latex provides stable dispersions.

2. Experimental

All chemicals were used as received from Aldrich Chemical without further purification.

Poly(methyl methacrylate)-blok-poly(acrylic acid) (PMMA-b-PAA) core-shell latex has been prepared by hydrolysis of poly(ethyl acrylate) blok in poly(methyl methacrylate) blok poly(ethyl acrylate) which was prepared using cupper mediated ATRP technique [7]. GPC traces of the first blok indicates M_n: 33.000 Da's with 1.15 polydispersity. M_n of the final blok copolymer was 57.000 having 1.23 overall polydispersity. 10 grams of this polymer was dissolved in 30 mL dioxane and 20 mL of 30% H_2SO_4 solution was added portionwise to the mixture while refluxing. By this way polyethylacrylate blok were hydrolysed to give PMMA-b-PAA. Degree of hydrolysis was checked by conductometric titration of the polymer in acetone-water (1:1) solution and found as 14.45 mmol g^{-1}. This result is in good agreement with the predicted one from GPC.

Pyrrole was oxidatively polymerized in the presence of PMMA-b-PAA core shell latex in THF:H_2O (1:4) mixture. Oxidation of pyrrole was performed by using hyrogen peroxide which was 2.33 times of monomer, and the PMMA-b-PAA was kept as 0.4 times of pyrrole concentration. Polymerization solution was vigorously

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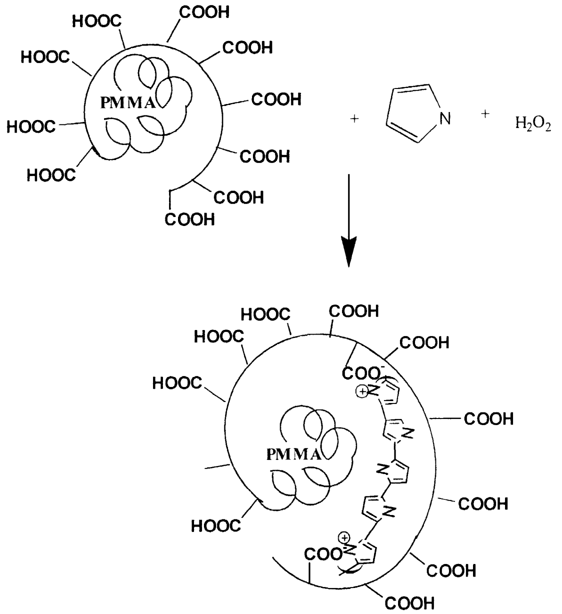
stirred with a magnetic stirrer and the kinetics of the polymerization was followed with a Shimadzu 160A UV-visible spectrophotometer. Polymer films were casted by spin coating on the Pt button electrode for electrochemistry and on ITO coated glass substrates for spectroelectrochemistry from the resulting polymer solution. Electrochemistry and spectroelectrochemistry of the polymers were performed in 0.1 M $LiClO_4$/PC where the resulting polymer was not soluble.

3. Results and Discussion

In the FT-IR spectra of the hydrolyzed product of PMMA-b-PEA, the broad carbonyl stretching vibration shifts from 1714 cm^{-1} to 1640 cm^{-1} due to hydrolysis yielding carboxyl functions. Carbonyl groups of the PMMA segment in the same region has been broadened with the new band emerging. Also broad OH stretching vibration centered 3400 cm^{-1} is an additional evidence for the formation of carboxyl groups in the hydrolysis product. Conductometric titration of 0.105 g hydrolyzed polymer sample in presence of 30 mL of 0.049 M NaOH yields 22.4 mL of 0.05 M HCl consumption indicating 10.45 mmol carboxyl function per gram of the polymer. This result implies that the number of acrylic acid units in the block copolymer is 4.22 per MMA unit. Since molecular weight of the PMMA segment is 37.000 (MwD = 1.23) molecular weight of the hydrolyzed block copolymer is found as 150.000.



Scheme 1. Stabilization mechanism of PPy particles in solution.

Polymerization of the pyrrole (10^{-2} M) was performed oxidatively with hydrogen peroxide in the presence of poly(methyl methacrylate)-blok-poly(acrylic acid) (PMMA-b-PAA). Amount of the PMMA-b-PAA was selected as the amount of carboxyl groups to be 40% of the pyrrole units. Positively charged (oxidized) short chain PPy particles are stabilized with the negatively charged carboxylate groups on the PMMA-b-PAA backbone in the solution without precipitation. Stabilization mechanism of the PPy particles can be depicted in Scheme 1.

The solution was followed with the UV-vis spectrophotometer for 3 hours starting form the beginning of the polymerization (See Figure 1). A linear and sharp increase in time was observed at the wavelength of 470 nm indicating that the soluble and charged PPy particles are suspended by the carcoxylate groups in the PMMA-b-PAA. It is surprising that there is no absorption at higher wavelengths than 470 nm and the spectrum is completely clear after 700 nm. The very well defined and sharp peak observed at 470 nm indicates that molecular weight of the PPy particles have a narrow distribution. Since the molecular weight of the PPy nanoparticles is not high enough (low conjugation), the polymer films show relatively low conductivities, 10^{-2} Scm^{-1}, measured with four-point probe technique.

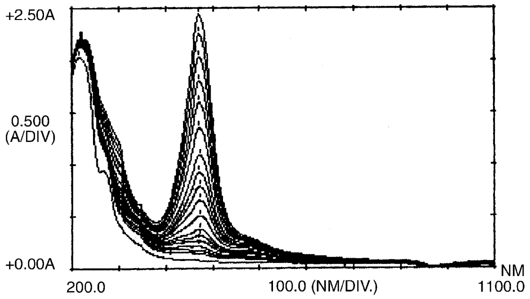


Figure 1. Uv-visible spectrum of the solution during the polymerization.

Cyclic voltammogram of thin PPy films prepared from the final polymerization solution on the Pt button electrode have shown well defined and reversible redox processes at the scan rates between 50 and 500 mV s^{-1} in 0.1M $LiClO_4$/PC. $E_{1/2}$ of the polymer was found as +0.26 V *vs.* SCE. Scan rate dependence of the anodic and cathodic peak currents show a linear dependence as a function of the scan rate. Note that the ability to be switched reversibly in a non-diffusion limited process at scan rates as high as 500 mV s^{-1} is rather unusual for conducting polymers and may stem from the thickness and porous structure of the polymer films.

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