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Preparation and characterization of new optically active poly(*N*-acryloyl chloride) functionalized with (*S*)-phenylalanine and pendant pyrene

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Abstract

The synthesis and characterization of the poly(*N*-acryloyl chloride) derivatives containing amino acid, carboxyl groups and pyrene in the side chain of the backbone introduced by a post-modification with suitable compounds are reported. Alkaline hydrolysis of the ester groups in poly(*N*-acryloyl (*S*)-phenylalanine benzyl ester-acrylic acid-acryloyloxymethyl-pyrene) (PAcPheBz-Py) or its reducing with H_2 in the presence of Pd/C (10%) was carried out to prepare terpolymers with free carboxyl groups (PAcPhe-Py1, PAcPhe-Py2), whose structure and composition are similar. Investigation of such structures by the fluorescence spectroscopy indicates a clear dependence of the fluorescence on the polymer structure, the solvent nature, temperature and pH, with a significant increasing of the monomer emission upon addition of CH_3OH to the PAcPhe-Py1 solution in THF. Varying the composition and the pH of the debenzylated polymer solution, a conformational change reflected through increasing and decreasing of the fluorescence intensity of the side chain fluorophore was evidenced. Also, the sensing capability of the above pyrene-polymers determined by measuring the fluorescence quenching suggested that these acrylate analogues could find practical applications for detection of amine molecules.

Keywords: Poly(*N*-acryloyl (*S*)-phenylalanine-acrylic acid-acryloyloxymethyl-pyrene); Fluorescence; Diethylaniline quencher; Quenching kinetic

1. Introduction

In recent years, the incorporation of α-amino acids into synthetic polymers has generated considerable interest, because it can lead to new biomaterials with a wide range of properties that can be easily modulated by varying the components in the building block of the macromolecular backbone during synthesis [1–5]. Examples of amino acid-derived organic polymers on the basis of (co)polyacrylates, polyisobutylenes, polyurethanes, polyacetylenes or hydrogels have been developed for applications that include controlled drug delivery systems, affinity based separators and optobioelectronic devices [6–11]. The most materials can be obtained through direct polymerization of vinyl monomers carrying (*S*)-amino acid moieties in the side chains [8,12–15] or reacting amino acid diesters functionalized with suitable monomers [10,16–19]. This latter approach was successfully applied in preparing of polyesteramides and polyurethanes. Alternatively, the amino acid sequences were covalently attached, for example, on a polyurethane backbone by a post-modification of the precursor that offers an opportunity to introduce a variety of functions useful in promoting of favorable cell-polymer interactions [20–22]. When methacrylamides with and without (*S*)-amino acid in the side chains and/or *N*-(meth)acryloyl (*S*)-amino acids were (co)polymerized, novel optically active polymers were obtained [3,12,23], for which the relationship between the polymer structure, properties and conformational changes was interpreted in terms of molecular architecture and contribution of the chiral monomers. With the aiming a deeper insight into this aspect, it appeared of interest to check whether the replacement of leucine/glycine by phenylalanine in the forementioned poly(acryloyl chloride), could produce analogous chiroptical effects as clear indicative of significant conformational homogeneity of the polymeric chains. Additionally, the presence of luminescent fluorophore on the same backbone, like pyrene rings directly linked through the ester group to the acrylic system, would create the

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possibility of synthesizing optically active and photo luminescent polymers potentially suitable for applications in biology, biomedicine, analytic techniques and optical devices. Moreover, in the light of new micro(nano)structured materials, the fluorescence technique provides a particularly useful tool for studies of microscopic dynamics and conformation of the polymers [24].

Our group has recently reported a number of new bio(photo)polyurethanes with biologically active sequences as dipeptide [25], hydroxamic acids [26], ammonium/pyridinium groups [27] in tandem with the study of pyrene-, stilbene-, triazene polymers [28–33] and azobenzene ionomers [34,35]. In the current work, we presented a first study on the synthesis and structure of poly(*N*-acryloyl chloride) modified with phenylalanine benzyl ester and pyrene methanol, accompanied of a fluorescence quenching study. To test the behavior in solution of the poly(*N*-acryloyl phenylalanine benzyl ester-acrylic acid-acryloyloxymethyl-pyrene), including its self-assembly ability, the synthesized polymer was converted into the corresponding acid derivatives that could be further used as a macromolecular support and carrier for drugs or in chemosensor applications.

2. Experimental

2.1. Materials

All chemicals (Aldrich) were used as received without purifications.

2.2. Synthesis

(*S*)-*phenylalanine benzyl ester tosylate* (*PheBzTos*) was prepared by the condensation of (*S*)-phenylalanine (10 g, 0.06 mol) with benzyl alcohol (16.36 g, 0.15 mol) in toluene and in the presence of *para* toluene sulfonic acid (11.46 g, 0.06 mol). The reaction mixture was heated to reflux, the formed water being collected in a Dean Stark trap for about 5–6 h. The solution was diluted with diethyl ether (500 mL) and the resulting precipitate was collected on a filter, and then recrystallized from methanol/diethyl ether (1:5, v/v).

^{1}H NMR, PheBzTos in $CDCl_3$ (δ, ppm): CH_3 from tosylate, 7.25 and 7.15 (m, 10H, aromatic protons from Phe and phenyl of benzyl group), 4.95 (q, –COO–C<u>H</u>$_2$–C_6H_5) 4.28 (m, <u>CH</u>–COO–CH_2–C_6H_5 from Phe), 3.25 (m, CH_2–C_6H_5 from Phe), 2.25 (s, CH_3 from tosylate).

FT-IR, PheBzTos (cm^{-1}): 3304 (NH), 1734 (lactame), 1699 (C=O ester), 1662 (amide I), 1545 (amide II), 1287 (C–O, ester).

Poly(*acryloyl chloride*) was obtained using a conventional radical polymerization of acryloyl chloride (10 g, 0.11 mol) in dioxane (40 mL) in the presence of AIBN (2‰). The homopolymerization of acryloyl chloride was realized into glass ampoules that were sealed in the flame. They were allowed to react for 3 days at 60 °C. After purification of the polymer by precipitation in *n*-hexane, the conversion was determined gravimetrically (8.3 g, $\eta = 83\%$). IR (cm^{-1}): 2980–2850 (CH_2, C–H), 1788 (CO–Cl), 770 (C–Cl).

Preparing of poly(*N-acryloyl* (*S*)*-phenylalanine-acrylic acid-acryloyloxymethyl pyrene*) (*PAcPheBz-Py*) was carried out in DMF solution (90 mL) using poly(acryloyl chloride) (2 g, 22 mmol), (*S*)-phenylalanine benzyl ester (5.5 g, 12.88 mmol) and pyrene-methanol (0.51 g, 2.2 mmol). The reaction was realized in the presence of triethylamine (4 mL, 29 mmol) under stirring at room temperature for 24 h, and then it was prolonged for another 2 h at 50 °C. The formed polymer (*PAcPheBz-Py*) was precipitated in 0.01 m HCl solution (300 mL), collected by filtration and vacuum-dried.

Removal of protecting benzyl group from PAcPheBz-Py was performed by adding KOH solution (0.2 g, 5 mmol) to the polymer solution in THF (1 g polymer/10 mL) and stirring at room temperature for 15 h. After neutralization with HCl solution (0.13 g, 3.5 mmol), the obtained copolymer (PAcPhe-Py1) was then precipitated in water, filtered and dried.

Other polyacrylate (PAcPhe-Py2) was also synthesized through reduction of PAcPheBz-Py (1 g,) in DMF:methanol (1:1, v/v) using H_2 in the presence of 0.1 g Pd/C (10%) for 3 days. After filtration, the polymer was precipitated in diethyl ether, filtered and dried.

All copolymers are soluble in common organic solvents such as chloroform, dichloromethane, THF and DMF.

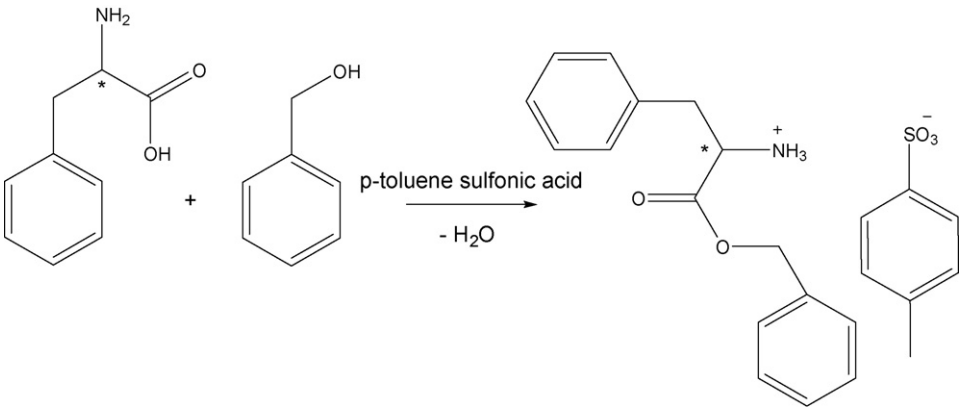
2.3. Characterization

The structure of monomers and polymers was verified by ^{1}H NMR and FT-IR spectroscopy using a Bruker 400 MHz spectrometer and a Bruker Vertex 70 spectrophotometer, respectively. The average molecular weight was determined in DMF by GPC analysis consisting of a PLEMD 950 apparatus equipped with two PL gel mixed columns using polystyrene standards.

The fluorescence spectra were recorded with an SLM 8000 spectrofluorimeter (Japan) and the quenching study was carried out using *N*,*N*-diethylaniline (DEA). Thermal transitions were measured on a Perkin-Elmer differential scanning calorimeter and were performed with a heating rate of 0.5° min^{-1}. Optical rotation measurements were carried out in DMF ($c = 1.0$ g dL^{-1}) at 20 °C by the use of an polarimeter (Jasco).

3. Results and discussion

Usually simple, in the first step phenylalanine benzyl ester that contains a reactive amine functionality is employed as chiral coupling reagent to poly(acryloyl chloride), prior prepared upon conventional radical polymerization of acryloyl chloride in the presence of AIBN. Synthesis of amino acid derivative (*PheBzTos*) implies protecting of the carboxylic group from (*S*)-phenylalanine with benzyl alcohol, according to Scheme 1. A variation of the N-acylation reaction is subsequently achieved for an additional coupling of PheBzTos and 1-hydroxymethyl pyrene to the acrylic backbone to give a photopolymer, which contains both phenylalanine and pyrene rings in the side chains. Therefore, pyrene as a molecule capable of emitting a signal is used for labeling chemically modified poly(acryloyl chloride), the molar fraction in the above polymer that affords a photon-emitting material being of approximately 10 mol%. Finally, if this polymer has yet in structure reactive site, like CO–Cl it can be exploited by its convertibility to free carboxylic groups. Thus,

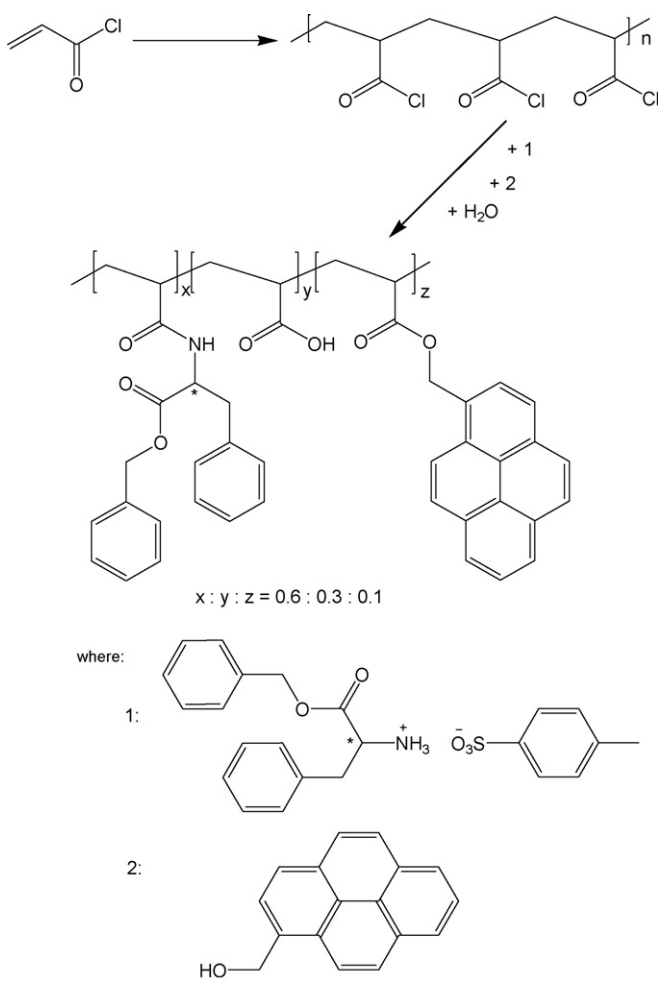


Scheme 1. Synthesis of (*S*)-phenylalanine benzyl ester tosylate (PheBzTos).

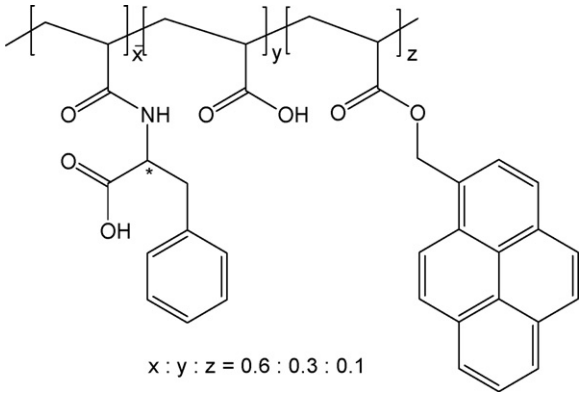
using a hydrolysis reaction in aqueous solution under adequate conditions, a terpolymer with acrylic acid units (PAcPheBz-Py) has been obtained (see Scheme 2).

Furthermore, to create a certain number of residues of amino acid with free carboxyl groups useful for design of new chemically functional materials (for instance, attaching of drugs/biomolecules), a controlled deblocking reaction of the ester group was performed by treatment of PAcPheBz-Py with KOH solution. The structure of newly formed copolymer (PAcPhe-Py1) can be schematically represented in Scheme 3. An increase in the content of pendent carboxyl groups when passing from PAcPheBz-Py to PAcPhe-Py1 as well as the interaction between the anionic polymer side chains is expected to be reflected in a modification of the optical rotation. In fact, the so-obtained polymers can be characterized by a mixture of hydrophilic moieties (carboxyl) and hydrophobic acryloyl sequences bearing pyrene and phenylalanine along the hydrocarbon backbone. The structural confirmation of polymers comes from ^{1}H NMR and FT-IR spectroscopic techniques, DSC, GPC and elemental analysis.

In the ^{1}H NMR spectrum of the polymer (PAcPheBz-Py) presented in Fig. 1, can be identified characteristic peaks to the constituent protons as follows: at 8.40–7.96 ppm (m, aromatic protons from pyrene), 7.33–7.23 ppm (m, aromatic protons from PheBz), 5.26 ppm (s, methylene protons from ester Py–CH_2–OCO), 5.0 ppm (s, methylene protons from Bz), 4.5 ppm (s, CH protons from phenylalanine), 3.25 ppm (m, protons from phenylalanine) and those in the zone 1.3–2.35 ppm (m, CH_2–CH–COO protons from acrylic and acryloyl amino acid). From the integral ratio of the pyrene protons, phenylalanine protons and aliphatic protons (CH_2–CH–COO) it was estimated the polymer composition in acryloyl phenylalanine



Scheme 2. Synthesis of poly(*N*-acryloyl (*S*)-phenylalanine benzyl ester-acrylic acid-acryloyloxymethyl-pyrene) (PAcPheBz-Py).



Scheme 3. Structure of poly(*N*-acryloyl) (*S*)-phenylalanine-acrylic acid-acryloyloxymethyl pyrene (PAcPhe-Py1).

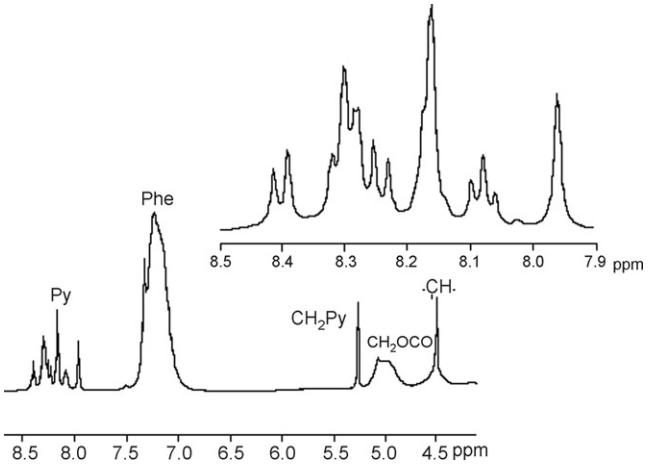


Fig. 1. ^{1}H NMR spectrum of poly(*N*-acryloyl (*S*)-phenylalanine benzyl ester-acrylic acid-acryloyloxymethyl-pyrene) (PAcPheBz-Py).

benzyl ester/acrylic acid/acryloyl pyrene as being of 0.6/0.3/0.1. Following then the integral of carboxylic protons at 12.4 ppm, it was found that the polymer contains about 30 mol% poly(acrylic acid) in the backbone, confirming thus the mentioned structure. Compared to PAcPheBz-Py, in the ^{1}H NMR spectrum of PAcPhe-Py1 (unshown) the signal of CH_2 benzyl protons located about 5 ppm significantly decreased as result of releasing of the benzyl unit from phenylalanine that allows the formation of free carboxyl group on amino acid in the side chain. To make a difference between the carboxyl groups belonging to the acrylic sequence from polymer and those of amino acid, we have taken in consideration the integral of CH and CH_2 benzyl protons of amino acid derivative that indicated a hydrolysis degree of the ester function from PAcPheBz-Py of 90%. Moreover, the resonance peak at 5.26 ppm, contributed by the methylene protons from pyrene-ester function remaining unmodified, it could be an argument in the favor of selective hydrolysis of the benzyl ester group. It is obvious, therefore, that the undesired attack of the nucleophilic reagent OH^- on the ester is sterically impeded of pyrene rings, but in the presence of base it is possible a loss of the chiral purity through the asymmetric carbon atoms of phenylalanine from polymers.

GPC analysis of both polymers indicates relatively high molecular weights of the synthesized poly(*N*-acryloyl (*S*)-phenylalanine benzyl ester-acrylic acid-acryloyloxymethyl-pyrene) (Mw: 72,300) and poly(*N*-acryloyl (*S*)-phenylalanine-acrylic acid-acryloyloxymethyl pyrene) (Mw: 65,000), that agree with the hydrolysis degree determined by NMR spectroscopy.

Another way for the removal of protecting group from the PAcPheBz-Py polymer was reducing with H_2, in the presence of Pd/C (10%) through a procedure usually encountered in the peptide chemistry. It became undoubtedly that hydrogenolysis of the *S*-benzyl ester generates amino acid with free carboxyl function.

Analyzing the ^{1}H NMR spectrum of the latter polymer (PAcPhe-Py2), it was found that deprotection of the benzyl ester part which accompanies free carboxyl group forming occurred about 85%. In Fig. 2 is given the ^{1}H NMR spectrum of the

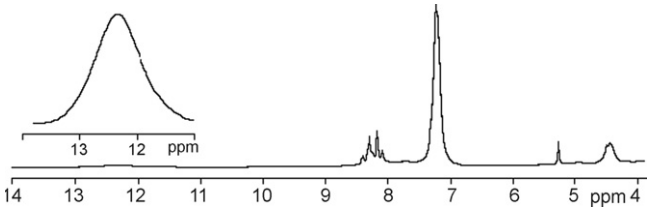


Fig. 2. Partial ^{1}H NMR spectrum of poly(*N*-acryloyl (*S*)-phenylalanine-acrylic acid-acryloyloxymethyl pyrene) (PAcPhe-Py2) obtained by the reducing procedure.

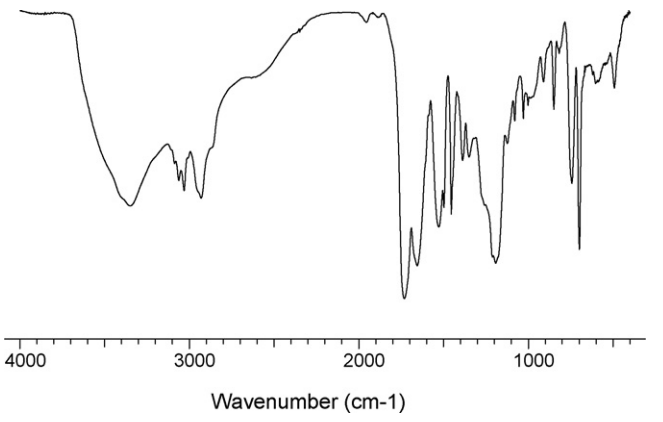


Fig. 3. FT-IR spectrum of poly(*N*-acryloyl (*S*)-phenylalanine-acrylic acid-acryloyloxymethyl pyrene) (PAcPhe-Py1).

carboxylic polymer resulted through reduction (PAcPhe-Py2), where it is clear that the benzyl protons integral from the ester group decreased due to deprotection of the benzyl ester unit under the experimental conditions applied in this study. Interesting is comparison of PAcPhe-Py2 and PAcPhe-Py1 polymers which confirms that these are identical in structure, composition and average molecular weight (PAcPhe-Py2, Mw: 66,000).

The FT-IR spectra of the acrylic polymers exhibited absorption bands sustaining the structure of functional groups. For example, poly(*N*-acryloyl phenylalanine-acrylic acid-acryloyloxymethyl pyrene) (PAcPhe-Py1) showed peaks at 3350 cm^{-1} attributed to the stretching vibration of the NH group, 1650 cm^{-1} to the amide I, 1529 cm^{-1} to the amide II and at 1200 cm^{-1} for the ester group (Fig. 3). The stretching vibration

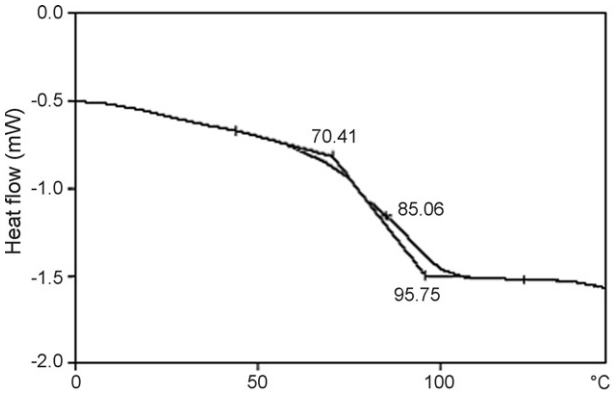


Fig. 4. DSC thermogram of poly(*N*-acryloyl (*S*)-phenylalanine-acrylic acid-acryloyloxymethyl pyrene) (PAcPhe-Py1).

of the aromatic ring appears at 700–750 cm^{-1} and that of the carbonyl group at 1732 cm^{-1}.

Since these polymers offer a possibility to use the carboxylic acids for binding different active molecules, resulting thus a wide range of desired biological activities, it is important to investigate the thermal data collected by differential scanning calorimetry (DSC). At this point, we report that PAcPhe-Py1 exhibits in the DSC curve a single glass transition at about 85.06 °C on the second run heating rate (0.5 °C/min), while in the first run just a transition at 70.85 °C was measured (Fig. 4). The last transition is associated to the melting point, indicating rather an amorphous nature of the polymer. It appears that the size, polarity of the amino acid and pyrene entities prevent even partial crystallization of the polymer because the conformational possibilities of a chain are limited for a close packing.

On the other hand, the specific optical rotation measurements in PAcPheBz-Py ($[\alpha]_D^{20} = +18.51°$) compared to the phenylalanine derivative used in synthesis PheBzTos ($[\alpha]_D^{20} = +4.73°$) was not in agreement with the negative values obtained for the most poly(*N*-acryloyl amino acids), excepting the tyrosine and phenylalanine based polymers [36]. The fact that in the debenzylated form (PAcPhe-Py1), the optical rotation has a lower value $[\alpha]_D^{20} = +9.98°$ suggests the role played by the basic hydrolysis of the ester moiety from PAcPheBz-Py on the polymer conformation into a manner similar to other poly(amino acids), but this point will be examined in a forthcoming paper.

3.1. Fluorescence properties

Emission and excitation spectra of the polymers were measured in DMF, THF and solid state, after prior registration of the exciting fluorescence of the polyacrylate useful in choosing the most proper excitation wavelengths. When the polymer solution is excited in DMF at 340 nm, PAcPheBz-Py shows only an intense monomer emission located at 381, 400 and 422 nm corresponding to pyrene monomers (Fig. 5). The general features of the spectra are similar in THF, but in this solvent the spectrum is less structured than in DMF. This could be due to protection of the monomer fluorescence from solvation in a moderately polar solvent (THF) in which the polar polymer chains are probably contracted. At first glance, the "monomer emission" can be a consequence of the isolation effect between pyrene moieties distributed in a small number onto an acrylic backbone with phenylalanine in the side chain, where the interaction of fluorophore molecules to form excimers is restricted. For example, in organic solutions pyrene excimer formation is a well-known concentration-dependent phenomenon [37]. Comparison with the UV absorption spectra of polymer solution reveals that the excitation spectrum for the monomer fluorescence corresponds to the UV absorption with maxima centered at 280, 300, 312, 328 and 344 nm. Exciting then with 365 nm, the monomer fluorescence maximum is shifted towards blue with about 2 nm suggesting the existence of aggregates in polymer solution. On the other hand, the excitation spectra monitored at 335 and at 319 nm produce a pattern of the emission spectra, which is qualitatively the same with that above mentioned, but the maximum of monomer emission decreased in PAcPheBz-Py solution.

Although pyrene excimer is not evidenced in organic solution of the polymer before debenzylation (PAcPheBz-Py), a different behavior was unexpectedly observed in the case of the polymer obtained after the debenzylation reaction (PAcPhe-Py1). Here, besides the corresponding monomer fluorescence appears an excimer fluorescence positioned at 486 nm. Similarly to the polymer solution, both excimer and monomer fluorescence were also found for PAcPhe-Py1 in the solid state at various excitation wavelengths. The results are summarized in Fig. 6.

In order to see if there is a fluorescence dependence on the solvent-induced changes, we examined the methanol-induced conformational change of the PAcPhe-Py1 polymer related to the fluorescence properties. As shown in Fig. 7, by rising of methanol quantity to a polymer solution in THF, the monomer fluorescence intensity in the presence of 30% methanol was approximately three times larger than that in the absence of methanol. This finding may indicate that PAcPhe-Py1 suffers a change of conformation by means of polar solvent, like CH_3OH, known for its ability to cleavage the intramolecular hydrogen bonds between the amide groups along the side chains. A further

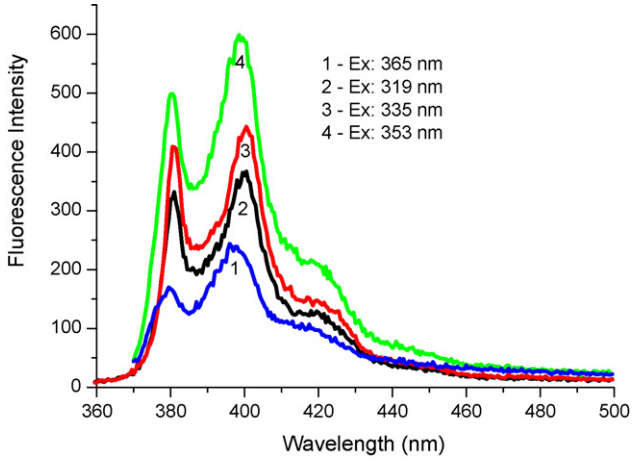


Fig. 5. Fluorescence spectrum of poly(*N*-acryloyl (*S*)-phenylalanine benzyl ester-acrylic acid-acryloyloxymethyl-pyrene) (PAcPheBz-Py) in DMF.

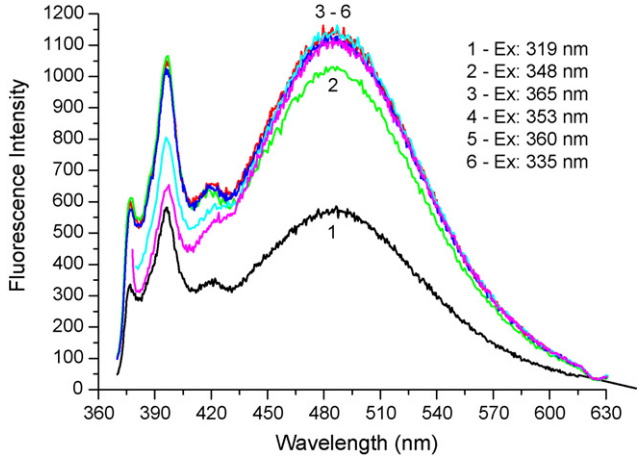


Fig. 6. Fluorescence spectrum of poly(*N*-acryloyl (*S*)-phenylalanine-acrylic acid-acryloyloxymethyl pyrene) (PAcPhe-Py1) in the solid state.

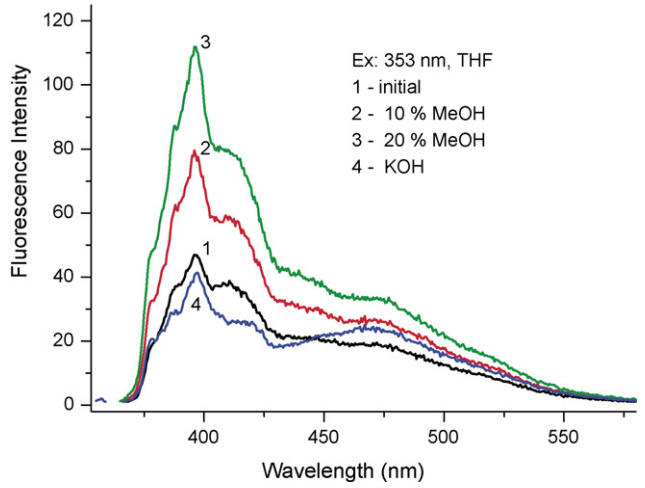


Fig. 7. Variation of fluorescence spectra of poly(*N*-acryloyl (*S*)-phenylalanine-acrylic acid-acryloyloxymethyl pyrene) (PAcPhe-Py1) with solvent composition.

addition (i.e. one drop) of 10^{-4} M KOH solution in methanol to the above mixture (THF:CH_3OH, 70:30, v/v) had as effect an almost complete returning of the monomer fluorescence to the initial one before KOH addition, with an easy increasing of excimer fluorescence. Again, such response of the polymer seems to be caused of a conformation change induced of the electrostatic repulsion between carboxyl and carboxylate anion groups from the side chains. In a similar fashion, continuing with the addition of HCl to the above solution it was noticed that there is the same tendency of returning of the fluorescence intensity. Like the case of polyacetylenes carrying amino acids [38], it is assumed that there is a reversible conformational change of the PAcPhe-Py1 polymer with pH, but this assumption demands to be checked.

PAcPhe-Py1 was also employed in a study of varying the fluorescence properties with temperature. All the fluorescence spectra were made in solid state. So, at excitation with 351 nm and a temperature of 20 K, the fluorescence spectrum in solid state of the polymer PAcPhe-Py1 shows a large maximum at 330–480 nm attributed to the monomer fluorescence besides another two maxima located at 480–520 nm and, respectively, 540–680 nm corresponding to the excimer fluorescence. It is also evidenced that variations of temperature during the cooling of sample at 300 K influence the fluorescent properties of the polymer in solid state. In the case of excitation with 632 nm only excimer derived predominantly from preformed ground state dimers or higher aggregates was detected. A similar result has been also visualized at excitation of 488 and 514 nm ($T = 20$ K), when the pyrene molecule emits just excimer fluorescence. The influence of temperature on the emitted fluorescence for PAcPhe-Py1 is given in Fig. 8.

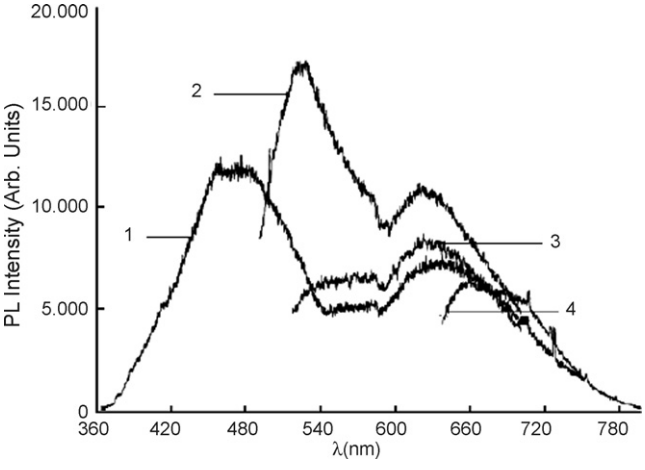


Fig. 8. Fluorescence profile for poly(*N*-acryloyl (*S*)-phenylalanine-acrylic acid-acryloyloxymethyl pyrene) (PAcPhe-Py1) in solid state for $\lambda_{ex} = 351$ nm (1), $\lambda_{ex} = 488$ nm (2) and $\lambda_{ex} = 514$ nm (3) at $T = 20$ K or for $\lambda_{ex} = 632$ nm (4) at $T = 300$ K.

3.2. Fluorescence quenching by DEA

In order to obtain information about the microenvironment around the pyrene moieties, the fluorescence quenching was compared between copolymers and pyrene excited molecule by use of *N*,*N*-diethylaniline (DEA) as quencher. Thus, in a last set of experiments, DEA was added to a solution of PAcPheBz-Py in DMF to observe the evolution of the fluorescence as the

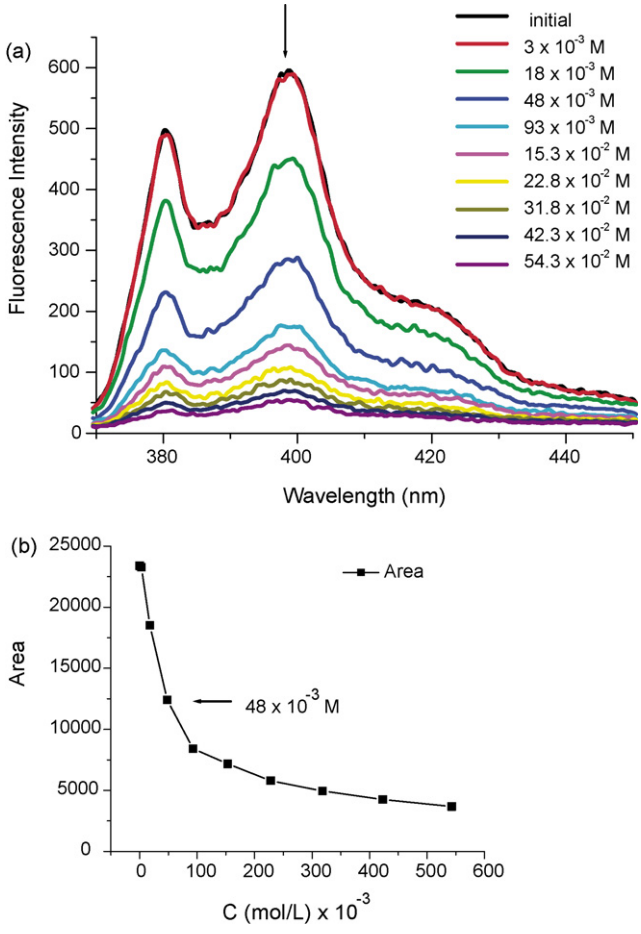


Fig. 9. Effect of *N*,*N*-diethylaniline on the fluorescence quenching in the solution of poly(*N*-acryloyl (*S*)-phenylalanine benzyl ester-acrylic acid-acryloyloxymethyl-pyrene) (PAcPheBz-Py) in DMF (a) and(b), evolution of the total area.

quantity of quencher was risen (Fig. 9, plot a). It is to be noted that by adding a solution of 48×10^{-3} mol/L DEA, the pyrene monomer fluorescence of the polymer in DMF is quenched with about 55%. Consequently, the evolution of the total area sustains the decreasing of the fluorescence intensity with a gradual increase in the DEA concentration (Fig. 9, plot b).

Returning to PAcPhe-Py1 solution, the analogous response by adding of amine was observed. In fact, the fluorescence of PAcPhe-Py1 in DMF is quenched through DEA, when the intensity of both excimer and monomer emission decreases with increasing the concentration of DEA solution to 47.17×10^{-4} M (Fig. 10, plot a). It was confirmed that this concentration of quencher affects 55% of the monomer and excimer fluorescence in a fashion similar to the PAcPheBz-Py polymer (Fig. 10, plot b) due to the interactions of electron-donor/ electron acceptor type between excited pyrene and amine molecules. Other aspects concerning the synthetic poly(*N*-acryloyl amino acids) with and without pyrene in structure as potential biologically active polyanions are under investigation and will be published elsewhere.

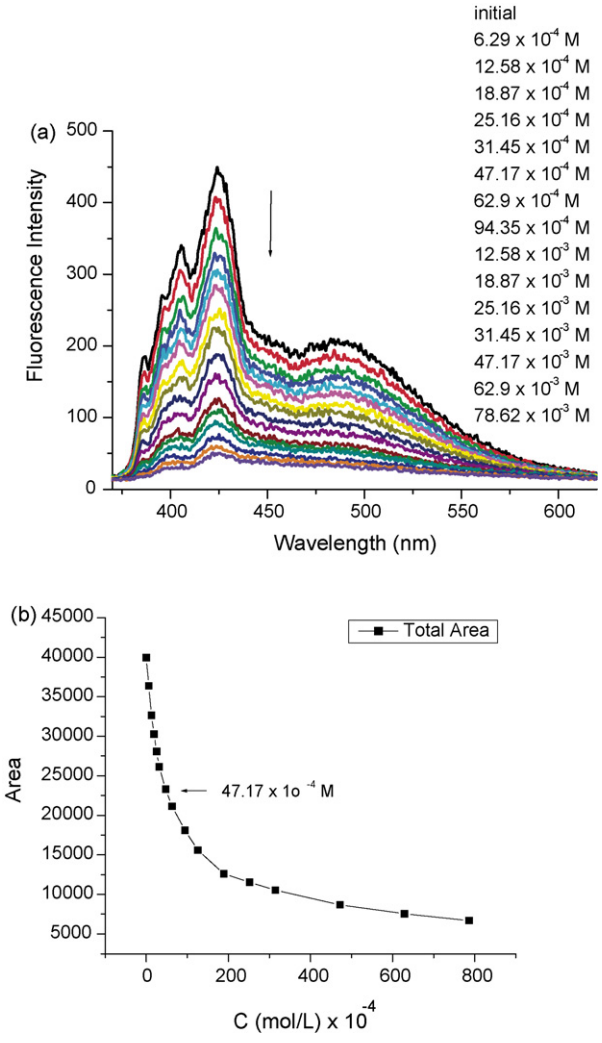


Fig. 10. Effect of *N*,*N*-diethylaniline on the fluorescence quenching in the solution of poly(*N*-acryloyl (*S*)-phenylalanine-acrylic acid-acryloyloxymethyl pyrene) (PAcPhe-Py1) in DMF (a) and (b), evolution of the total area.

4. Conclusions

In conclusion, we have synthesized pyrene-functionalized poly(*N*-acryloyl phenylalanine-acrylic acid) (PAcPhe-Py1) with well-defined composition and controlled structure varying the number of carboxyl groups by alkaline hydrolysis of the benzyl ester function from amino acid or a reduction with H_2 in the presence of Pd/C. Factors that influence the fluorescence properties such as the solvent nature, pH and temperature were studied by means fluorescence spectroscopy. Depending on pH, the polymer resulted after debenzylation undergoes reversible conformational change that could open a way to obtain pH-responsive systems. Moreover, in the presence of *N*,*N*-diethylaniline (47.17×10^{-4} M) the fluorescence emission of the polymer in solution can be quenched to around 55%, and consequently, a promising chemosensor for amine could be developed.

References

[1] K. Raman, R. Ramamoorthy, B.S.R. Reddy, React. Funct. Polym. 62 (2005) 215.
[2] A.A. Vaidya, B.S. Lele, M.G. Kulkarni, R.A. Mashelkar, Biotech. Bioeng. 34 (1999) 418.
[3] M.V. Deshmuch, A.A. Vaidya, M.G. Kulkarni, P.R. Rajamohanan, S. Ganapathy, Polymer 41 (2000) 7951.
[4] J.E. Puskas, Y. Chen, Y. Dahman, D. Padavan, J. Polym. Sci. Part A: Polym. Chem. 42 (2004) 3091.
[5] N. Vyavahare, J. Kohn, J. Polym. Sci. Part A: Polym. Chem. 32 (1994) 1271.
[6] A. Nathan, S. Zalipsky, J. Kohn, J. Bioact. Compat. Polym. 9 (1994) 239.
[7] H.B. Lin, W. Sun, D.F. Mosher, C. Garciaecheverria, K. Schaufelberger, P.I. Lelkes, S.L. Cooper, J. Biomed. Mater. Res. 28 (1994) 329.
[8] F. Salhi, J.W.Y. Lam, K.K.L. Cheuk, J.A.K. Cha, B.Z. Tang, Polym. Prepr. 41 (2000) 1185.
[9] C. Sumner, S. Krause, A. Sabot, K. Turner, C.J. McNeil, Biosens. Bioelectr. 16 (2001) 709.
[10] N. Arabuli, G. Tsitlanadze, L. Edilashavili, D. Kharadze, T. Goguadze, V. Beridze, Z. Gomurashvili, R. Katsarava, Macromol. Chem. Phys. 195 (1994) 2279.
[11] L. Angiolini, D. Caretti, L. Giorgini, E. Salatelli, A. Altomare, C. Carlini, R. Solaro, Polymer 39 (1998) 6621.
[12] F. Sanda, T. Abe, T. Endo, J. Polym. Sci. Part A: Polym. Chem. 35 (1997) 2619.
[13] F. Sanda, M. Nakamura, T. Endo, Macromolecules 29 (1996) 8064.
[14] H. Murata, F. Sanda, T. Endo, Macromolecules 30 (1997) 2902.
[15] C. Methenitis, G. Pneumatikakis, M. Pitsikalis, J. Morcellet, M. Morcellet, J. Polym. Sci. Part A: Polym. Chem. 33 (1995) 2233.
[16] G.A. Skarja, K.A. Woodhouse, J. Biomater. Sci. Polym. Ed. 12 (2001) 851.
[17] G.A. Skarja, K.A. Woodhouse, J. Appl. Polym. Sci. 75 (2000) 1522.
[18] S. Fumio, G. Guangzheng, M. Toshio, Macromol. Biosci. 4 (2004) 570.
[19] T. Kartvelishvili, G. Tsitlanadze, L. Edilashavili, N. Japaridze, R. Katsarava, Macromol. Chem. Phys. 198 (1997) 1921.
[20] H. Chen, X. Jiang, L. He, T. Zhang, M. Xu, X. Yu, J. Appl. Polym. Sci. 84 (2002) 2474.
[21] J.P. Santerre, J.L. Brash, Ind. Eng. Chem. Res. 36 (1997) 1352.
[22] A. Nathan, S. Zalipsky, J. Kohn, Polym. Prepr. 31 (1990) 213.
[23] F. Sanda, M. Nakamura, T. Endo, J. Polym. Sci. Part A: Polym. Chem. 36 (1998) 2681.
[24] M.C. Kramer, C.G. Welch, J.R. Steger, C.L. McCormick, Macromolecules 28 (1995) 5248.
[25] E.C. Buruiana, T. Buruiana, J. Biomater. Sci. Polym. Ed. 15 (2004) 781.
[26] T. Buruiana, D. Spiridon, E.C. Buruiana, V. Hefco, C.V. Uglea, J. Biomater. Sci. Polym. Ed. 10 (1999) 1159.
[27] T. Buruiana, E.C. Buruiana, J. Polym. Mater. 19 (2002) 29.

[28] E.C. Buruiana, T. Buruiana, V. Pohoata, J. Photochem. Photobiol. A: Chem. 180 (2006) 150.
[29] E.C. Buruiana, T. Buruiana, G. Strat, M. Strat, J. Polym. Sci. Part A: Polym. Chem. 43 (2005) 3945.
[30] E.C. Buruiana, T. Buruiana, G. Strat, M. Strat, J. Photochem. Photobiol. A: Chem. 162 (2004) 23.
[31] E.C. Buruiana, T. Buruiana, G. Strat, M. Strat, J. Polym. Sci. Part A: Polym. Chem. 11 (2002) 1918.
[32] E.C. Buruiana, T. Buruiana, L. Hahui, J. Polym. Sci. Part A: Polym. Chem. 44 (2006) 5271.
[33] E.C. Buruiana, V. Melinte, T. Buruiana, T. Lippert, H. Yoshikawa, H. Mashuhara, J. Photochem. Photobiol. A: Chem. 171 (2005) 261.
[34] T. Buruiana, E.C. Buruiana, J. Appl. Polym. Sci. 96 (2005) 577.
[35] T. Buruiana, E.C. Buruiana, J. Polym. Sci. Part A: Polym. Chem. 42 (2004) 5463.
[36] A. Bentolila, I. Vlodavsky, R.I. Michaeli, O. Kovalchuk, C. Haloun, A.J. Domb, J. Med. Chem. 43 (2000) 2591.
[37] R.C. Dorrance, T.F. Hunter, J. Chem. Soc. Faraday Trans. 70 (1974) 1572.
[38] F. Sanda, K. Terada, T. Masuda, Macromolecules 38 (2005) 8149.