Journal of Photochemistry and Photobiology A: Chemistry 213 (2010) 107–113

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Polyacrylates containing dansyl semicarbazide units sensitive for some structures in solution and film

Emil C. Buruiana*, Andreea L. Chibac, Tinca Buruiana

"Petru Poni" Institute of Macromolecular Chemistry, 41 A Grigore Ghica Voda Alley, 700487 Iasi, Romania

ARTICLE INFO

Article history:
Received 1 February 2010
Received in revised form 12 May 2010
Accepted 12 May 2010
Available online 21 May 2010

Keywords:
Copolymerization
Polyacrylates
Dansyl semicarbazide
Fluorescence

ABSTRACT

Two dansylated copolymers have been synthesized by free radical polymerization of *N-methacryloyloxyethylcarbamoyl-5-(dimethylaminonaphthalene-1-sulfonohydrazine)* (DnsSA) and N-dodecylacrylamide or methyl methacrylate with 1,1′-azobis (cyclohexanecarbonitrile) as the initiator. The structure and the chemical composition of the formed copolymers (DnsSA-DA; DnsSA-MMA) were confirmed by spectral analysis (^{1}H NMR, FTIR, UV/vis), thermal methods, GPC measurements, and AFM technique. Compared with DnsSA (λ_{em} = 525 nm/DMF; 515 nm/$CHCl_3$), the emission spectra of DnsSA-DA in DMF exhibited a time- and concentration-dependent monomer and excimer fluorescence (430 nm; 520 nm), while in $CHCl_3$ only the excimer form exists for both copolymers. The sensing ability of these copolymers in both the solvents has been investigated by fluorescence spectroscopy in tandem with quenching experiments using various metal ions (Cu^{2+}, Fe^{2+}, Ni^{2+}) and nitroaromatics (picric acid, p-nitrotoluene, o-nitrophenol, dinitro-m-xylene, nitrobenzene), which suggested that such polymeric fluorophores could find applications for detection of some metal ions as well as nitro-derivatives in DMF solutions, the most efficient quencher being Cu^{2+} and picric acid in the case of DnsSA-DA. The fluorescence study showed that the fluorescence emission in film state can be also quenched by nitrobenzene vapors, and further, an excellent reversibility of this process was observed.

1. Introduction

In recent years, a number of reports have surfaced aspects regarding the photophysics of 1,5-dimethylaminonaphthalene sulfonamide (dansyl, Dns) derivatives, which are often useful as molecular probe in the exploration of biological systems (proteins, lipozomes, micelles) and synthetic polymers [1,2] including polymeric films [3] or glass fibers [4,5]. Moreover, the ability of the Dns molecule to manipulate the behavior of materials by changing the environmental conditions surrounding the probe has been widely exploited for constructing fluorescent chemosensors for organic molecules, upon the binding to β-cyclodextrine [6] and derivatives of sol–gel type [7], or chemical immobilization of self-assembled monolayers on glass slide surfaces, to name a few [8].

In particular, the design and development of more sensitive and efficient systems for the selective detection of divalent metal ions (Cu^{2+}, Pb^{2+}, Fe^{2+}, Ni^{2+}) in comparison with other transition metal ions [9–11] identified in environmental and biological processes have earned special attention. For example, LB films of dansylated peptide lipids [12], Dns-D,L-phenylalanine [13], Dns-poly(propylene amine) dendrimers [14], and Dns-cyclodextrinamino acid [15] were obtained to be investigated as suitable fluorescent indicators of enantiomeric purity or for molecular recognition. One very sensitive fluorescent sensor for heavy metal ions was also synthesized by dansylation of the 3-[2-(2-aminoethylamino)ethylamino]propyl-trimethoxysilane receptor, where the covalent attachment of dansyl-modified polyamine into silica colloids allowed the creation of a nanoscale architecture that could be developed for multifunctional nanomaterials [16]. Unfortunately, so far, few studies have been devoted to the acrylic polymers labeled with the fluorescent dansyl moiety, whose feature was involved only in investigating the binding behavior of the group and the complex formation [17]. Aiming to improve the knowledge and to develop sensors for the optical detection of acidity, we have previously reported a dansylated copolyacrylate, following the relationship between the structure and the peculiar response generated of the dansyl photophysics to the protonation of the amino group [18]. As a continuing effort in search of the new photopolymers with pyrene, stilbene, or anthracene units in their backbone [19–23], this paper presents the synthesis and intrinsic properties of two acrylic copolymers containing dansyl semicarbazide groups with focus on the fluorescence response of the polymer solution and film upon exposure to metal ions and nitroaromatics.

---

* Corresponding author. Tel.: +40 232 217454; fax: +40 232 211299.
E-mail address: buruiana.emil@yahoo.com (E.C. Buruiana).

1010-6030/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2010.05.008

2. Experimental

2.1. Materials

5-(Dimethylamino)naphthalene-1-sulfonyl hydrazine, 2-isocyanatoethyl methacrylate, dodecylamine, acryloyl chloride and methyl methacrylate (MMA) were used as received (Aldrich) without any purification.

2.2. Synthesis of N-methacryloyloxyethylcarbamoyl-5-(dimethylaminonaphthalene-1-sulfonohydrazine) (DnsSA)

To a well-stirred solution of 5-(dimethylamino)naphthalene-1-sulfonyl hydrazine (2.99 g, 10.7 mmol) in 15 mL THF, 10.7 mmol of 2-isocyanatoethyl methacrylate (1.55 mL) was added to yield a dansylated monomer. The mixture was kept under stirring at room temperature for 24 h and then at 35 °C for others 24 h. The formed product was concentrated under reduced pressure and further purified by repeated washings with diethyl ether.

^{1}H NMR of DnsSA in $CDCl_3$ (δ, ppm): 8.27, 7.56, 7.2 and 6.85 (aromatic protons); 6.1 and 5.57 (olefinic protons in trans and cis configuration); 3.75 (methylene protons from CH_2CH_2OCO); 3.11 (CH_2CH_2OCO); 2.88 (methyl protons from $N(CH_3)_2$); 1.88 (methyl protons from methacrylate).

FTIR (cm^{-1}): 1639 (C=C); 1710 (carbonyl group); 3406 (urethane group); 650–945 (aromatic ring); 1168 and 1341 (SO_2N group); UV ($CHCl_3$): 354 nm.

Fluorescence emission (λ_{exc} = 300 nm): 525 nm (DMF); 515 ($CHCl_3$).

2.3. Synthesis of dodecylacrylamide (DA)

The dodecylacrylamide monomer was obtained from reaction of a solution of acryloyl chloride (2.26 mL, 26.7 mmol) in 5 mL THF added dropwise to a 20 mL THF solution of dodecylamine (5 g, 26.7 mmol) at 0 °C, in the presence of triethylamine (3.73 mL, 26.7 mmol). This mixture was stirred at room temperature for 24 h and then the product was filtered and the solvent was removed under reduced pressure. The resulting product was recrystallized from n-hexane.

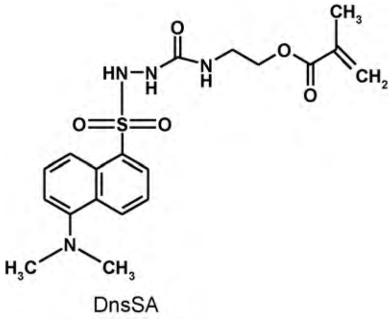
^{1}H NMR of DA in $CDCl_3$: 1.25 ppm (aliphatic CH_2); 0.88 ppm (methyl protons); 3.32 ppm ($-CH_2-NH-$), 7.26 ppm ($-CH_2-NH-$), 6.25 ppm (olefinic proton in trans CH_2), 6.1 ppm (olefinic proton CH); 5.6 ppm (olefinic proton in cis).

FTIR of DA: 3270 cm^{-1} (ν_{NH} NH group); 1652 cm^{-1} ($\nu_{C=O}$ amide I); 1551 cm^{-1} (amide II); 2956 cm^{-1}, 2871 cm^{-1} and 1469 cm^{-1} (CH_3 group); 2921 cm^{-1}, 2849 cm^{-1} and 721 cm^{-1} (CH_2); 1650 cm^{-1} ($\nu_{C=C}$ carbonyl group).

2.4. Polymers' synthesis

DnsSA-co-DA was prepared through a conventional radical polymerization of DnsSA (0.7 g, 1.67 mmol) and dodecylacrylamide (4 g, 16.7 mmol) in dioxane (molar ratio between monomers: 1:10) using 1,1′-azobis (cyclohexanecarbonitrile) (2‰) as the initiator. The mixture was reacted at 80 °C for 72 h, under purified nitrogen and the resulting copolymer was concentrated under reduced pressure, purified by precipitation in water and dried at 60 °C for 24 h, and then under reduced pressure.

Under the same experimental conditions was prepared DnsSA-co-MMA using DnsSA (0.5 g, 1.19 mmol) and MMA (2.5 g, 24.97 mmol). The monomers' mixture was reacted at 80 °C for 24 h, under purified nitrogen. The resulting copolymer was purified by precipitation in diethyl ether and dried in stove at 60 °C for 24 h and then under reduced pressure.



Scheme 1. Structure of the N-methacryloyloxyethylcarbamoyl-5-(dimethylaminonaphthalene-1-sulfonohydrazine) (DnsSA).

^{1}H NMR signals for DnsSA-co-DA (MMA) in $CDCl_3$: 8.6, 8.37 and 7.6 ppm (aromatic protons); 3.64 ppm (methylene protons from ester); 3.35 ppm (methylene protons from CH_2NHCO); 2.9 ppm ($(CH_3)_2N-$); 1.55–0.86 ppm (aliphatic protons). For DnsSA-co-MMA, other chemical shifts at about 3.6 ppm and in the zone 2.0–0.85 ppm have been assigned to methyl protons from ester and methyl and aliphatic protons, respectively.

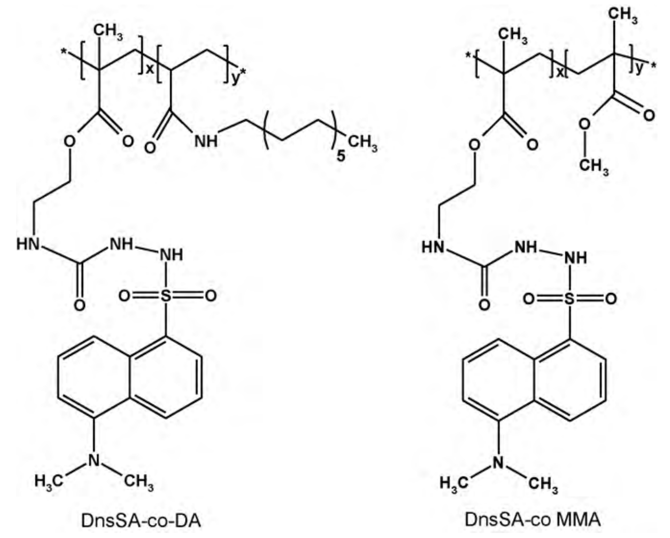
2.5. Measurements

The structure of all synthesized derivatives was verified by ^{1}H NMR, FTIR, and UV spectroscopy. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrophotometer in $CDCl_3$ at room temperature with TMS as an internal standard. FTIR spectra were recorded on a Specord M80 spectrophotometer. The UV absorption spectra were measured with a Specord 200 spectrophotometer in $CHCl_3$ solution. In order to obtain molecular weight of copolymers there were recorded the GPC chromatograms with a Polymer Laboratory MD-950 apparatus equipped with an evaporative mass detector and two PL gel 5 μm columns using DMF as a solvent and polystyrene standards for calibration. The thermal transitions were determined on a Perkin-Elmer differential scanning calorimeter by cooling of the copolymer to 5 °C and heating at a rate of 10 °C/min up to 120 °C. Thermogravimetric analysis (TGA) was conducted in air on a MOM derivatograph at heating rate of 10 °C. The surface morphology of the copolymers was examined by means of atomic force microscopic (AFM) technique using a SOLVER PRO-M AFM. The polymeric films for AFM experiment were prepared using a spin coater Model WS-400B-6NPP/LITE/10K from Laurel Tech at 3000 rpm, the images being registered in different points of the sample to check their reproducibility. The fluorescence intensity measurements were carried out with a Perkin-Elmer LS 55 spectrophotometer at room temperature in CCl_4 solution and in DMF solution.

3. Results and discussion

3.1. Synthesis and characterization

Preparing fluorescent monomer, *N-methacryloyloxyethylcarbamoyl-5-(dimethylaminonaphthalene-1-sulfonohydrazine)* (DnsSA, Scheme 1) involved a conventional addition reaction of 5-(dimethylamino)naphthalene-1-sulfonyl hydrazine with 2-isocyanatoethyl methacrylate. The structure and purity of DnsSA was confirmed by FTIR, ^{1}H NMR and UV spectroscopy. To obtain the copolyacrylates with dansyl semicarbazide entities covalently attached to polymeric backbone, DnsSA was radically copolymerized with N-dodecylacrylamide or methyl methacrylate using 1,1′-azobis (cyclohexanecarbonitrile) as the initiator. The structure of the formed copolymers (Scheme 2),



Scheme 2. Structure of the copolyacrylates with dansyl semicarbazide moieties.

N-methacryloyloxyethylcarbamoyl-5-(dimethylaminonaphthalene-1-sulfonohydrazine)-co-dodecylacrylamide (DnsSA-co-DA) and *N-methacryloyloxyethylcarbamoyl-5-(dimethylaminonaphthalene-1-sulfonohydrazine)*-co-methyl methacrylate (DnsSA-co-MMA), was examined by spectral and thermal analyses, AFM and fluorescence techniques. It must be noted that both the copolymers presented a high solubility in common solvents such as DMF, DMSO, chloroform, and dichloromethane. The major difference between these polymeric fluorophores is that the former has a long hydrocarbon chain attached to the acrylic sequence which could facilitate aggregation with effect on the fluorescence of DnsSA-co-DA.

The ^{1}H NMR signals for DnsSA-co-DA (MMA) given in the experimental part sustain the expected structure for both copolymers. The identification of structural composition in copolymers was achieved through analysis of the area ratio derived from aromatic protons signals (8.6–7.22 ppm) to the aliphatic protons signals (1.55–0.86 ppm for DnsSA-co-DA, and respectively, 3.6 ppm for DnsSA-co-MMA). Accordingly, it was estimated that the molar ratio of the monomeric units in the above copolymers was of 3:97 (DnsSA:DA) and of 2.4:97.6 (DnsSA:MMA), the content of dansyl units being smaller than that of the monomer feed ratio (1:10). The molecular weight of DnsSA-co-DA determined by GPC was estimated to be of 33,200, and of 65,000 for DnsSA-co-MMA.

The FTIR spectra of copolymers showed absorption bands around 3274 cm^{-1} (NH), 1652 cm^{-1} (amide I) and 1550 cm^{-1} (amide II), not including the stretching vibration of the C=C double bond, which confirms that the polymerization of monomeric units occurred (not shown). The UV–vis absorption spectra of dansylated copolymers are characterized by the same curve profile as that of the monomer, only visible difference being in the case of DnsSA-DA copolymer in $CHCl_3$ (Fig. 1), where besides the absorption maxima attributed to $\pi-\pi^*$ transition of the naphthalene ring (248 nm) appears a hypsochromic shift of about 10 nm of charge-transfer band (340 nm).

The thermal properties of these copolymers were assessed with thermogravimetric (TGA) and differential scanning calorimetry (DSC) analyses. As can be seen in Table 1, TGA traces revealed that such copolymers showed a two-stage and respectively, three-stage degradation pattern. The first and second stage of thermal decomposition (T_{onset}) starting at around 160 °C (DnsSA-co-DA) or 140 °C (DnsSA-co-MMA) may be attributed to the decomposition of dodecylamide (weight loss of 50 wt%) and respectively, ester groups (weight loss of about 20 wt%) from the synthesized copolymers. Their decomposition temperatures at which this process is finished (T_{endset}) were around 420 °C, and this result can be related to the decomposition of the polymeric main chain. Therefore, the use of DA as co-monomer led to the formation of acrylic photopolymer with a better thermal stability. The DSC thermogram for DnsSA-co-MMA displayed a single glass transition (T_g) at 60.83 °C, indicating the miscibility of dansyl and ester units in the amorphous phase, whereas the T_g for DnsSA-co-DA was observed at 75.95 °C.

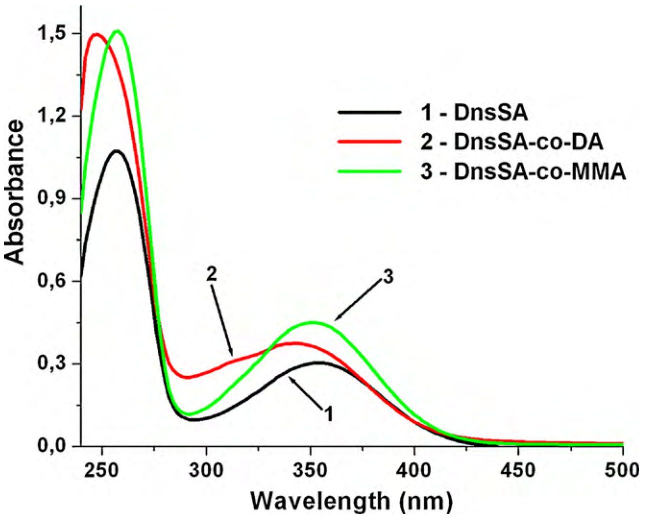


Fig. 1. UV absorption spectra of dansylated monomer and copolyacrylates in $CHCl_3$.

The morphology of the above copolymers is visualized by atomic force microscopy (AFM), the sample being prepared by spin coating on silicon wafers as described in Section 2. The bi- and three-dimensional AFM diagrams (Fig. 2) suggested a homogeneous morphology of the polymeric surfaces covered with small aggregates of regular shape with about 20 nm in height by one phase. Obviously, the existence of white domains could be associated to the crystalline component of the photopolymer distributed into an amorphous matrix, where the difficulty of packing of the macromolecular chains would be responsible for this low crystallinity.

3.2. *Fluorescence behavior of dansyl label*

Emission spectra of the dansyl-labeled acrylic copolymers were measured at first in solvents with different polarities (DMF, $CHCl_3$), since the position, shape, and intensity of the emission are sensitive to molecular mobility, solvation, and polarity of the environment around the fluorophore. When excited at 300 nm, each spectrum of the copolymers in DMF solution (10.3 mg L^{-1}) freshly prepared consisted of two emission bands. For instance, DnsSA-co-DA gave an emission spectrum in which the shorter wavelength strong band peaked at 430 nm is assigned to the ordinary monomer fluorescence emission from monomeric excited dansyl groups, while the longer wavelength band, centered near 520 nm (shoulder), may be due to the excimer fluorescence emission, originating from the attractive interaction of an excited dansyl moiety with another dansyl unit in the ground state or by direct excitation of the aggregated species. On the other hand, the profile of the fluorescence emission of dansyl molecule being basically dependent upon its concentration, we should note here that the intensities of monomer fluorescence (I_M) and excimer fluorescence (I_E) significantly increased at increasing concentrations of copolymer, but the excimer form is emitted preferentially up to a concentration of about 72.2 mg L^{-1} of DnsSA-co-DA. Considering that intermolecular hydrophobic aggregation of the dansyl fluorophores is responsible for increasing the population of excited dimers, it is

Table 1
Thermal data concerning dansyl-copolymers.

Sample	Stage	T_{onset} (°C)	T_{peak} (°C)	T_{endset} (°C)	W (%)	Residue (%)
DnsSA-co-DA	I	160	260	305	49.71	3.49
	II	360	415	420	46.8	
DnsSA-co-MMA	I	140	146	160	4.96	2.65
	II	220	238	240	14.46	
	III	360	404	420	77.93	

not surprising that the I_E/I_M ratio is enhanced. Normally, the introduction of copolymer over a given concentration (103 mg L^{-1}) is favorable to the formation of aggregates of dansyl groups, with effect on the fluorescence intensity, which decreased owing to the self-quenching phenomenon, appeared in the system (Fig. 3a). Moreover, the latter observation is similar to that found in the second experiment implying the monitoring of the emission band characteristic for dansylated copolymers with increasing temperatures. Thus, at temperatures of 20–70 °C the intensities of fluorescence emission for DnsSA-co-DA in DMF solution are significantly affected causing a decrease with 40% of the initial value (I_M) and 22% (I_E) respectively, compared to that found in DnsSA-co-MMA, where I_E attained a value of 26.4% (Fig. 4). A similar feature has been found in the case of poly(methyl methacrylate) doped with dansyl derivative, where the fluorescence decay time decreased with the increase in temperature, a result assigned to a change in free volume of the polymer [24].

Other interesting observation from this study is that related to the temporal changes appeared in the monomer emission from dansyl in copolymer which increased after 1 week of standing, more quickly than the excimer emission (Fig. 3b). Hence, the monomer emission predominated at the beginning of the experiment, whereas a new equilibrium between the monomer form and the association state needs times for reorganization. Further examination of the spectrum of DnsSA-co-MMA in DMF revealed that the ratio of monomer-to-excimer fluorescence intensity (I_{425}/I_{520}) is smaller compared to the former, most probably due to the conformation differences of the macromolecular chain leading to distinct average distances among the fluorophores. The fact that its emission spectrum is highly sensitive to solvent polarity is sustained of the change of the fluorescence emission spectrum of both copolymers in $CHCl_3$, when only the excimer emission at 500 nm (DnsSA-co-DA) and respectively, at 514 nm (DnsSA-co-MMA) was recorded (see latter). This means that, in nonpolar solvent, the fluorescence arises from the associated state of dansyl molecules located on the polymeric backbone. Notably absent is the monomer fluorescence in the case of DnsSA monomer, when the excimer fluorescence is emitted in the both solvents.

Based on this consideration, we attempted to investigate the ability of some metal ions to quench the fluorescence of dansyl-copolymers in DMF solution (after 1 week). Typical fluorescence emission spectra obtained for DnsSA-co-DA (72.2 mg L^{-1}) upon gradual addition of Cu^{2+} ions ($CuBr_2$ solution) are shown in Fig. 5a. Therefore, a quenching of fluorescence intensity was observed,

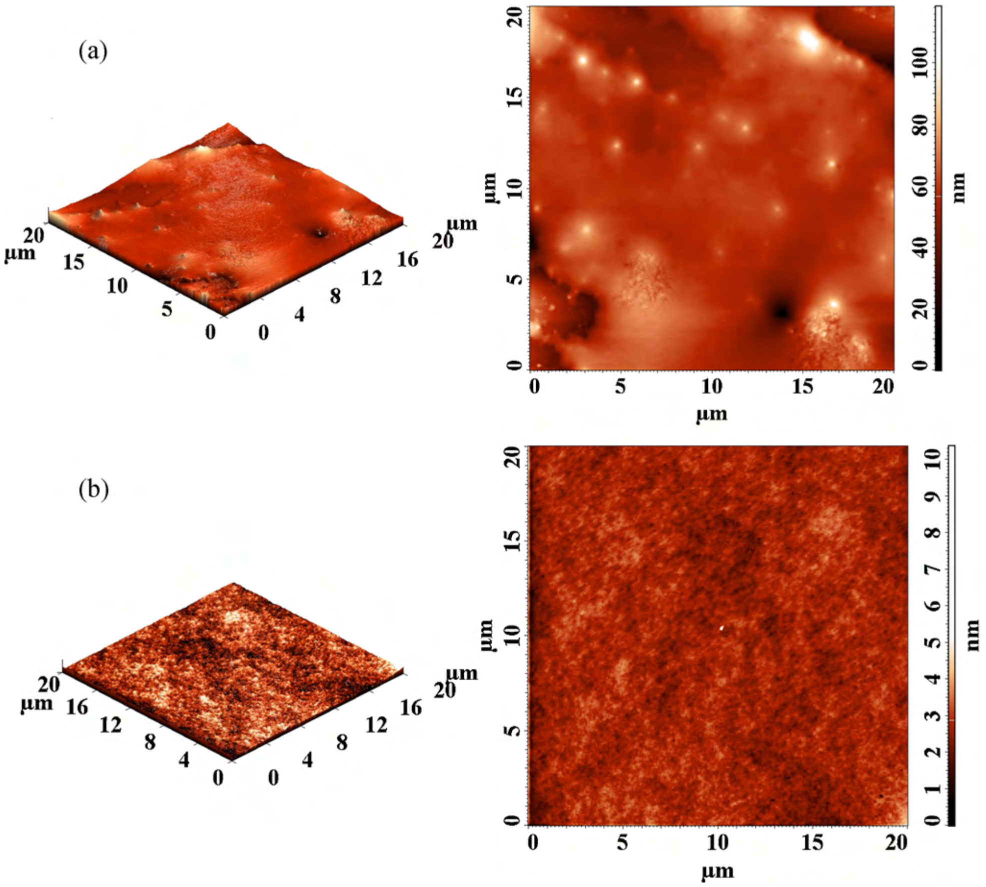


Fig. 2. AFM images for the dansylated copolyacrylates: DnsSA-co-DA (a) and DnsSA-co-MMA (b).

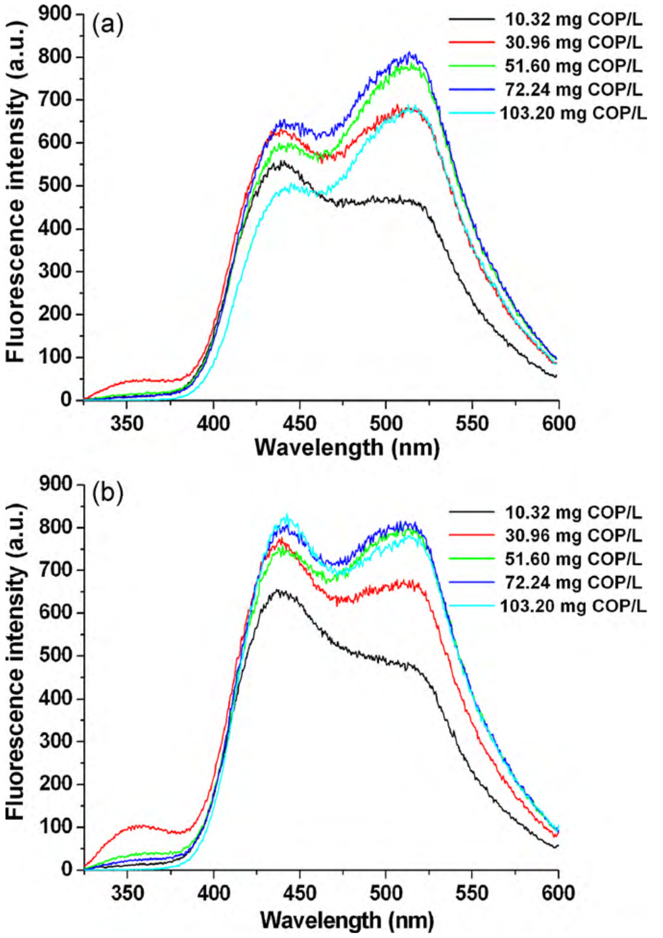


Fig. 3. Fluorescence spectra of DnsSA-co-DA in DMF at different concentrations of copolymer measured for fresh solutions (a) and after 1 week (b).

since the binding of a single metal cation can lead to the quenching of up to 10 surrounding dansyl molecule [25], so that at a concentration of 9.00×10^{-4} M Cu^{2+} a quenching efficiency of 93.5% was achieved. A similar behavior was recorded for DnsSA-co-MMA upon addition of 13.33×10^{-4} M Cu^{2+}, when the fluorescence intensity tends to reach equilibrium value at about 78.85%. On the other hand, the detection limit realized via fluorescence quenching was 0.33×10^{-4} M for DnsSA-co-DA and of 0.66×10^{-4} M for DnsSA-co-MMA, and this means that intermolecular quenching of the fluorescence accompanying coordination of Cu^{2+} is more efficient on DnsSA-co-DA than on the latter. Further evidence for this behavior is also supported by the experimental data obtained when other cations were introduced into polymer solution. The changes in relative fluorescence emission of the polymer solution (DnsSA-co-DA) in the presence of Cu^{2+}, Fe^{2+} and Ni^{2+} are summarized in Fig. 5b, where is illustrated the fluorescence quenching depending on the metal concentration.

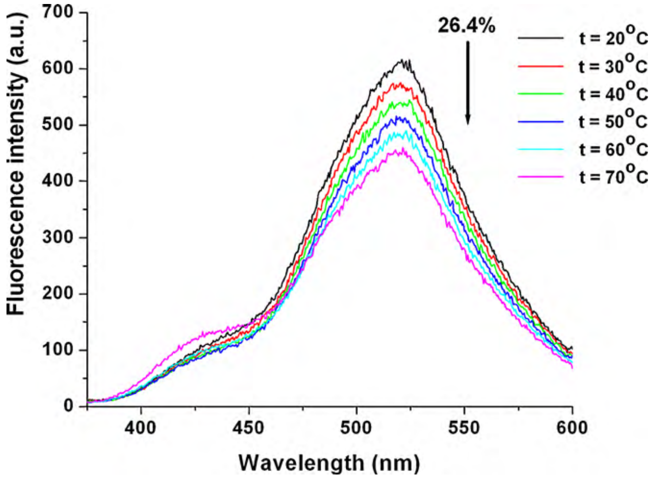


Fig. 4. Fluorescence spectra of DnsSA-co-MMA in DMF at different temperatures.

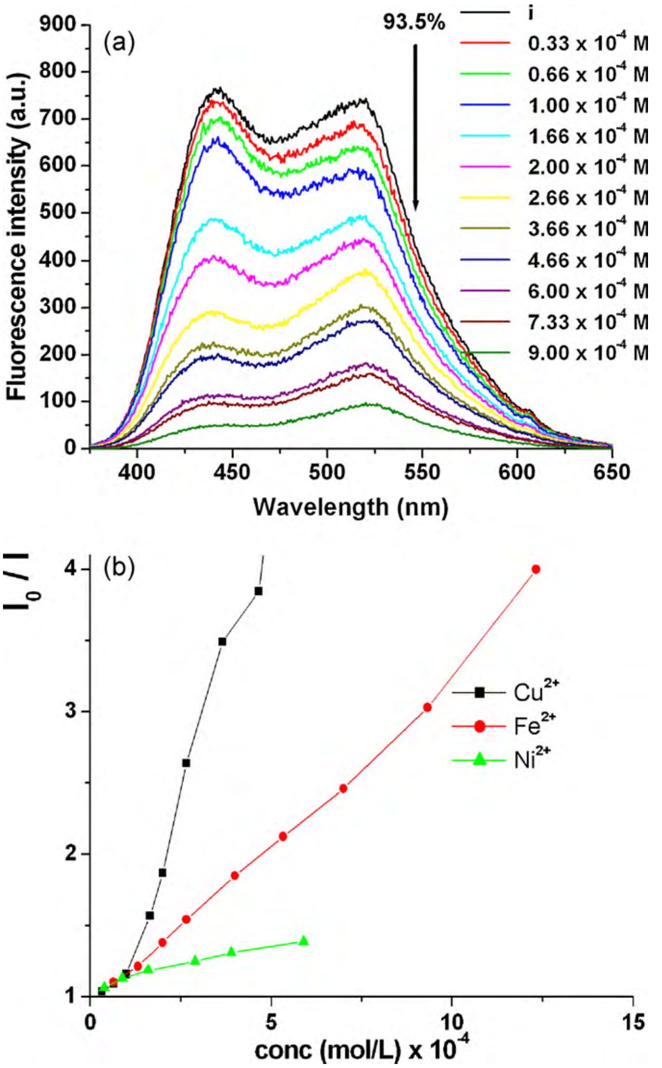


Fig. 5. (a) Fluorescence spectra of DnsSA-co-DA in DMF in the absence and presence of Cu^{2+} at different concentrations (λ_{ex} = 300 nm); (b) Stern–Volmer plots for DnsSA-co-DA and metal cations.

However, upon addition of 12.33×10^{-4} M Fe^{2+} to the DnsSA-co-DA the original fluorescence intensity drops to 75% and the smallest value of the quencher concentration identified was of 0.66×10^{-4} M. In the case of DnsSA-co-MMA, this parameter is easily increased to 78.36% (18.33×10^{-4} M Fe^{2+}) and the detection limit had the same value as in the former. If it is compared to the decrease of fluorescence emission intensity at a concentration of 11.33×10^{-4} M Fe^{2+} it is obvious that the quenching process is more favored in DnsSA-co-DA (75%) than in DnsSA-co-MMA (66%).

Examining the effect of Ni^{2+} (nickel acetate) it was detected that the quenching process was weaker than in the other cases namely, at 2.1×10^{-4} M Ni^{2+} the emission of DnsSA-co-MMA copolymer showed a decrease of about 20% of the initial value, and the detected

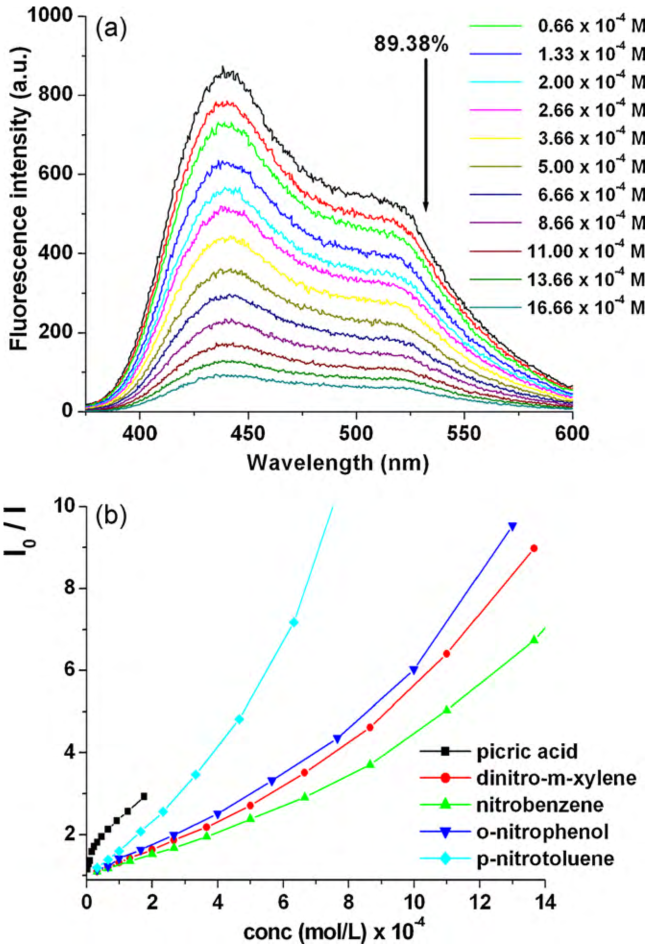


Fig. 6. (a) Fluorescence spectra of DnsSA-co-DA in DMF in the absence and presence of nitrobenzene at different concentrations ($\lambda_{ex} = 300$ nm); (b) Stern–Volmer plots for DnsSA-co-DA and nitroaromatic derivatives.

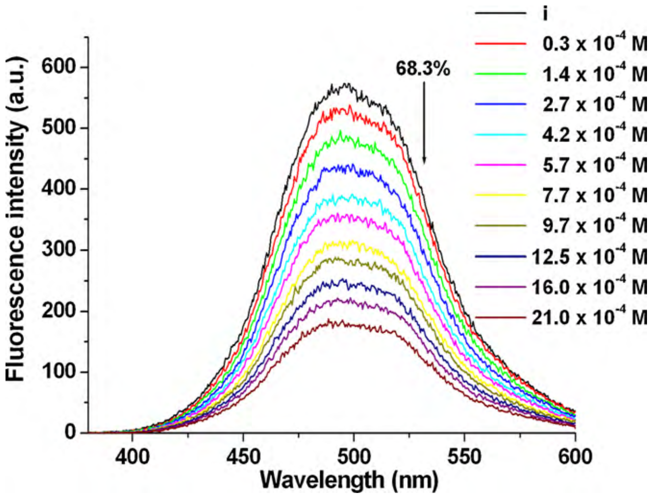


Fig. 7. Fluorescence spectra of DnsSA-co-DA in $CHCl_3$ in the absence and presence of nitrobenzene at different concentrations ($\lambda_{ex} = 300$ nm).

minimal concentration was 0.1×10^{-4} M. For the first copolymer, the fluorescence emission intensity decreased with 27.8% (for 5.9×10^{-4} M Ni^{2+}) and the detection limit was 0.4×10^{-4} M. Therefore, despite structural difference the effect observed here suggested that the Ni^{2+} cation had the close efficiency as quencher on the both dansyl-labeled copolymers. Moreover, the quenching process obeyed the Stern–Volmer relationship indicating that this is dynamic in nature at least in its linear part, and the efficiency of quenching decreased in the next order: Cu^{2+}, Fe^{2+} and Ni^{2+} for both copolymers. It appeared that the ability of metal cations to quench the fluorescence of the dansyl molecule from copolymers may be explained on the basis of photoinduced energy transfer processes involving the dansyl excited state and probably the orbitals d^9 (Cu^{2+}), d^6 (Fe^{2+}), or d^8 (Ni^{2+}) of the metal ion [26].

Additionally, the effect of nitroaromatics on the dansyl fluorescence in DMF polymer solution (10.3 mg L^{-1} DnsSA-co-DA) has been evaluated by fluorescence measurements against increasing concentration of each organic compound such as nitrobenzene, o-nitrophenol, p-nitrotoluene, dinitro-m-xylene and picric acid. Thus, the gradual addition of p-nitrobenzene in polymer solution suppressed the fluorescence emission up to 89.4% (16.6×10^{-4} M), but the shape of the emission bands did not change during the quenching process (Fig. 6a), for which the limit concentration was around 0.33×10^{-4} M. Under these conditions, p-nitrotoluene induced a more pronounced quenching of the dansyl fluorescence (92.6% at 9.0×10^{-4} M) and the limit concentration was almost the same as that in the case of nitrobenzene. When o-nitrophenol was present in the solution, the fluorescence intensity decreased to 89.5% (13.0×10^{-4} M), whereas the value generated of dinitro-m-xylene was of 88.86% (13.66×10^{-4} M). Again, the fluorescence and especially the monomer form were found to be strongly quenched by picric acid up to 70% at a lower concentration (17.6×10^{-5} M). Meanwhile, in the last case the monomer emission maximum was bathochromically shifted (40 nm) and this could be mainly related to complexation by acrylic copolymer with covalently linked semicarbazidedansyl fluorophore, when used together with picric acid in organic solution. Analyzing this finding it is obviously that the fluorescence response of the DnsSA-co-DA interaction with nitroaromatic compounds indicated comparable abilities of some of them, fact reflected of the quenching efficiency which decreased in the order: picric acid > p-nitrotoluene > o-nitrophenol ≥ dinitro-m-xylene > nitrobenzene. The data obtained by performing a Stern–Volmer analysis in each case are shown in Fig. 6b, where relatively linear plots between concentration of quencher and I_0/I for DnsSA-co-DA can be observed. In interpreting these observations, we can reasonably assume that quenching of florescence of the dansylated copolymer occurred through an electron transfer from the fluorophore in the excited state to nitroaromatics. By considering these observations it can be concluded that in the photochemical process the structure of quenchers and especially, the effects of steric shielding responsible for reagent accessibility towards fluorophore are not interconnected through the occurrence of a thermodynamically allowed charge-transfer to a closer unit.

As expected, the addition of nitroaromatics in solution of DnsSA-co-MMA produced effects similar to those reported above, reason for that all these structures could be operated as quencher agents (around 80%), but in the next order: p-nitrotoluene > nitrobenzene > dinitro-m-xylene ≥ picric acid > o-nitrophenol. Contrary to what happens by adding of nitroaromatics in the polymer solution, the quenching process of dansyl units was not detected in the presence of nitromethane and such effect may be attributed to specific changes in the microstructure of solution or in the probe surrounding. This is in accordance with data reported for a dansyl-based film sensor [27].

Concerning both the polymers in $CHCl_3$ solution (Fig. 7), the obtained results indicated that the excimer fluorescence of dansyl is quenched up to 68% (DnsSA-co-DA) and to 48%, respectively (DnsSA-co-MMA) by nitrobenzene (20×10^{-4} M), while over a certain concentration (44.6×10^{-4} M), the quencher efficiently quenched the fluorescence only in the latter copolymer (73%).

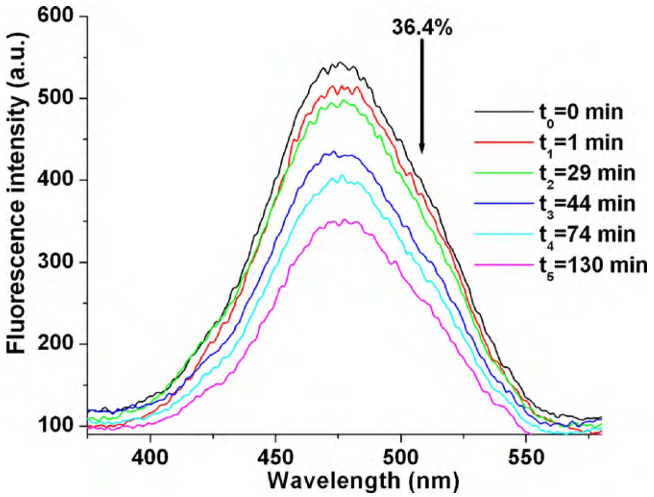


Fig. 8. Fluorescence spectra of DnsSA-co-DA film in the absence and presence of nitrobenzene in atmosphere after different period of time (λ_{ex} = 300 nm).

Obviously, the nitroaromatics had a higher degree of fluorescence quenching in a solvent with high polarity.

In another experiment, thin polymeric films were prepared to be investigated in the light of above results. Fluorescence spectrum of polymer DnsSA-co-DA in thin film showed that the fluorescence emission was bathochromically shifted with a single band at 476 nm. Polymer DnsSA-co-MMA displayed a similar emission in film (484 nm) and this emission spectrum suggests that aggregation takes place in the solid state. Following then the behavior of polymer films exposed to the saturated vapors of nitrobenzene it was observed that indeed, after 130 min of exposure, the fluorescence intensity of DnsSA-co-DA film decreased with time up to 36% (Fig. 8). When the latter film was exposed to vapors, the fluorescence quenching attained a maximum value of 12.5% (after 75 min), without to increase further. Moreover, a reversible process was found after few hours of standing of the films into clean atmosphere, and this behavior is reflected in the fluorescence spectra where the fluorescence again was restored to its initial profile. One difficulty in extending the data for films is that we have no direct proof of the assumption that these may be used in aqueous solutions containing various metal ions, because the observed effect seems to be negligibly small (5% quenching). This difference in sensitivity may be due to the additional factors which play an important role in the sensing aspects of the films to analyte concentrations in aqueous solution. To gain deeper insight for the photophysical process occurring in the film state further investigations are in progress in our laboratory.

4. Conclusions

A new dansyl semicarbazide-containing acrylate was prepared and further copolymerized free radically with N-dodecylacrylamide or methyl methacrylate, in order to demonstrate the potential of our approach for developing copolymers with dansyl pendant to be used in monitoring the metal ions and nitroaromatic derivatives in organic medium and less in film state (excepting nitrobenzene). The results suggested that the presence of a hydrophobic side alkyl chain in the fluorescent copolymer improves its molecule sensing ability.

Acknowledgement

Thanks to the Ministry of Research and Education for the financial support of this work by a project from The National Plan of Research & Development-PNII (IDEI Program: project no. 78/1.10.2007).

References

[1] W. Pfleiderer, S. Matysiak, F. Bergmann, R. Schnell, Acta Biochim. Pol. 43 (1996) 37–44.
[2] Hollaender, Surf. Interface Anal. 36 (2004) 1023–1026.
[3] K.J. Shea, D.Y. Sasaki, G.J. Stoddard, Macromolecules 22 (1989) 1722–1730.
[4] J. Gonzalez-Benito, J.C. Cabanelos, J.A. Aznar, M.R. Vigil, J. Bravo, J. Baselga, J. Appl. Polym. Sci. 62 (1996) 375–384.
[5] J. Gonzalez-Benito, A. Aznar, J. Baselga, J. Fluoresc. 11 (2001) 307–314.
[6] S. Pagliari, R. Corradini, G. Galaverna, S. Sforza, A. Dossena, R. Marchelli, Tetrahedron Lett. 41 (2000) 3691–3695.
[7] S. Pandey, G.A. Baker, M.A. Kane, N.J. Bonzagni, F.V. Bright, Chem. Mater. 12 (2000) 3547–3551.
[8] H. Li, J.P. Kang, L.P. Ding, F.T. Lü, Y. Fang, J. Photochem. Photobiol. A: Chem. 197 (2008) 226–231.
[9] M. Berton, F. Mancin, G.P. Stocchero, P. Tecilla, U. Tonellato, Langmuir 17 (2001) 7521–7528.
[10] S. Deo, H.A. Godwin, J. Am. Chem. Soc. 122 (2000) 174–175.
[11] M. Vehse, B. Liu, L. Edman, G.C. Bazan, A.J. Heeger, Adv. Mater. 16 (2004) 1001–1004.
[12] Y. Zheng, Q. Huo, P.F. Kele, M. Andrepoulos, S.M. Pham, R.M. Leblanc, Org. Lett. 3 (2001) 3277–3280.
[13] Y. Yan, M.L. Myrick, Anal. Chem. 71 (1999) 1958–1962.
[14] F. Vögtle, S. Gestermann, C. Kauffmann, P. Ceroni, V. Vicinelli, V. Balzani, J. Am. Chem. Soc. 122 (2000) 10398–10404.
[15] H. Ikeda, M. Nakamura, N. Ise, N. Oguma, A. Nakamura, T. Ikeda, F. Toda, A. Ueno, J. Am. Chem. Soc. 118 (1996) 10980–10988.
[16] M. Montalti, L. Prodi, N. Zaccheroni, J. Mater. Chem. 15 (2005) 2810–2814.
[17] B. Bednar, Z. Li, Y. Huang, L.C.P. Chang, H. Morawetz, Macromolecules 18 (1985) 1829–1833.
[18] E.C. Buruiana, M. Zamfir, T. Buruiana, J. Polym. Sci. A: Polym. Chem. 46 (2008) 3774–3782.
[19] E.C. Buruiana, T. Buruiana, V. Pohoata, J. Photochem. Photobiol. A: Chem. 180 (2006) 150–156.
[20] E.C. Buruiana, T. Buruiana, L. Hahui, J. Photochem. Photobiol. A: Chem. 189 (2007) 65–72.
[21] E.C. Buruiana, T. Buruiana, G. Strat, M. Strat, J. Photochem. Photobiol. A: Chem. 162 (2004) 23–31.
[22] E.C. Buruiana, M. Zamfir, T. Buruiana, Eur. Polym. J. 43 (2007) 4316–4324.
[23] E.C. Buruiana, M. Olaru, B.C. Simionescu, Eur. Polym. J. 43 (2007) 1359–1371.
[24] N.A. O'Connor, S.T. Sakata, H. Zhu, K.J. Shea, Org. Lett. 8 (2006) 1581–1584.
[25] J. Yin, X. Guan, D. Wang, S. Liu, Langmuir 25 (2009) 11367–11374.
[26] Q. Miao, X. Huang, Y. Cheng, Y. Liu, L. Zong, Y. Cheng, J. Appl. Polym. Sci. 111 (2009) 3137–3143.
[27] K. Jianping, D. Liping, L. Fengting, Z. Shujuan, F. Yu, J. Phys. D: Appl. Phys. 39 (2006) 5097–5102.