

Thin films from hydrophilic poly(N,N-dimethyl acrylamide) copolymers as optical indicators for humidity

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Abstract. In the present paper we study thin films from poly(N,N-dimethyl acrylamide)-poly(ethylene oxide) (PDMAA/PEO) copolymers of different composition and structure in order to implement them as sensitive media for optical indicators for humidity. PDMAA/PEO di- and triblock copolymers were synthesized via redox polymerization in aqueous media. Thin films were deposited on silicon substrates by spin coating method using polymers solutions with appropriate concentrations. Refractive index, extinction coefficient and thickness of the films are calculated from reflectance spectra of the films deposited on silicon substrates using non-linear curve fitting method. Sensing properties of the films were tested by films exposure to different humidity levels followed by *in-situ* monitoring of the changes in the optical properties. The influence of the polymer structure and postdeposition annealing on the optical and sensing properties of the films was investigated. The potential application of selected polymers for optical sensing of humidity were demonstrated and discussed.

1. Introduction

The quantity of water vapors found in the air can vary drastically from almost zero to the point of saturation. Low or high humidity, or changes in-between, can harm sensitive materials and objects, affect many manufacturing processes in industries or disturb human comfort. Traditional humidity sensors are generally resistive and capacitive one based on the electrical measurement. Despite some recent progress in room temperature sensing [1-4], generally electric sensors suffer from high working temperature and lack of selectivity. Besides, most of the traditional sensors have relatively low accuracy due to the cross-temperature feature. In recent years an optical sensing of humidity emerges as an alternative approach. It offers simplicity of detection, room temperature detection, high accuracy and sensitivity, and immunity to electromagnetic interference or explosion danger. Various measuring scheme have been developed so far that operate on the basis of fibre-optic technology [5-10], surface plasmon resonance [11], microring resonator and whispering modes [12-14], Fabry-Perot resonances [15, 16], holographic grating [17, 18], photonic crystals [19, 20], etc. Great variety of materials that change their refractive index, extinction coefficient or thicknesses are implemented as sensitive media: tungsten disulfide [6], SiO₂ nanoparticles [7], porous SiO₂ [11], undoped and dye doped polyvinyl alcohol [8, 15], polyimide [9], agarose gel and hydroxyethylcellulose / polyvinylidene fluoride [10], elastic polymer SU-8 [12], poly(acrylic acid) / polyethyleneimine polymers [13], polyacrylamide



microfiber rings [14], chitosan [16], undoped and zeolite doped self-developed polyacrylamide / poly(vinyl alcohol) photopolymer [17, 18], alternating thin films of titania and poly(2-hydroxyethyl methacrylate-co-glycidyl methacrylate) (PHEMA-co-PGMA) [19], PHEMA and epoxy based resist [20], self-assembled poly(styrenesulfonate-methylbutylene) (PStS-b-PMB) block copolymers with tailored hygroscopic properties [21], graphene oxide [4]. Among them, polymers are receiving considerable attention because of the tailored functionality, easy deposition and relatively low cost. When they are prepared in thin film form they offer additionally fast response due to the short diffusion path length.

In this study we have chosen poly(N,N-dimethyl acrylamide) (PDMAA) because it is a hydrophilic polymer well known for its biocompatibility and good mechanical and film-forming properties [22]. PDMAA is less polar than polyacrylamide and hence highly soluble in water as well as in large number of organic solvents. Therefore strong swelling can be expected when exposed to water vapors. We expected that the combination of PDMAA with another hydrophilic polymer such as poly(ethylene oxide) will extend further their ability for water sensing.

In this paper we propose and demonstrate experimentally the optical sensing ability of hydrophilic poly(N,N-dimethyl acrylamide) / poly(ethylene oxide) block copolymers. The optical and sensing properties of spin-coated films are studied as a function of postdeposition annealing temperature (60 °C, 120 °C and 180 °C) and relative humidity (5% RH and 95 % RH). The implementation of films as active media for color indicators for humidity is demonstrated and discussed.

2. Experimental part

2.1. Synthesis of PDMAA and PEO-PDMAA copolymers

The monomer N,N-dimethylacrylamide (DMAA) and the initiator diammonium cerium(IV) nitrate were purchased from Sigma-Aldrich (Germany). Poly(ethylene oxide) methyl ether (PEO-ME) and poly(ethylene oxide) (PEO) both of molar mass 2000 g/mol were supplied from Fluka (Switzerland). The solvents and other reagents used were of standard laboratory reagent grade.

Double hydrophilic di- and triblock copolymers were synthesized by means of redox polymerization of DMAA in deionized water when using 3.3 g/L PEO-ME or respectively PEO as initiating moiety. The reaction mixture was purged with nitrogen for 30 min at ambient temperature and the initiator diammonium cerium (IV) nitrate (0.01 equiv. in respect to the PEO precursor) was added. The polymerization was carried out at 35 °C under nitrogen atmosphere and the obtained copolymers were purified by dialysis against water and finally isolated by freeze-drying. The reaction schemes of the synthetic procedures are shown in figure 1.

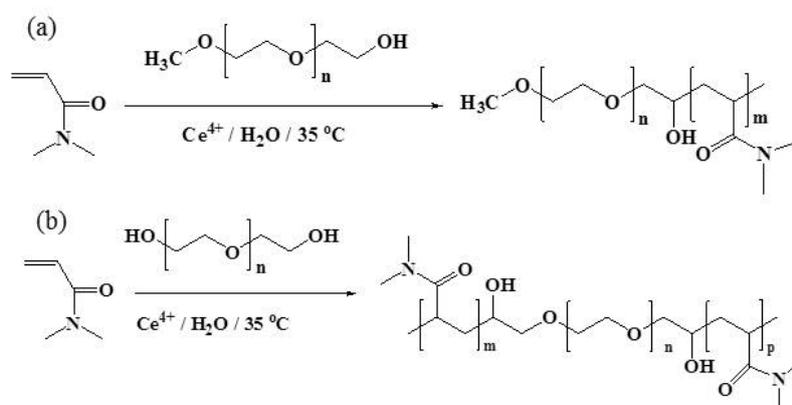


Figure 1. Reaction schemes of the synthesis of double hydrophilic block copolymers: (a) PEO-*b*-PDMAA; and (b) PDMAA-*b*-PEO-*b*-PDMAA.

PDMAA homopolymer was synthesized by aqueous free radical polymerization of DMAA initiated by 4,4-azobis (4-cyanovaleric acid) (ABCVA). The reaction was carried out at 60 °C under nitrogen atmosphere for 6 hours. The reaction mixture was evaporated and the obtained polymer was purified by precipitation from dichloromethane in cold diethyl ether.

The structure and composition of the prepared copolymers were analyzed by Nuclear Magnetic Resonance (NMR). The molar masses were calculated based on the integrated proton spectra when comparing the integrals of the signals of PEO and PDMAA repeating units. The compositions and molar masses (M_n) of diblock and triblock copolymers were PEO₄₅-*b*-PDMAA₃₇, $M_n = 5700$ g/mol and PDMAA₂₈-*b*-PEO₄₅-*b*-PDMAA₂₈, $M_n = 7500$ g/mol, respectively.

2.2. Thin film deposition and characterization

Polymer solutions of concentration 0.5 wt. % were prepared. PDMAA and PEO-*b*-PDMAA were dissolved in methanol-water mixture (80:20 volume ratio), while chloroform was used as a solvent for PDMAA-*b*-PEO-*b*-PDMAA. Thin films were deposited by the method of spin coating by dropping 0.2 ml of the polymer solutions onto preliminarily cleaned Si-substrates and spinning at a rate of 3000 min⁻¹ for 30 s. Prior to characterization all films were subjected to annealing at temperatures of 60 °C, 120 °C and 180 °C for 30 min.

Optical constants (refractive index, n and extinction coefficient, k) along with film thickness, d were determined through non-linear curve fitting of reflectance spectra measured at normal light incidence by UV-VIS-NIR spectrophotometer (Cary 5E, Varian) [23]. The experimental errors for the three parameters, n , k and d were 0.005, 0.003 and 2 nm, respectively.

The humidity sensing performance was evaluated by measuring the reflectance spectra of the films at relative humidity (RH) of 5% and 95% using homemade bubbler system for generation of vapors from liquids [24]. The predetermined humidity levels were established in the measuring cell through flow of dry argon in the case of 5 % RH and flow of argon saturated with water vapors for reaching 95% RH. The measured reflectance spectra at both humidity levels were further used for determination of n , k and d of the films.

3. Results and discussion

The dispersion curves of the refractive index of the studied polymer films for three different postdeposition annealing temperatures (60 °C, 120 °C and 180 °C) are calculated from the measured reflectance spectra of the films [23] and are presented in figure 2. All films exhibit normal dispersion, i.e refractive index decreases with wavelength, that can be expected considering that films are transparent in the studied spectral range. The values of the extinction coefficient (k) vary in the ranges $k=0.007 - 0.015$. For all studied polymers there is no change of film thickness at 60 °C, while for 120 °C and 180 °C a decrease is observed for both di- and triblock polymers and no change for PDMAA films. For (PEO-*b*-PDMAA) the thickness changes from 61 nm (60 °C) to 49 nm at 120 °C and reaches value of 46 nm at 180 °C, while for PDMAA-*b*-PEO-*b*-PDMAA thin films d decreases from 90 nm at 60 °C to 87 nm and 77 nm for 120 °C and 180 °C, respectively.

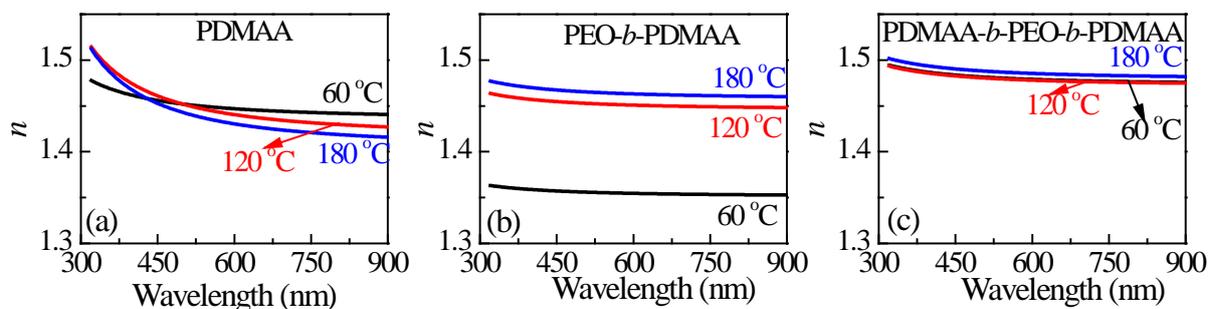


Figure 2. Refractive index of PDMAA (a), PEO-*b*-PDMAA (b) and PDMAA-*b*-PEO-*b*-PDMAA (c) thin films as a function of wavelength at denoted postdeposition annealing temperatures.

The dependences of n and k (at wavelength of 600 nm) on the annealing temperature are displayed in figure 3. It is seen that the post deposition annealing influences in a different way the optical properties of polymer films. A decrease in n for PDMAA films is observed starting from 1.457 (60 °C), going through 1.440 (120 °C) and finally reaching 1.430 (180 °C), while for PEO-*b*-PDMAA and PDMAA-*b*-PEO-*b*-PDMAA films n increases substantially in the first case — starting from 1.355 going through 1.451 and reaching 1.463, and slightly for the second one: from 1.479, through 1.478 to 1.485 (all values are for wavelength of 600 nm).

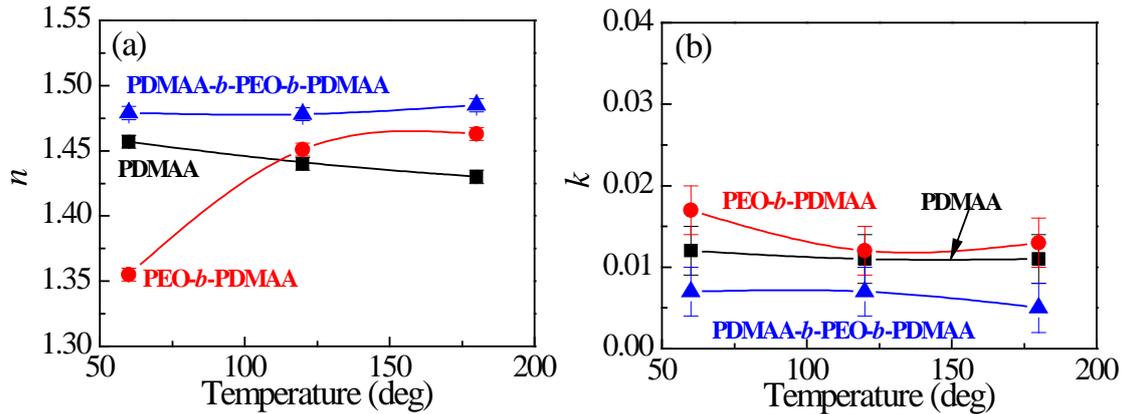


Figure 3. Refractive index (a) and extinction coefficient (b) at wavelength of 600 nm with respective errors as a function of post deposition annealing temperature.

Usually the postdeposition annealing leads to densification of the films due to the removal of residual solvent and consequent contraction of the film that is consistent with the reduction of film thickness. This is the possible reason for optical behavior of PEO-*b*-PDMAA and PDMAA-*b*-PEO-*b*-PDMAA films where n increases at higher annealing temperatures due to the increase of film density. It is seen from figure 3(a) that the change is mostly pronounced for diblock copolymer films that have been prepared using methanol:water mixture as solvent as compared to triblock copolymer films prepared using the more volatile compound (chloroform). The observed decrease in n for PDMAA thin films indicates no contraction of the film with temperature that is confirmed with the obtained similar values for the thickness at different temperatures. Thus the removal of residual solvent accompanied with no contraction lead to an increase of free volume of the film and decrease of its effective refractive index.

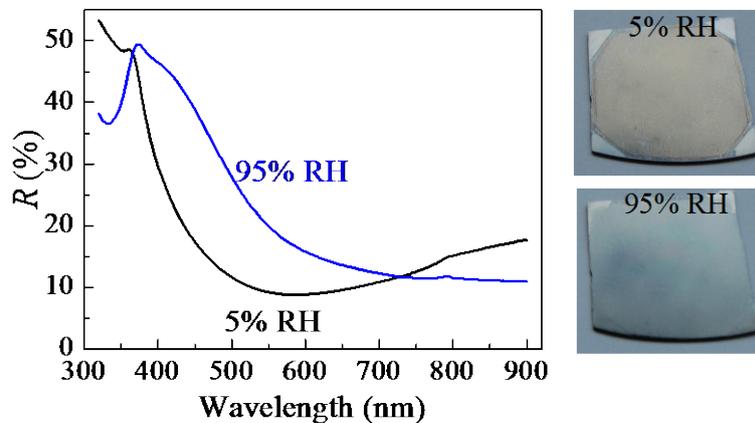


Figure 4. Reflectance spectra of PDMAA-*b*-PEO-*b*-PDMAA thin film measured at relative humidity of 5% and 95% and pictures of respective sample at denoted humidity.

According to the extinction coefficient, there is no dependence on the annealing temperature, or on the polymers structure. The k -values vary from 0.007 for the triblock copolymer films to 0.011 and 0.012 for PDMAA and diblock copolymer, respectively and are almost the same in the framework of the experimental errors (Fig. 3(b)).

Figure 4 presents the typical example for the sensing experiments. The reflectance spectra of the film (PDMAA-*b*-PEO-*b*-PDMAA is chosen for illustration) are measured at two different levels of relative humidity, 5% RH and 95% RH, supplied by the bubbler system explained elsewhere [24]. At high humidity there is a significant red shift of the spectra that leads to a considerable change of the color of the film from light brown to light blue. The change of the color is instant and reversible. This means that there is no condensation of water inside the film; otherwise the film will be destroyed from the local dissolution of the polymer. Therefore no increase of refractive index can be expected due to replacement of air inside the film with water. Then the swelling of polymer is the only reason for the observed red shift.

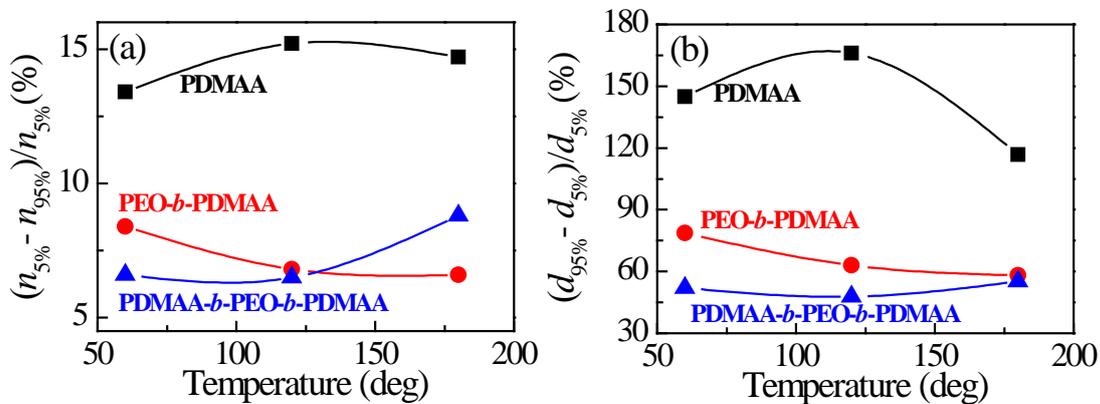


Figure 5. Relative change in refractive index (a) and thickness (b) of denoted thin polymer films due to exposure to relative humidity from 5% RH to 95% RH as a function of temperature of postdeposition annealing.

Reflectance spectra of all films are measured and the change of refractive index and thickness are calculated using already developed programs [23]. The results are shown in figure 5 as a function of postdeposition treatment. For all films there is a decrease in n and increase in d when relative humidity changes from 5% to 95% RH. The strongest humidity response is obtained for PDMAA films annealed at 120 °C: n and d change with 15% and 166%. However compared to the homopolymer, the block copolymers offer possibility to improve the film properties particularly by optimizing macromolecular characteristics and block copolymer architecture (linear, branched, graft, etc.) which will be explored in the following studies of team. For PEO-*b*-PDMAA films the strongest response of n (8.4%) and d (79%) are obtained at 60 °C, while for PDMAA-*b*-PEO-*b*-PDMAA the preferred treatment is annealing at 180 °C where the changes in n and d are 8.8% and 55.1%, respectively. As expected significant swelling of all polymers is obtained that is accompanied with decrease of n due to the density reduction. The increase of relative humidity leads to an increase of extinction coefficient mostly pronounced for PDMAA films, where k changes almost twice - from 0.011 to 0.021.

It is also worthwhile to note that PEO homopolymer films have also been investigated. However the thin films are unstable and even small amounts of humidity present in the air dissolved them.

Conclusion

The successful application of thin films of poly(N,N-dimethyl acrylamide) copolymers as optical indicators for humidity is demonstrated. The change in humidity from 5% to 95% RH leads to color change of films that can be detected by naked eye. The color change is due to significant film swelling

resulting in red shift of the reflectance spectra minimum. The swelling is also accompanied with decrease of refractive index owing to the reduction of film density. It is revealed that the structure and annealing temperature influence in different ways the optical response of polymer films. The highest changes are obtained for PDMAA films annealed at 120 °C where the thickness increases from 59 nm to 157 nm while the refractive index decreases from 1.47 to 1.25 (the values are for wavelength of 600 nm). However, the copolymers' performance can be improved considerably by optimization of the molar mass, chemical composition and structure, etc. The easy preparation, good sensitivity and fast response of hydrophilic poly(N,N-dimethyl acrylamide) copolymers provide promising opportunity for their application as optical indicators for humidity.

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