



From solutions to porous film: Influence of the media on fluorescent acridine end-capped polystyrene photophysical properties



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ABSTRACT

Nitroxide-mediated radical polymerization (NMP) was used to synthesize polystyrene (PS) in the presence of N-tert-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl)nitroxide (SG1) as a control agent and the BlocBuilder[®] alkoxyamine as an initiator. The α -telechelic carboxylic acid PS was further functionalized by the fluorescent 9-aminoacridine moiety (9AA) to synthesize α -functional fluorescent polystyrene (PS-9AA). The 9-aminoacridine end-capped PS was characterized by size exclusion chromatography, two dimensional heteronuclear multiple-bond correlation nuclear magnetic resonance and fluorescence spectroscopy. The PS-9AA α -telechelic polymer was used to prepare fluorescent continuous and porous polymer films *via* the Breath Figure (BF) method. The fluorescence properties of PS-9AA in solution were compared to the corresponding one in the continuous and porous polymer films.

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1. Introduction

Polymer films with ordered porous structures have gained increasing scientific interest due to their potential applications such as photo-active surfaces or materials for (bio)sensors, electronic/fluorescent flexible films, or photonic iridescent biomimetic surfaces [1–6]. In 1994, Widawski et al. first reported the highly ordered porous film formation using the Breath Figure (BF) technique [7]. Since 1994, it has emerged from literature that this formation is favored by complex polymer architectures [1–5,8–10], BF is also mainly an interesting process for inducing preferential positioning of the polymer polar functions at the surface of the pores leading to functional porous polymer films [11–16]. Our group recently took advantage of this property to design photo-active structured porous films from Rose Bengal-based polystyrene [17]. The grafted Rose Bengal proved to be an efficient photosensitizer to produce singlet oxygen under irradiation that catalyzed photo-oxidation of organic molecules in the presence of the porous substrate [17].

The present work aims at investigating the impact of the surrounding matter (polarity of solvent, presence of covalently linked polymer or structured porous polymer film) on the photophysical properties of the 9-aminoacridine fluorescent probe. To achieve this goal, the α -carboxylic acid end-capped linear polystyrene (PS-COOH) will first be synthesized by nitroxide-mediated radical polymerization (NMP) using a carboxylic acid-based alkoxyamine [18–20]. Secondly, the fluorescent end-functionalized polystyrene will be synthesized by amidification of PS-COOH with 9-aminoacridine (9AA) prior to characterization of the functional polymer by 2-dimensional HMBC NMR and electronic spectroscopy. The choice of 9-aminoacridine molecule was driven by two criteria: its molecular structure (*i.e.* fluorescent nitrogen heterocyclic bases, see Fig. 1) allowing chemical modification of PS-COOH and its intrinsic photophysical properties. The photophysical and photochemical properties of this chromophore and its derivatives have been extensively investigated for applications in biological and materials fields [21–24].

The photophysical properties, and especially the fluorescence lifetimes, of grafted fluorophores might be useful to probe the local environment and the polymer structuration, as well as to develop fluorescence lifetime assays [25]. It may be noted that the preparation of luminescent porous films has been previously reported [26–28], but the photo-physical properties of the corresponding

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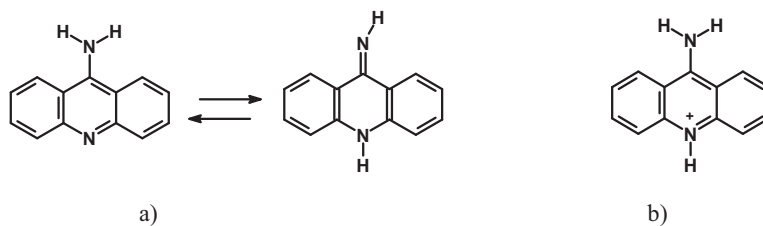


Fig. 1. (a) Neutral and (b) monoprotonated forms of 9-aminoacridine (9AA).

polymer have never been studied neither in solution nor into the films.

In the present work, the absorption, excitation and emission spectra together with the photosensitizer lifetime of the well-defined fluorescent polystyrene end-capped with 9-aminoacridine will be thoroughly compared: (i) in solution with different organic solvents, (ii) in non-porous polymer films and (iii) in porous films prepared by the fast BF process (Scheme 1).

2. Experimental

2.1. Materials

Styrene (S, Sigma Aldrich, >99%), tetrahydrofuran (THF, VWR PROLABO), 9-aminoacridine (9AA, Sigma Aldrich, >99%), N,N'-dicyclohexylcarbodiimide (DCC, Fluka, $\geq 99\%$), N-hydroxysuccinimide (NHS, Fluka, $\geq 97\%$), carbon disulfide (CS₂, Aldrich, $\geq 99.9\%$), dichloromethane (CH₂Cl₂, stabilized with 0.2% of ethanol, VWR PROLABO), chloroform (CHCl₃, Sigma Aldrich), were used as received. N-(2-methylpropyl)-N-(1-dimethylphosphono-2,2-dimethylpropyl)-O-(2-carboxylprop-2-yl)hydroxylamine MAMA BlocBuilder[®] was kindly provided by Arkema.

2.2. Synthesis of polystyrene with carboxylic chain end (PS-COOH)

Synthesis of the PS-COOH is reported. The BlocBuilder[®] alkoxyamine (0.331 g, 0.875 mmol) was added to a 25 mL round bottom flask containing styrene (18.202 g, 175 mmol). The mixture was degassed for 20 min prior immersing the round bottom flask into an oil bath set at 115 °C for 3 h. After 3 h, the flask was transferred into an ice bath to stop the reaction. Styrene conversion was calculated by analyzing the crude sample by nuclear magnetic resonance (conversion = 39%). PS-COOH was collected by precipitation drop by drop into 500 mL of ethanol, then filtered under vacuum by Büchner.

2.3. Functionalization of PS-COOH by 9-aminoacridine (PS-9AA)

PS-COOH was then functionalized by 9AA in two steps: PS-COOH (0.7 g, 13.2 mmol, 1 eq.), DCC (0.023 g, 11 mmol, 1.2 eq.), NHS (0.019 g, 11 mmol, 1.2 eq.) were introduced into a 50 mL round bottom flask. The mixture was subjected to nitrogen bubbling for 10 min, then 22 mL of dry THF was added to the flask. The flask was then placed in an oil bath at 50 °C for 72 h and stirred at 500 rpm. The product was precipitated in 200 mL ethanol to remove the impurities. The precipitate was then filtered by Büchner and dried under vacuum.

9AA (0.022 g, 11 mmol, 1.2 eq.) was added to the product in a 50 mL round bottom flask and subjected to nitrogen bubbling for 10 min, and then 22 mL of dry THF was added. The flask was placed in an oil bath at 50 °C for 144 h and stirred at 500 rpm. Drop by drop precipitation was performed 3 times in 200 mL ethanol, with 15 min centrifugation at 3000 rpm after each precipitation. After

the removal of free 9AA, the functionalized PS-9AA was collected and dried under vacuum for 24 h.

2.4. Preparation of porous films

The porous films were prepared by casting 5 drops of a polymer solution (5 g L⁻¹ in carbon disulfide) onto a glass substrate at 20 °C under a humid air flow (flow rate of 20 cm³ s⁻¹, 55% of relative humidity). The films were obtained within 30 s due to the high volatility of the solvent.

2.5. Preparation of continuous films

The continuous films were prepared by casting 5 drops of a polymer solution (5 g L⁻¹ in tetrahydrofuran) onto a glass substrate at 20 °C in the absence of any humid air flow.

3. Characterization methods

3.1. Nuclear magnetic resonance (NMR) spectroscopy

Proton, carbon and heteronuclear multiple-bond correlation (HMBC) spectra were recorded in deuterated chloroform as a solvent using a Brüker 400 MHz spectrometer at 25 °C.

3.2. Size exclusion chromatography (SEC)

Characterization of all the polymers samples was performed by using THF solvent as an eluent with a flow rate of 1 mL min⁻¹. The SEC was equipped by a refractive index detector and an ultraviolet detector (used at 404 nm wavelength which is the absorption wavelength of 9AA). The polymer samples were prepared at 5 g L⁻¹ concentration and filtered through a PTFE 0.45 μm filters.

3.3. Optical microscopy

Pictures were taken in reflection with a Leica DM/LM microscope using a 50× dry objective and a Leica DFC280 video camera. Standard image processing was performed with the Image Manager IM50 software. The 2-dimensional fast transform was performed with the 2D FFT function available in Igor Pro[®] software.

3.4. Absorption spectroscopy

The absorption spectra were recorded at room temperature with a double beam Cary 5000 spectrophotometer in steps of 0.5 nm in the range 250–800 nm using a 1 cm quartz optical cell (Hellma). The diffuse reflectance spectra of the films were measured with a Perkin-Elmer 860 spectrophotometer fitted with a 15 cm diameter integrating sphere with the sample holder in the bottom horizontal position. They were recorded at room temperature in steps of 1 nm, in the range 250–800 nm with a bandwidth of 2 nm. The instrument was calibrated with a certified Spectralon white standard (Labsphere, North Sutton, USA).

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