Polymer Chemistry

Cite this: *Polym. Chem.*, 2012, **3**, 2619

www.rsc.org/polymers

PAPER

A photoresponsive fluorescent glycopolymer†

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Received 29th May 2012, Accepted 17th June 2012
DOI: 10.1039/c2py20375h

Herein we report a new photoresponsive amphiphilic glycopolymer, poly(pyrenylmethyl methacrylate)-*b*-poly(3-*O*-4-vinylbenzoyl-D-glucopyranose) (PPy-*b*-PBG), synthesized *via* atom transfer radical polymerization (ATRP). The aggregation behaviour of PPy-*b*-PBG was investigated in dilute aqueous solutions by dynamic light scattering and fluorescence spectroscopy. Formation of spherical aggregates was observed in solutions under controlled conditions due to the amphiphilic nature of the polymer. The presence of strong pyrene excimer emission in aqueous solution indicated the aggregation of pyrene units. Irradiation of these glycosomes with UV light resulted in the photo-solvolysis of 1-pyrenylmethyl esters accompanied by the disruption of the polymer aggregates due to the hydrophilic nature of the residual polymer. The morphology of the polymer aggregates before and after UV irradiation was examined by AFM, SEM and TEM. Encapsulation of hydrophobic Nile Red molecules by the glycosomes resulted in successful fluorescence modulation and UV irradiation resulted in the controlled release of the entrapped dye into water.

1. Introduction

The self-assembly of amphiphilic building blocks in aqueous solution has attracted great attention of interdisciplinary scientists due to the possibility of attaining well-defined nanostructures such as micelles and vesicles with unique physical and chemical properties.[1–7] Supramolecular assembly in such materials is controlled by a fine balance between various non-covalent interactions.[8–12] Compared to low-molecular-weight molecules, block copolymer aggregates offer advantages and broaden their potential for technological applications in a variety of areas, such as in biology, colloid science, and encapsulation technology.[13–17] In bulk, the immiscibility of the constituent blocks leads to microphase separation with the formation of a variety of nanoscale periodic patterns including spheres, cylinders, bicontinuous phases, and lamellae, with sizes comparable to the chain dimensions.[18–20] When these block copolymers are dispersed in a selective solvent, micellar aggregates are formed. These aggregates are very similar to those formed by the low-molecular-weight surfactants.[21–24] The resultant micellar structures are stabilized in solution through the interactions of the soluble block with the solvent molecules.[25,26]

Currently, research on polymeric micelles capable of responding to external stimuli has been very active as these materials can be effectively used as delivery vehicles for controlled encapsulation and release.[14,27–31] Polymer micelles or vesicles have been classified according to the stimuli to which they respond. Compared to pH or redox responsive micelles/vesicles, light responsive materials offer the advantage, in the controlled release of encapsulated molecules, that no extra chemical substances are needed to induce the response. Moreover, light provides a very broad range of tunable parameters, *e.g.*, wavelength, duration, and intensity, which can be modulated in the potential applications.[32] A suitable chromophore can be incorporated into these molecules to render them susceptible to external stimuli, which is desirable for controlled delivery application, by using UV light as an external trigger.[33–40]

Recently, increasing attention has been paid to synthetic polymers containing pendant saccharide moieties (so called glycopolymers) as biological recognition signals.[41–44] Two general methods for synthesizing glycopolymers involve either polymerizing a carbohydrate based monomer[45–47] or post-functionalization of a polymer with a saccharide.[48–50] In both cases, exquisite control over chain-length and carbohydrate density over the back-bone can be attained by making use of atom transfer radical polymerization (ATRP).[51–53] Synthetic carbohydrate polymers with biocompatible and biodegradable properties are now increasingly used in tissue engineering and control drug-delivery applications.[54,55] Many of them are also used as surfactants,[56] biologically active polymers[57] and for investigating glycopolymer–protein interactions.[58] Recently Pasparakis and Alexander reported self-assembling glycopolymer vesicles that can communicate with bacterial cells through a glycocode as well as through dye molecules that were previously placed in the vesicles.[59]

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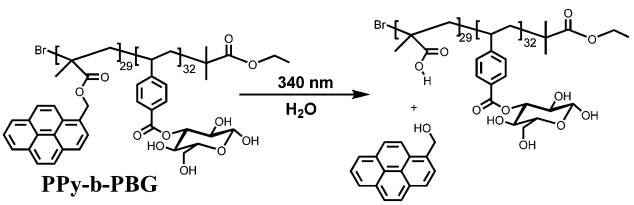
† Electronic supplementary information (ESI) available: Materials and methods, synthetic steps and characterization details of PPy-*b*-PBG, AFM and TEM images of PPy-*b*-PBG aggregates. See DOI: 10.1039/c2py20375h

In this report, by making use of ATRP we have successfully synthesized a well-defined photoresponsive amphiphilic block copolymer containing photolabile poly(pyrenylmethyl methacrylate) as the hydrophobic block and poly(3-*O*-4-vinylbenzoyl-D-glucopyranose) as the hydrophilic block. The resultant polymer has 29 Py and 32 BG units. Introduction of glucose segments into the hydrophilic block can impart biocompatibility[41–44] whereas hydrophobic pyrenylmethyl methacrylate can incorporate photoresponsivity to the block copolymer.[37,39] It was expected that this block copolymer could self-assemble into ordered aggregates in solution. UV light irradiation of an aqueous solution of this block copolymer results in the photo-solvolysis of pyrenylmethyl ester giving rise to 1-pyrenemethanol, which converts the hydrophobic PPy block into hydrophilic poly(methacrylic acid) (PMA). UV irradiation results in the chemical transformation of the initial amphiphilic block copolymer into a double hydrophilic block copolymer thereby solubilizing the polymer and precipitating the cleaved 1-pyrenemethanol. Thus photo-solvolysis was expected to bring about a decrease in the overall hydrophobicity of the resultant block copolymer, thereby resulting in the disruption of the polymer aggregates. Such a property would make the polymer a useful candidate for controlled release systems. Scheme 1 demonstrates this strategy.

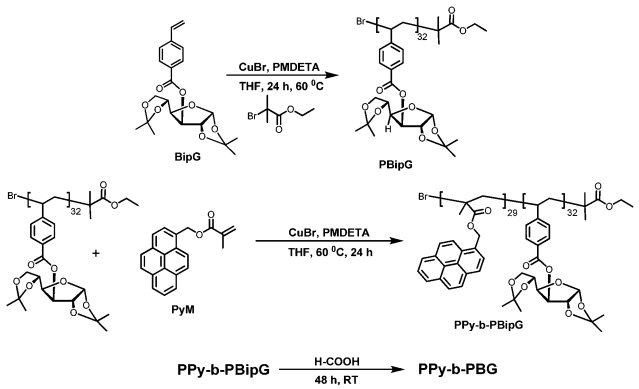
2. Results and discussion

Synthesis and characterization of PPy-*b*-PBG

Scheme 2 outlines the synthesis of the diblock copolymer PPy-*b*-PBG. The isopropylidene group protected glucose monomer BipG was polymerized under ATRP conditions using CuBr/PMDETA with ethyl 2-bromoisobutyrate at 60 °C in THF for 24 hours. The number-average molecular weight (M_n) of PBipG as determined by conventional GPC was 12 297 which corresponds to 32 BipG units and the polydispersity index (PDI) was 1.19. Copolymerization of PyM was conducted using CuBr/PMDETA with PBipG as the macroinitiator at 60 °C in THF for 24 hours. The resultant polymer PPy-*b*-PBipG had a M_n value of 21 194 and a PDI value of 1.46. Fig. 1 shows the GPC trace of PPy-*b*-PBipG together with that of the homopolymer PBipG. It can be seen that the molecular weight of PPy-*b*-PBipG shifts towards the high molecular weight region without any trace of the low molecular weight macroinitiator. This shows that PBipG is effective in copolymerizing PyM to give a well-defined diblock copolymer PPy-*b*-PBipG. The polydispersity, however, increases slightly during the second polymerization stage. The diblock copolymer PPy-*b*-PBipG was purified by reprecipitating three times from THF into methanol. The resulting polymer PPy-*b*-PBipG was composed of 29 units of Py and 32 units of BipG.



Scheme 1 Chemical structure of PPy-*b*-PBG and its photo-solvolysis under UV light irradiation.



Scheme 2 Synthesis of PPy-*b*-PBG.

The molecular weight and the comonomer composition of the copolymer determined by GPC using linear polystyrene standards are just the apparent ones due to the compact nature of branched macromolecules and lack of suitable standards. A more reliable value for the Py content in the copolymer obtained by ATRP could be obtained from the ^{1}H NMR spectra by comparing the peaks at 0.69 ppm attributed to the three methyl protons of the PPy segment and the peak at 6.40 ppm corresponding to the aromatic protons of PBipG segment (Fig. 2b). The content of Py as determined by ^{1}H NMR was found to be 43 units. Copolymers with variable amounts of PPy can be obtained by varying the feed ratio. Reactivity of Py was found to be greater than that of its precursor PBipG which is probably due to the higher reactivity of methyl methacrylate when compared with that of styrene.[60]

Hydrolysis of the isopropylidene groups in PPy-*b*-PBipG was performed by treating the samples with formic acid as reported elsewhere.[45] The final product PPy-*b*-PBG was obtained by freeze-drying following dialysis of the deprotected polymer against distilled water. The structures of the polymers PBipG, PPy-*b*-PBipG and PPy-*b*-PBG were confirmed by ^{1}H NMR. Fig. 2 shows the ^{1}H NMR spectra of the respective polymers. The characteristic peaks at 1.2–1.4 (isopropyl protons), 6.3–6.5 (aromatic protons), 7.4–7.7 ppm (aromatic protons) are clearly seen in PBipG. In the case of the copolymer PPy-*b*-PBipG, besides the signals of the PBipG segment, the PPy signals appear at 5.1–5.3 attributable to methylene protons and at 7.2–7.6 ppm corresponding to the pyrene aromatic protons. This confirmed

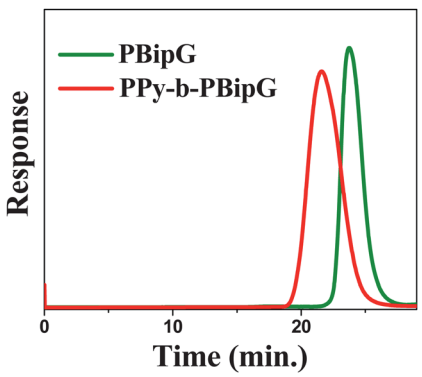


Fig. 1 GPC (in THF) curves of PPy-*b*-PBipG and the corresponding precursor PBip.

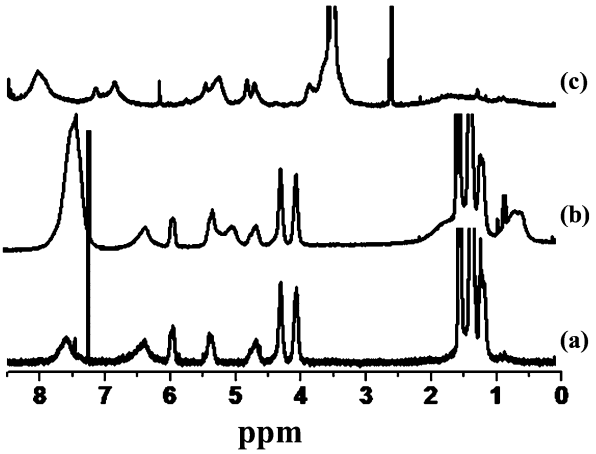


Fig. 2 ^{1}H NMR spectra of (a) PBipG in $CDCl_3$ (b) PPy-*b*-PBipG in $CDCl_3$ and (c) PPy-*b*-PBG in DMSO-d_6 at room temperature.

the presence of both PPy and PBipG blocks in the resultant copolymer. The structure of the deprotected polymer could be determined by ^{1}H NMR in DMSO-d_6. Fig. 2c reveals that the signals of the isopropylede protons (1.2–1.4 ppm) completely disappear after the hydrolysis of PPy-*b*-PBipG and a broad signal corresponding to the anomeric hydroxyl groups of the sugar moieties (6.5–7.0 ppm) appears. This indicates the quantitative deprotection of the isopropylidene protecting groups. PPy block could not be clearly observed in the ^{1}H NMR spectrum of PPy-*b*-PBG in DMSO-d_6 which indicates that the PPy block is strongly aggregated in DMSO-d_6.

Morphological investigation of PPy-*b*-PBG aggregates

To study the aggregation behavior of the PPy-*b*-PBG block copolymer in water, 1 mg of the dried block copolymer was dissolved in 1 mL of DMF. To this, 1 mL of deionized water was added at a rate of 500 μL h^{-1} with gentle stirring. When the addition of this water was complete, 10 mL of water was added quickly to quench the aggregates. The sample was then put into a dialysis bag (molecular weight cut: 3500) and dialyzed against deionised water for 2 days to remove DMF. The solution was filtered through a 0.45 μm filter (Millipore Millex-HV) before use. DLS measurements of the resultant solution showed the presence of well-defined spherical particles with an average diameter of 473 nm with a PDI of 0.094. Fig. 3 shows the size distribution of PPy-*b*-PBG in water.

Photoinduced formation and disruption of polymer aggregates were confirmed by AFM, SEM and TEM. For AFM and SEM measurements part of the micellar solution after dialysis was drop-cast on a mica sheet and dried. Another part of the solution was exposed to UV light for 2 hours and then drop-cast and dried on a mica sheet. Fig. 4 and 5 show the AFM and SEM images obtained from the two solutions respectively. Spherical aggregates with an average diameter of 500 nm were observed in the AFM images of the dried film obtained from the solution unexposed to UV light. SEM images revealed that these spherical aggregates are hollow, as seen from the images of the broken aggregates, probably formed under high vacuum conditions during SEM analysis, which indicated that these spherical

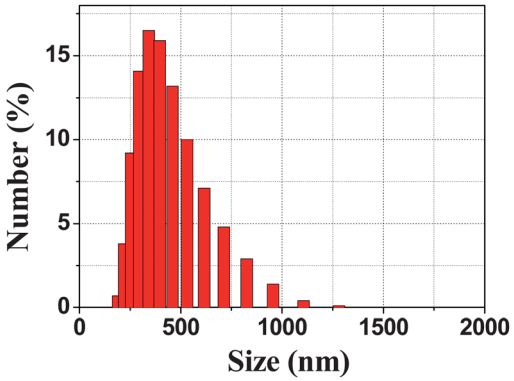


Fig. 3 Size distribution of PPy-*b*-PBG aggregates in water.

aggregates are, in fact, vesicles. In contrast no aggregates were observed in the dried film obtained from the solution which was exposed to UV light for 2 hours. TEM images of the aggregates confirmed the vesicular nature of these aggregates as there was a clear contrast difference between the core and the periphery of the aggregates (Fig. 6).

The above results clearly confirmed that glycosomes (glycopolymer vesicles) formed from the diblock copolymer PPy-*b*-PBG become unstable and get dissociated when the colloidal solution was exposed to UV light. This instability arises from the photo-solvolysis reaction resulting in the conversion of PPy block to PMA block resulting in a substantial increase in the overall hydrophilicity of the polymer.

Investigation of the aggregation behavior of PPy-*b*-PBG using fluorescence spectroscopy

Photochemical cleavage of pyrene entities from PPy-*b*-PBG was confirmed by fluorescence spectroscopy. Fig. 7 shows the decrease in fluorescence of the colloidal solution of PPy-*b*-PBG in water following irradiation. As seen from the figure, aqueous solution of the diblock copolymer PPy-*b*-PBG showed a very

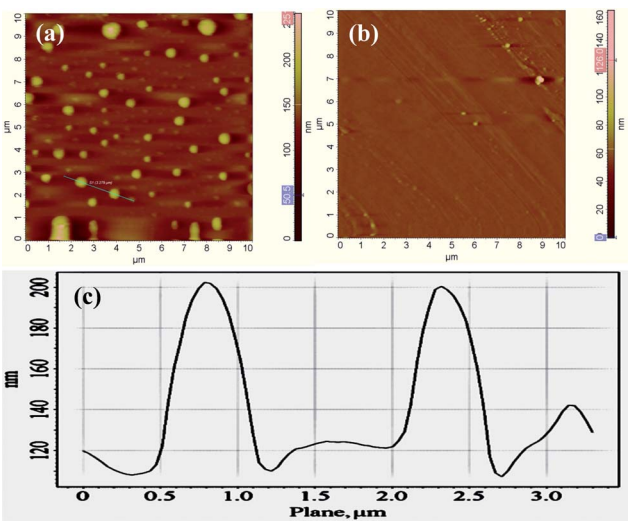


Fig. 4 (a) AFM image of the air-dried PPy-*b*-PBG aggregates obtained from the aqueous suspension before UV irradiation, (b) AFM image obtained after 2 h of UV irradiation and (c) height profile of the aggregates.

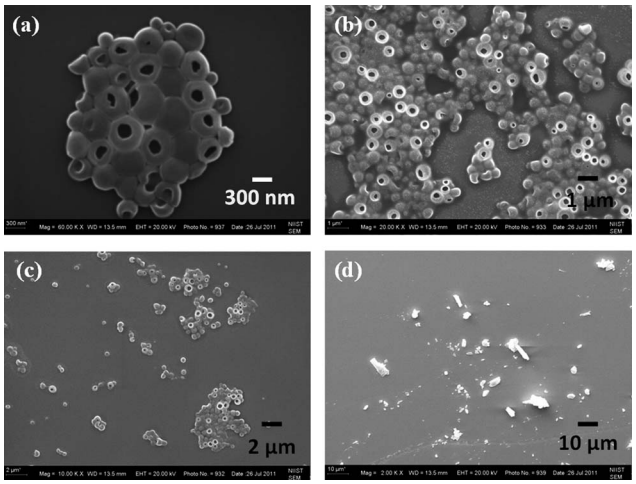


Fig. 5 (a, b and c) SEM images of the air-dried PPy-*b*-PBG aggregates obtained from the aqueous suspension before UV irradiation and (d) SEM image obtained after 2 h of UV irradiation.

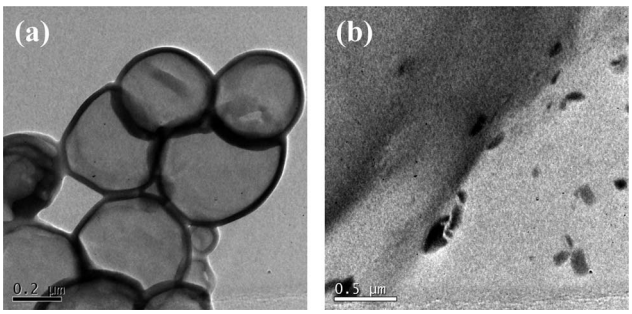


Fig. 6 (a) TEM image of the air-dried PPy-*b*-PBG aggregates obtained from aqueous suspension before UV irradiation and (b) TEM image obtained after 2 h of UV irradiation.

strong excimer emission at about 486 nm with negligible monomer emission. This indicates that the pyrene units are tightly held in the aggregated state of PPy-*b*-PBG. Following UV irradiation, however, there was a dramatic decrease in excimer emission with a slight increase in monomer emission around 380–410 nm. Since the byproduct of the photosolvolysis reaction *i.e.* 1-pyrenemethanol is sparingly soluble in water we observe only a slight increase in the pyrene monomer emission. These results clearly confirm the photosolvolysis reaction which results in the cleavage of pyrene moieties from the polymer main chain thereby disrupting the micellar structure.

The ability of PPy-*b*-PBG to encapsulate hydrophobic dyes and release them was also demonstrated using Nile Red. Fig. 8 shows the extent of overlap between the absorption spectra of Nile Red in THF and the emission spectra of PPy-*b*-PBG in water. Since there is good overlap between the absorption spectra of Nile Red and emission of PPy-*b*-PBG it was felt that a non-radiative energy transfer process between the PPy-*b*-PBG donor and Nile Red acceptor would be effective after dye encapsulation.

In order to encapsulate Nile Red inside PPy-*b*-PBG aggregates, 1 mg of the copolymer and 0.1 mg of Nile Red were first dissolved in 1 mL of DMF. The solution was gently stirred and 1 mL of deionised water was added into it at a rate of 500 μL h^{-1}. When the addition of this water was complete, 10 mL water was added quickly to quench the aggregates. Then the sample was put into a dialysis bag (molecular weight cut: 3500) and dialyzed against deionised water for 2 days and filtered before use. When the Nile Red encapsulated solution was excited at 350 nm the solution showed a strong emission at 655 nm corresponding to that of Nile Red with a drastic decrease in the excimer emission of pyrene. Irradiation with UV light results in cleavage of 1-pyrenemethanol and simultaneous release of encapsulated Nile Red. Since both compounds are water insoluble a dramatic decrease in the fluorescence emission occurs. Fig. 9a indicates the fall in the emission of a Nile Red encapsulated colloidal solution of PPy-*b*-PBG during UV irradiation. Fig. 9b shows the fluorescence emission spectra of the colloidal solution with encapsulated Nile Red before and after UV light exposure (excitation wavelength, 350 nm); for comparison, the emission spectrum of the colloidal solution without Nile Red, prepared under the same conditions, is also shown in Fig. 9b.

Emission of Nile Red from dye loaded PPy-*b*-PBG aggregates could also be observed by directly exciting the dye at its absorption maxima. The absorption spectra of the dye encapsulated colloidal solution exhibited a peak at 561 nm which corresponds to the absorption of Nile Red trapped inside the polymer aggregates. Irradiation with UV light resulted in a fall in

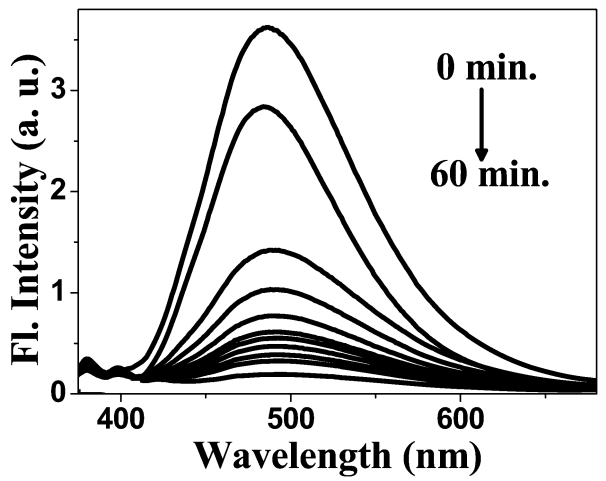


Fig. 7 Change in fluorescence emission spectra of PPy-*b*-PBG in water, following UV irradiation.

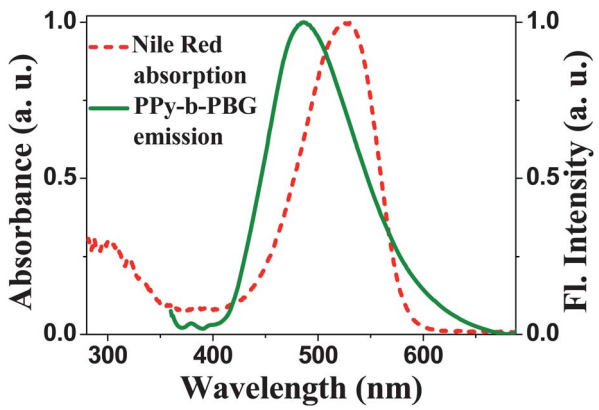


Fig. 8 Comparison of the absorption spectra of Nile Red in THF with the fluorescence spectra of PPy-*b*-PBG in water.

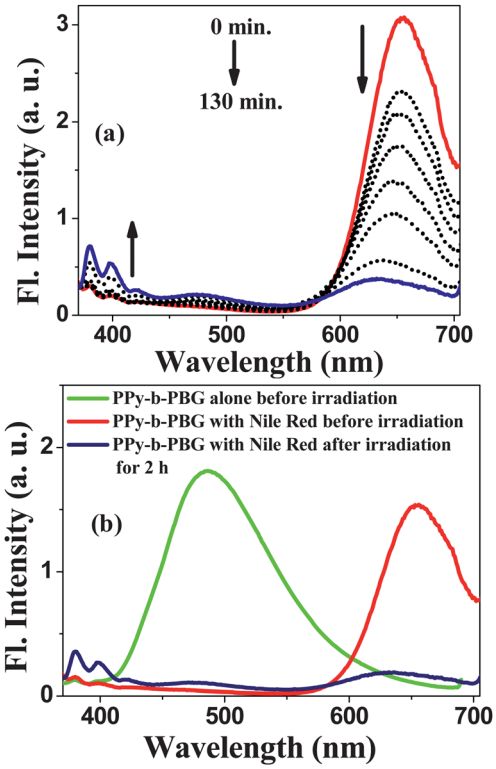


Fig. 9 (a) Changes in the fluorescence emission spectra ($\lambda_{ex} = 350$ nm) of Nile Red loaded polymer aggregates in water upon UV irradiation and (b) fluorescence emission of the Nile Red encapsulated aggregate solution compared with that of the non-encapsulated solution.

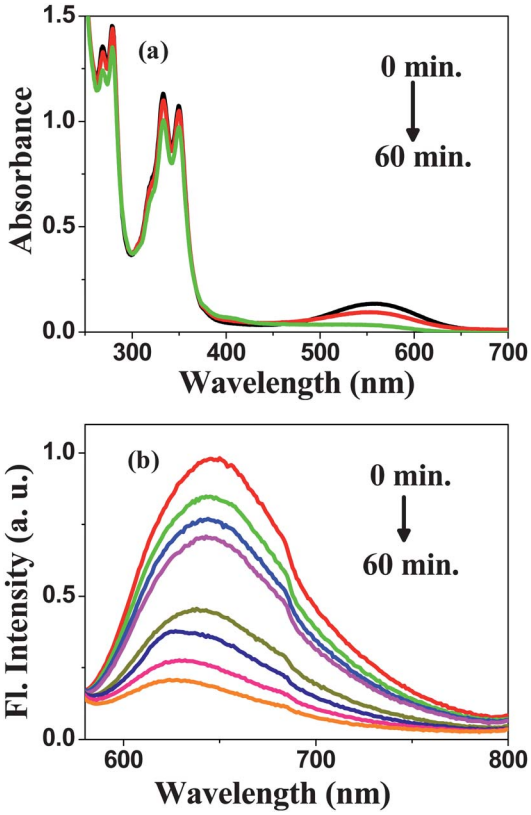


Fig. 10 (a) Changes in the absorption spectra of Nile Red loaded polymer aggregates in water upon UV irradiation and (b) changes in the fluorescence emission spectra ($\lambda_{ex} = 550$ nm) of Nile Red upon UV irradiation of Nile Red loaded polymer aggregates in water.

the absorption dye due to its release into water (Fig. 10a). Similarly, upon excitation at 561 nm, the dye encapsulated solution emitted at 647 nm which kept on decreasing upon continued UV irradiation with a concomitant release of dye into water (Fig. 10b).

The excitation spectra of the Nile Red loaded solution indicated that the Nile Red emission was maximum when the solution was excited at the absorption maxima of pyrene (Fig. 11a). Thus excitation spectra provided additional evidence for the encapsulation of Nile Red by the glycosomes. Fig. 11b shows a photograph of an aqueous solution of PPy-*b*-PBG before and after Nile Red encapsulation. This decrease in the excimer emission of pyrene upon Nile Red encapsulation is indicative of fluorescence resonance energy transfer (FRET) taking place from pyrene to Nile Red. The FRET process requires that the emission band of the donor overlaps with the absorption band of the acceptor and the distance between them should be within the Förster distance which is usually 15–60 Å.[61,62] Since the excimer emission band (415–650 nm) of pyrene overlaps well with the absorption band (420–600 nm) of Nile Red, energy transfer from pyrene excimer to Nile Red is possible provided they are in close proximity with each other. Thus FRET is indicative of the encapsulation of Nile Red by the hydrophobic PPy block. Irradiation with UV light results in cleavage of 1-pyrenemethanol and simultaneous release of encapsulated Nile Red. Since both compounds are water insoluble a dramatic decrease in the fluorescence emission occurs. The Nile Red fluorescence intensity at 655 nm decreases exponentially with irradiation time (See Fig. S5 of ESI†). It was found that the Nile Red loaded polymersomes were stable in the absence of UV light for up to six months as there was no

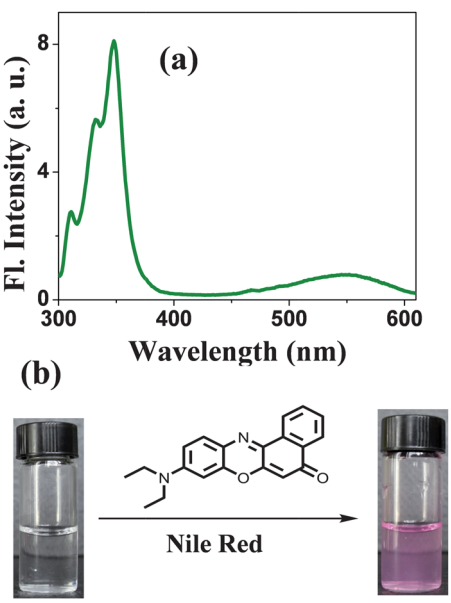


Fig. 11 (a) Fluorescence excitation spectra (emission collected at 655 nm) of Nile Red loaded polymer aggregates in water and (b) photograph showing an aqueous solution of PPy-*b*-PBG; (left) without Nile Red and (right) in the presence of Nile Red.

appreciable decrease in Nile Red fluorescence intensity during this period. The stability of the vesicles was also checked using DLS and microscopic analysis which confirmed that there was no detectable change in the size of the particles during storage even up to a period of six months.

3. Conclusions

In conclusion, we have synthesized a novel photoresponsive fluorescent glycopolymer which can form well-defined uniform spherical aggregates in water. Irradiation with UV light brings about a decrease in hydrophobicity of the polymer which results in breakage of polymer aggregates. These amphiphilic block copolymer aggregates have the property of encapsulating hydrophobic dyes in their core which can be subsequently released upon UV irradiation. This property makes PPy-*b*-PBG a good candidate for a light-sensitive nanodevice having tunable encapsulating properties. They can also act as scaffolds for the FRET process which make them useful for biological sensing and cellular imaging.

Acknowledgements

Research grants from the Department of Science and Technology (DST), India and the Council of Scientific and Industrial Research Task Force Program (NWP 23) are gratefully acknowledged. We thank Dr Bhoje Gowd, E. for his valuable suggestions. We also thank Dr J. D. Sudha for GPC, Mr C. K. Chandrakanth for SEM and Mr Kiran Mohan for TEM measurements. This is contribution no. PPD-320 from NIIST-PPG. S. M. thank UGC, Government of India for research fellowships.

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