Aggregation and photoresponsive behavior of azobenzene–oligomethylene–glucopyranoside bolaamphiphiles[☆]

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Abstract

The self-aggregation behavior of a series of photoresponsive bolaamphiphiles consisting of a central azobenzene moiety linked to terminal sugar groups via oligomethylene spacers in water/DMSO mixed solvents are reported. Changes in the absorption spectra in these solvent mixtures indicated the formation of tightly packed H-aggregates. The ease of formation and the stability of the aggregates were observed to increase with increase in the length of the oligomethylene spacers. Microscopic studies indicated the formation of vesicles or fibers depending upon the length of the oligomethylene spacers. Disruption of the aggregates induced by photoisomerization of the azobenzene unit and their reformation via the subsequent thermal *cis* to *trans* isomerization was also investigated.
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Keywords: H-Aggregates; Bolaamphiphiles; Photoisomerization; Self-assembly

1. Introduction

Bolaamphiphiles (bolas) have been receiving increasing attention in recent years in view of their potential to form a variety of supramolecular architectures and biomimetic materials [1–3]. Interest in bolaamphiphiles arises mainly from the fact that they can simulate the architecture of monolayered membranes of Archaebacteria in the manner of placement of their hydrophobic and hydrophilic parts [2]. Archaebacteria are microorganisms capable of surviving extreme conditions such as high salt concentration or high temperatures [4]. An interesting feature of naturally occurring lipids found in Archaebacteria is the high proportion of glycosylated structures [5]. This aspect as well as the ability of sugars present in the glycocalix of biomembranes to participate in intracellular recognition processes and thus induce affinity for target cells [6], has motivated several groups to synthesize and study supramolecular assemblies of sugar derived bolas [7–10].

The strength of supramolecular assemblies of amphiphilic molecules can be enhanced by introducing various assembling units, which can self-aggregate via different non-covalent interactions [1,11–14]. Introduction of mesogenic units into amphiphiles is known to substantially stabilize nanostructures obtained from them [1,4,15,16]. As a part of our ongoing studies on investigating the correlations between molecular structure and self-assembly of molecules containing photoresponsive mesogenic units [17–20], we report here a detailed study on the self-aggregating properties of a series of sugar-based bolaamphiphiles [20] (Scheme 1), in which the sugar moieties are linked to an azobenzene chromophore via oligomethylene spacers. The presence of azobenzene chromophore in self-assembling materials is known to impart unique photoswitchable properties to them [21–26]. In the present manuscript, the role of the oligomethylene spacers and π-stacking ability of the azobenzene chromophore, as well as the effect of the *trans* to *cis* photoisomerization and the subsequent thermal *cis* to *trans* isomerization of the azobenzene chromophore in controlling the nature of

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azo-bis 5: n = 3   **azo-bis 8**: n = 6   **azo-bis 10**: n = 8
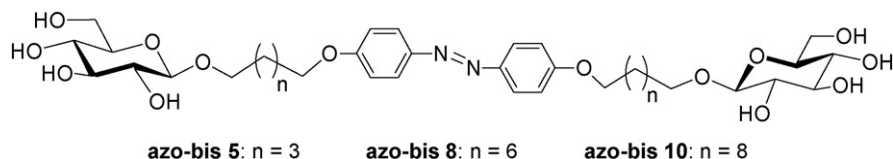
Scheme 1.

the supramolecular aggregates formed in solutions have been investigated.

2. Experimental

2.1. Materials and methods

Ultraviolet–visible (UV–vis) and circular dichroism (CD) spectra were recorded in quartz cuvettes. UV–vis spectra were recorded on a Shimadzu UV-2401 PC UV–vis scanning double beam spectrophotometer. CD spectra were recorded in the Jasco J-810 spectropolarimeter equipped with Jasco PTC-423S Peltier type temperature control system. (1S)-(+)-10-Camphorsulfonic acid, ammonium salt (0.06% aqueous solution, 1 cm light path) was used for calibration of the spectropolarimeter sensitivity and wavelength (CD = +190.4 mdeg at 291.0 nm). The CD exciton couplet amplitude was calculated as $A_{CD} = CD_{first\ Cotton}$ (at the long-wavelength maximum of the couplet) $- CD_{second\ Cotton}$ (at the short-wavelength maximum) [27,28]. The CD spectra obtained were similar in stirred and un-stirred sample solutions. Contribution from linear dichroism (LD) was negligible since the aggregate solutions placed at different angles had no effect on the type of Cotton effect and the solutions were clear at the temperatures studied. ^{1}H NMR experiments were carried out in a 300 MHz Bruker Avance DPX or a Bruker Avance DRX 500 spectrometer equipped with a Bruker BVT 3000 digital temperature controller. TMS was the internal standard and spectra were recorded without sample spinning. At higher D$_2$O volumes, the residual proton resonance in DMSO was used for calibration since the TMS peak was difficult to locate. The *trans* to *cis* photoisomerization in DMSO solution was investigated by irradiating with 364 nm monochromatic light isolated from a 450 W ozone free Xe lamp using the excitation monochromator of SPEX Fluorolog-2. Laser irradiation was carried out with 355 nm laser pulses (10 Hz, 6 ns pulse width) from a Spectra-Physics Quanta-Ray GCR-12S Nd:YAG laser. GC–MS analysis was carried out in a Shimadzu GC–MS QP 2010 analyzer. CHN analysis was carried out in a Carlo-Erba 1106 elemental analyzer.

Size distribution measurements of aggregates in solution were performed in a Malvern Instruments Nano-ZS by dynamic light scattering (DLS) employing a 633 nm He–Ne laser. Each experiment was repeated three times and the data was averaged.

Atomic force microscopy (AFM) was performed under normal atmosphere using tapping and contact mode probes on a Digital Instruments NanoScope IV MultiMode scanning probe microscope (tapping mode—model: Veeco RTESP/material: phosphorus (n) doped silicon, resonance frequency of 299 kHz and a spring constant of 20–80 Nm^{-1}; contact mode—model:

Veeco NP-20/material: silicon nitride). The samples for AFM studies were obtained by drop-casting and air-drying aggregate containing solutions on freshly cleaved mica. Blank experiments were conducted with only solvent mixtures on freshly cleaved mica to rule out any artefacts. Transmission electron microscope, TEM bright-field images were obtained using a Hitachi H-600 instrument operating at an accelerating voltage of 75 kV with sample solutions drop-cast and air-dried on copper grids (mesh 200) having a formvar carbon support film. Scanning electron microscope, SEM (signal: SEI) images were obtained using the JEOL JSM-5600 LV at 10 kV with the samples drop-cast and air-dried on a flat surface of cylindrical brass stubs and coated with gold in a JEOL JFC-1100 ion sputter, prior to viewing.

Solvents were of spectroscopy grade. Water was doubly distilled and deionized (resistivity of 18.2 MΩ cm) using a Millipore Milli-Q-Plus water purifier. The solutions containing aggregates were prepared from stock solutions of compounds in DMSO. To a constant volume pipetted out from the stock solution, various volume fractions of DMSO/water were added.

Aggregates were spontaneously formed upon adding non-solvent to the stock solution of azo-bola, without the need for ultrasonication or any other special treatment. The solutions containing aggregates exhibited a slight blue hue due to the scattering of white light. The percentages of water/DMSO mentioned in the text refer to volume percentage of water. On adding water to DMSO solutions of the compounds, exothermicity ($\Delta H = -715$ cal mol^{-1} for 0.36 mol fraction DMSO in water at 22–25 °C) [29], caused the solutions to warm up. The solutions were left to equilibrate at room temperature for 1 h after preparation before carrying out further studies.

2.2. Synthesis

The synthesis, characterization and thermotropic liquid crystalline properties of the azo-bolas have been reported by us [20]. The synthesis and detailed characterization of the model compound 10,10′-[(1E)-Azobis(4,1-phenyleneoxy)]bis[1-decanol] is provided in the electronic supplementary material (See the Electronic Supplementary Material).

3. Results

3.1. Spectroscopic characterization of supramolecular aggregates in solution

3.1.1. UV–vis and CD measurements

The azo-bolas were highly soluble in DMSO and practically insoluble in water. Fig. 1 shows the absorption spectra of 2.5×10^{-5} M solutions of azo-bis 10 in water/DMSO solvent
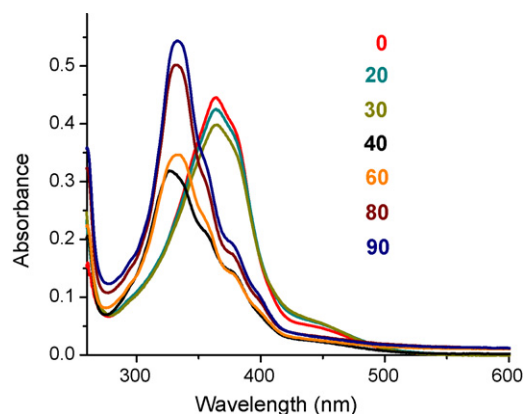
Fig. 1. Effect of varying water content on the UV–vis spectra of azo-bis 10 in water/DMSO solvent mixtures (2.5×10^{-5} M). Volume percentage of water in the solvent mixture is indicated in the figure.

Fig. 2. Effect of varying water content on the CD spectra of azo-bis 10 in water/DMSO solvent mixtures (2.5×10^{-5} M; solutions in pure DMSO and solvent mixtures containing up to 30% water were CD silent). Volume percentage of water in the solvent mixture is indicated in the figure.

mixtures with varying water content. In pure DMSO, azo-bis 10 exhibited a typical azobenzene monomer absorption spectrum [14,30,31] with a weak $n \rightarrow \pi^*$ transition at 454 nm and an intense $\pi \rightarrow \pi^*$ transition moment along the long-axis (A band) at 364 nm. Increase of water content in these solutions resulted initially in a steady decrease in intensity and a blue shift ($\Delta\lambda_{max} = 31$ nm) of the main absorption band centered at 364 nm (Fig. 1).

With subsequent increase in water content, the blue shift was accompanied by an increase in intensity and narrowing of the band. In solvent mixtures containing 90% water, the full width at half-maximum was narrower than that of the corresponding monomer band by 658 cm^{-1}. Similar results were observed for azo-bis 8 (See the Electronic Supplementary Material). For azo-bis 5 however, only a slight decrease in the intensity of absorption and a small blue shift of 4 nm was observed in the water rich solvent mixtures (See the Electronic Supplementary Material). Formation of a blue shifted band by amphiphilic azobenzene derivatives in aqueous or water rich media is attributed to the formation of H-aggregates, which essentially consist of a "card pack" array of transition moments of the individual molecules [32]. The blue-shifted band of H-aggregated species is normally wider and less intense than the monomer band, as is indeed observed in most of the azobenzene derivatives hitherto investigated [33–38]. When the excitons are strongly coupled however, due to a high degree of ordering of the constituent molecules, a large hypsochromic shift of the band accompanied by an increase in intensity and narrowing of the band are observed [39,40]. Such aggregates are referred to as H*-aggregates, of which there are only very few reports in the literature [39,41].

The absorption band attributable to the aggregates was CD active indicating a chiral arrangement of the transition moments of the azobenzene segment within the aggregates. Fig. 2 shows the CD spectra of azo-bis 10 aggregates in the water/DMSO solvent mixtures. Whereas solutions of azo-bis 10 in pure DMSO was CD silent, a positive first Cotton effect and negative second Cotton effect was observed for solutions containing water, indicating a right-handed chiral arrangement of the transition moments of the azobenzene chromophores within the aggregates. The CD spectra were observed only when the
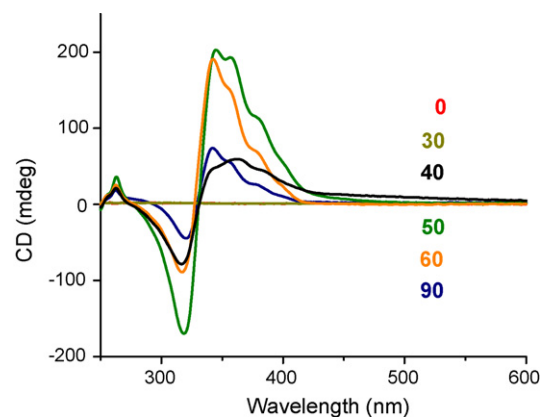
blue-shifted absorption spectrum attributable to the aggregate was present. The zero-crossing point was close to the absorption maximum of the aggregated chromophore, indicating the CD spectra to be due to the exciton coupling bands of the aggregate.

The tendency for aggregation of the azo-bolas was chain-length dependent. Whereas azo-bis 5 solutions were CD silent indicating a much lesser tendency to form strongly coupled H*-aggregates, onset of CD activity for azo-bis 8 occurred in 50% water/DMSO solutions. For azo-bis 10 the onset of CD activity was from solvents containing 40% water. In this context it is interesting to note that in bolaamphiphilic systems, where the terminal sugar molecules were linked to a central azobenzene via an arylamide unit [14], aggregation only resulted in a 15 nm blue shifted band of lower intensity. Thus the presence of the oligomethylene linker units of a suitable length was observed to be essential for the formation of the H*-aggregates.

3.1.2. Effect of temperature on the UV–vis and CD spectra

The formation of strongly coupled aggregates in azo-bis 10 was also indicated by the persistence of the aggregate band and CD acitivity at very high temperatures (Fig. 3). The blue shifted band exhibited a slight decrease in intensity and considerable broadening, indicating a weakening of the interaction among the azobenzene transition moments in the aggregate. Above 90 °C, however a considerable decrease in intensity and red shift in the band indicated break-up of the aggregate to the monomer form. Interestingly the CD amplitude (A_{CD}) increased by about 4.3 times on heating until the temperature reached 80 °C, after which a decrease was observed (Figs. 3b and 4). To the best of our knowledge, such an effect, namely increase in the CD intensity accompanied by broadening of the absorption band of the aggregate, is unprecedented. In general, for chiral supramolecular assemblies, the CD intensity decreases on heating [42,43]. A possible explanation for the observed results is schematically shown in Fig. 4. At room temperature, a near parallel face-to-face stacking of the transition moments of the H*-aggregates would be stabilized by intermolecular hydrogen bonding between the
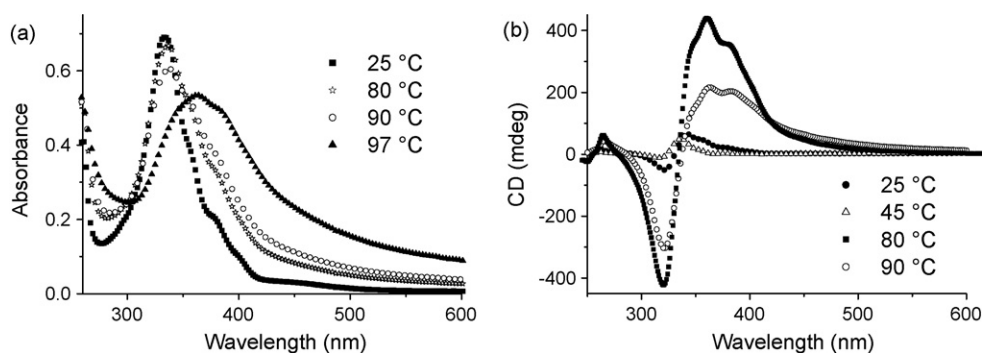
Fig. 3. Effect of temperature on (a) UV–vis spectra; (b) CD spectra of azo-bis 10 in 80% water/DMSO (2.5×10^{-5} M).

sugar groups. With increasing temperature, weakening of the intermolecular hydrogen bonding between the sugar moieties could result in a shift of the transition moments from a near parallel face-to-face stacking to a chiral arrangement (Fig. 4), resulting in broadening of the absorption band and enhancement in the CD intensity. It is known that the A_{CD} value is maximal when the angle of interacting moments is ~70° [27]. Further increase in temperature could result in the break-up of the aggregates leading to reduction in A_{CD} due to formation of the monomer.

Similar results were observed for azo-bis 8 (See the Electronic Supplementary Material), whereas azo-bis 5 solutions only a hyperchromic effect on the absorption spectrum was observed with increase in temperature (See the Electronic Supplementary Material), indicating break up of the weakly bound aggregates to the monomer form.

3.1.3. Proton NMR characterization of the aggregates

^{1}H NMR spectra of the aggregates were examined to gain further insight into the mode of molecular packing within the aggregates. Aggregation of molecules can make their motion anisotropic, and reduced rate of motion of molecular parts in solution can lead to long correlation times [44,45]. For the NMR studies, aggregation was induced by adding D_2O to a d_6-DMSO solution of azo-bis 8. The spectrum of azo-bis 8 in pure d_6-

DMSO displayed the expected resonances (Fig. 5a) [20,46]. On addition of D_2O a slight resonance broadening occurred in the aromatic ($\delta = 7.10$ and 7.82 ppm) and oligomethylene ($\delta = 1.21–1.83$ ppm) peaks. Further addition of D_2O, resulted in a coalescence of the aromatic doublets until finally the aromatic peaks collapsed and the region became featureless, indicating total loss of freedom of movement in the aromatic segment as a result of strong aggregation. The line broadening and decrease in intensity was much lesser for the oligomethylene peaks, indicating that this part of the molecules was less tightly packed within the aggregates, and retained considerable amount of their flexibility.

The onset of the collapse of the aromatic peaks in the NMR spectra on addition of D_2O was chain-length dependent. For a 16 mM solution of azo-bis 8 in d_6-DMSO, the aromatic peaks collapsed when the D_2O concentration reached 40%, whereas for an azo-bis 10 solution of the same concentration, the collapse occurred at a concentration of 30% D_2O. At high temperatures (>75 °C) the aromatic and oligomethylene resonances of azo-bis 8 and azo-bis 10 became well resolved indicating break-up of the aggregate.
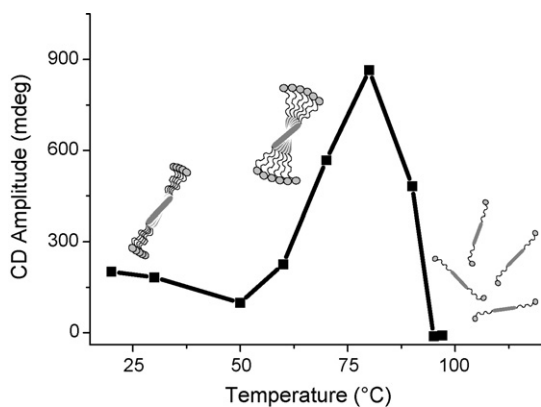

Fig. 4. Changes in CD amplitude with temperature of the azo-bis 10 aggregate in water/DMSO (For CD spectrum, see Fig. 3b). Also shown is a schematic representation of the probable arrangements of the molecules at various temperatures.
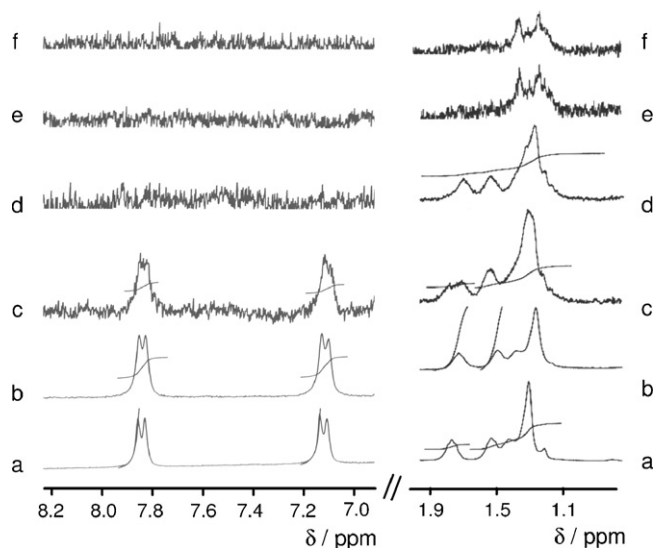

Fig. 5. ^{1}H NMR spectra of azo-bis 8 showing aromatic and oligomethylene protons: (a) in pure d_6-DMSO (16 mM); (b–f) changes upon adding D_2O in 100 μL increments ($T = 27$ °C).
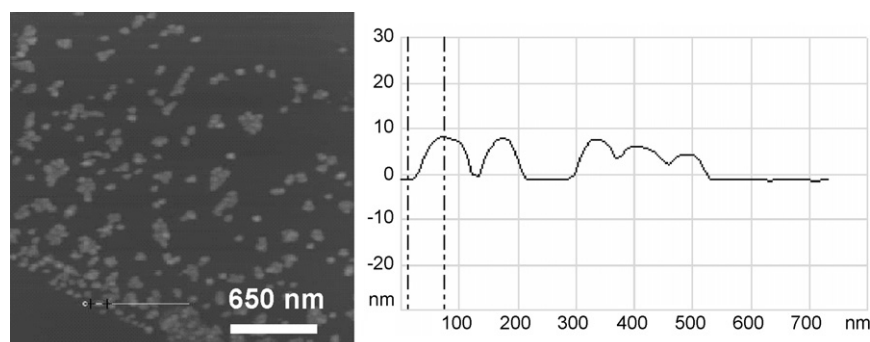
Fig. 6. Vesicles of azo-bis 8 (2.7×10^{-5} M) imaged by contact mode AFM and their cross-section analysis.

3.2. Morphology of the aggregates

Dynamic light scattering studies of solutions of azo-bis 8 in water/DMSO indicated the presence of polydisperse aggregates ranging from 200 nm to 1.5 µm (See the Electronic Supplementary Material). Microscopic (AFM, SEM and TEM) investigations of the solutions were carried out in order to visualise the morphology of the aggregates. AFM images of films deposited on mica by drop-casting 10^{-5} M solutions of azo-bis 8 in 90% water/DMSO indicated the presence of spherical aggregates existing singly as well as in the clustered state (Fig. 6). The spherical particles were also observed in the SEM images (Fig. 7a). The spherical particles were confirmed to be vesicles by TEM analysis which showed a clear electron contrast between the membrane and centre of the vesicles (Fig. 7b) [47–51]. The heights of the spheres estimated by cross-section analysis of the

AFM images were in the range of 8.2–9.4 nm which was equal to or little more than twice the length of the all *trans* form of azo-bis 8 ($l = 3.8$ nm). This is indicative of a bilayer stacking, which can occur in collapsed vesicles possessing a monolayer membrane structure.

Formation of vesicles was also observed in water/DMSO solutions of azo-bis 5 (See the Electronic Supplementary Material). For azo-bis 10 the morphology of the aggregates was found to be dependent on the method of preparation of the solution. Films deposited from solutions of azo-bis 10 in water/DMSO prepared under identical conditions, viz by adding water to DMSO solutions of the azo-bola, indicated the presence of fibers (Figs. 8a and 9a) instead of vesicles. Formation of fibers and tubular structures have been reported for a large number of sugar based amphiphiles and bolaamphiphiles [1,2,12,52]. However films deposited from the same solutions which had been
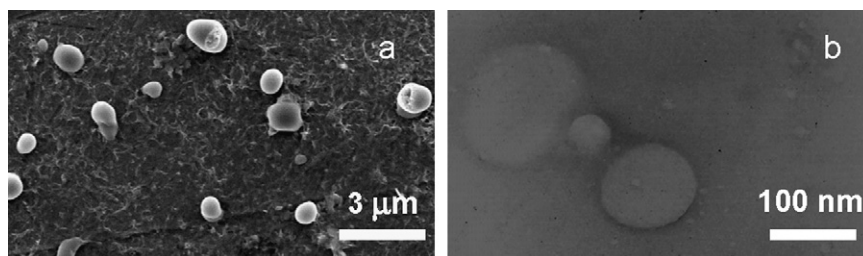

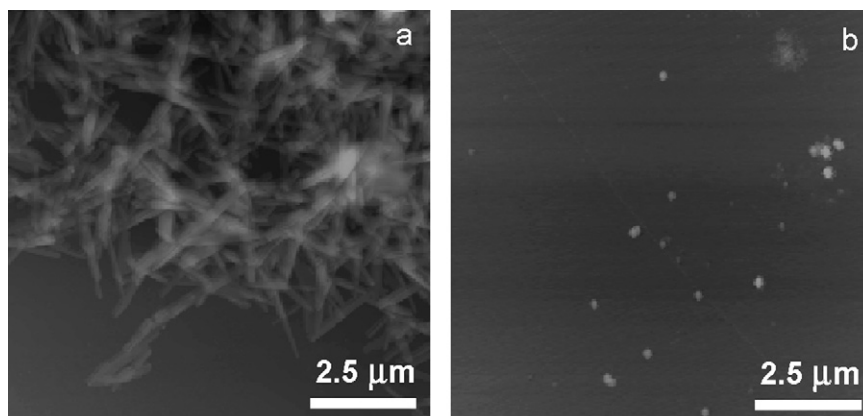Fig. 7. Vesicles of azo-bis 8 (2.7×10^{-5} M) viewed by (a) SEM and (b) TEM.

Fig. 8. Tapping mode AFM images of aggregates formed by azo-bis 10 (2.5×10^{-5} M): (a) fiber morphology when drop-cast in freshly prepared state; (b) vesicular morphology when drop-cast after heating to 97 °C and cooling.
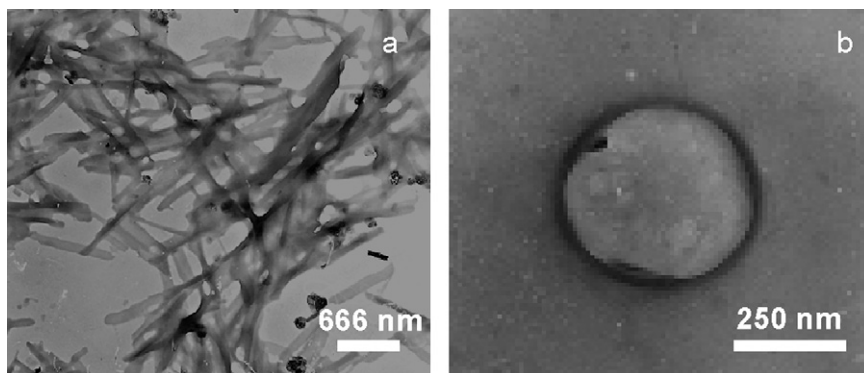
Fig. 9. TEM images of aggregates formed by azo-bis 10 (2.5×10^{-5} M): (a) fiber morphology in films cast from a freshly prepared solution; (b) vesicular morphology observed in a film deposited from solutions heated to 97 °C and cooled to ambient temperature.
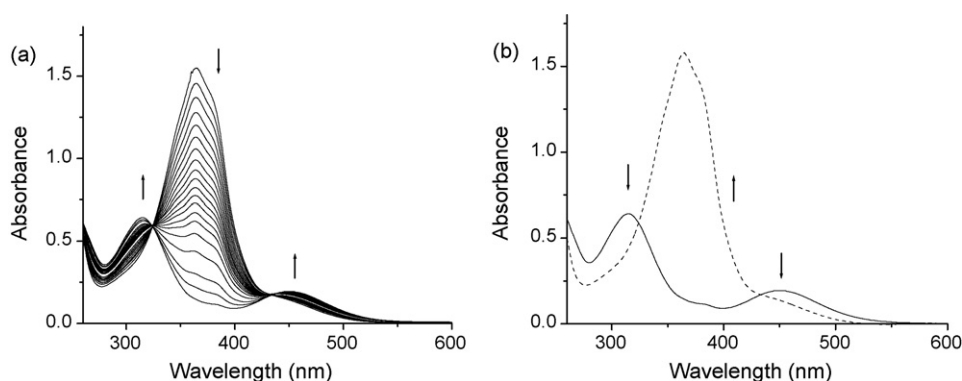

Fig. 10. UV–vis spectra of azo-bis 10 in DMSO showing (a) *trans* to *cis* photoisomerization change from all *trans* to photostationary state over a period of 14 min on irradiation with 364 nm monochromatic light; (b) *cis* to *trans* thermal isomerization; (—) photostationary state, (- - -) spectra obtained after 24 h.

heated to 97 °C and cooled to room temperature did not contain fibers, with only vesicles being observed (Figs. 8b and 9b).

3.3. Photoinduced break up of the aggregates

In pure DMSO solutions, the azo-bolas underwent *trans* to *cis* photoisomerization when irradiated with 364 nm light isolated from a 450 W Xe lamp (Fig. 10a). The reverse isomerization (*cis* to *trans*) occurred in the dark over a period of 24 h (Fig. 10b).

In the H-aggregated state, the azobenzene chromophore is known to be resistant to photoisomerization [34]. Thus photoisomerization was not observed on irradiation with the UV light output of the Xe lamp. On exposure of a solution of azo-bis 8 in water/DMSO, to 355 nm laser pulses ($\sim$50 mJ pulse^{-1}), however, a decrease in intensity of the 339 nm band and appearance of a broad band centred at 450 nm attributable to the n $\rightarrow$ π* transition of the *cis*-isomer was observed (Fig. 11). Changes in the UV–vis spectrum were accompanied by a significant reduction in the scattering nature of the solution. These observations clearly point to the disruption of the aggregate due to *trans* to *cis* photoisomerization of the azobenzene moiety. Recovery of the blue shifted aggregate band was observed when the irradiated solutions were kept in the dark for 24 h. However the final spectra were less intense and also slightly broader, suggesting a difference in the nature of the aggregated species formed.

Disruption of the aggregates due to photolysis was also indicated by changes in the ^{1}H NMR spectrum (Figs. 5f and 12). A new broad peak centred at $\delta = 6.79$ ppm appeared in the aromatic region on exposure of the solution containing aggregates to 355 nm laser pulses ($\sim$70 mJ pulse^{-1}). This could be attributed to multiplet of the *cis*-isomer by comparison with the NMR spectra of irradiated solutions of a model compound, 10,10′-[(1E)-Azobis(4,1-phenyleneoxy)]bis[1-decanol]
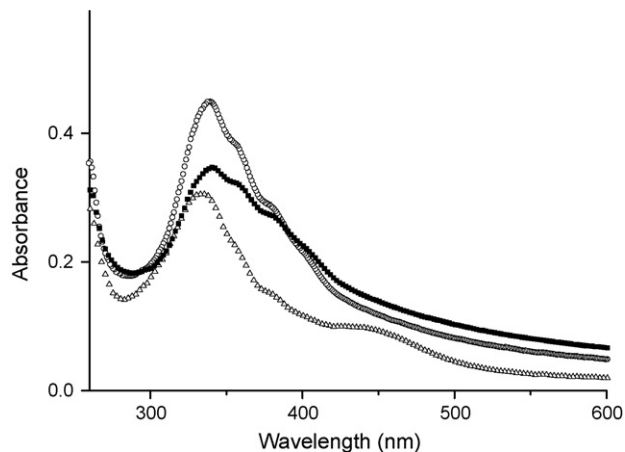

Fig. 11. Effect of irradiation on the UV–vis spectra of the aggregate of azo-bis 8 (2.7×10^{-5} M) in 90% water/DMSO: (○) before irradiation; (△) after irradiation; (■) Irradiated solution kept in dark for 24 h.
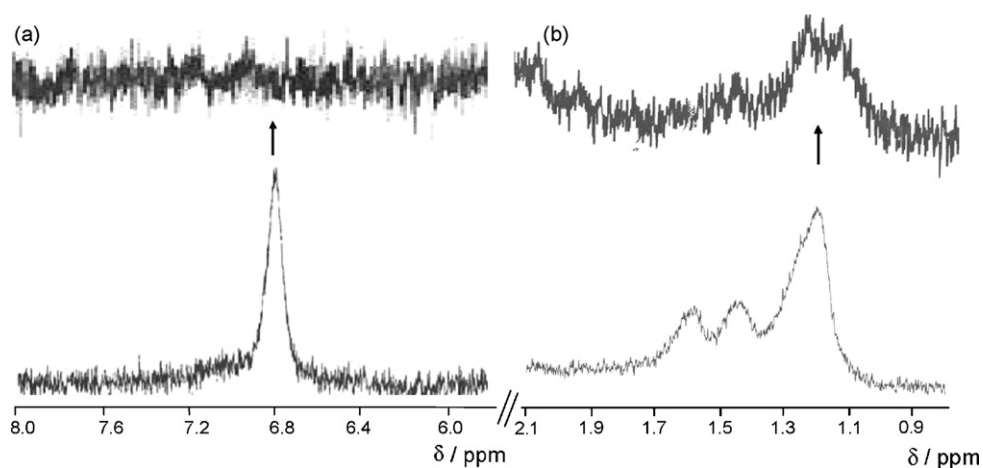
Fig. 12. Changes in ^{1}H NMR (a) aromatic protons; (b) oligomethylene protons of azo-bis 8 aggregate upon irradiation with 355 nm laser pulses (bottom) and recorded after keeping irradiated solution in the dark for 24 h (top; 7.5 mM, $T = 27\,^{\circ}$C).

(See the Electronic Supplementary Material). Irradiated solutions of the model compound also showed doublets at $\delta = 7.10$ and 7.82 ppm attributable to the residual *trans*-isomer (See the Electronic Supplementary Material). Peaks attributable to the *trans*-isomer were however not observed in irradiated solutions of the aggregated azo-bis 8, indicating the strong tendency of the residual *trans*-isomers to remain in the aggregated state. On keeping the irradiated solution at room temperature for 24 h, the peak due to the *cis*-isomer disappeared, implying thermal isomerization to the *trans*-isomer and subsequent aggregation (Fig. 12). At high temperatures (>75 $^{\circ}$C) appearance of the peaks attributable to the *trans*-isomer indicated that no permanent chemical transformation had occurred on laser irradiation. Similar effects were also observed for azo-bis 10 (See the Electronic Supplementary Material).

TEM images of the films cast from solution of azo-bis 8 in 90% water/DMSO indicated the presence of vesicles (Fig. 13a). The same solution was initially exposed to 355 nm laser pulses to induce *trans* to *cis* photoisomerization of the azobenzene moiety. The solution was kept in the dark for 24 h to allow the thermal recovery of the *trans* isomers. For these solutions, recovery of the aggregated form was indicated in both the UV–vis and NMR spectra. TEM images of aggregates obtained from these solu-

tions indicated mainly the existence of a large number of flat sheets and fibers alongside a few vesicles (Fig. 13b). On heating this solution to 97 $^{\circ}$C and cooling under ambient conditions, however the TEM images indicated the formation of vesicles, as observed in the freshly made un-photolyzed solutions.

4. Discussion

Sugar based amphiphiles and bolaamphiphiles have been shown to be very useful for generating a wide range of self-assembled structures. Recently Shimizu and co-workers have shown that the morphology of the self-assembled structures of some amphiphilic sugars could be controlled by controlling the structure of the seed materials used [53]. Thus crystalline materials precipitated from methanol gave rise to tapes, whereas solid films of the same materials obtained by evaporating a DMF solution gave rise to nanotubes. In both cases the self-assembled materials were obtained by preparing hot aqueous dispersions (100 $^{\circ}$C) of the two solids. These studies indicate that the supramolecular structural information stored in the seed materials are retained at least partially at the high temperatures allowing the materials to self assemble into different structures on cooling. In the azo-bolas investigated in the present study, the
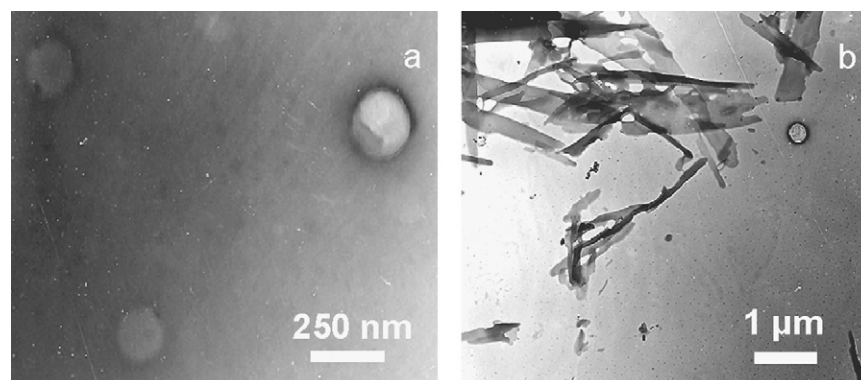

Fig. 13. TEM images for azo-bis 8 solutions (2.7×10^{-5} M) in 90% water/DMSO showing photoinduced changes in aggregation: (a) before irradiation; (b) following irradiation at 355 nm and keeping in the dark for 24 h.

presence of the azo chromophore made it possible to monitor the stability of the aggregates formed as a function of the length of the intervening oligomethylene spacer and temperature. The ease of formation of the highly ordered H*-aggregates, which as indicated by the formation of an intense, narrow, blue-shifted band compared to that of the azobenzene monomer, increased with increase in the length of the oligomethylene spacers. The stability of the aggregates as a function of temperature was also dependent on the length of the spacers. Whereas the absorption spectra of azo-bis 5 indicated complete break-up of the aggregate to the monomer form on heating, in the absorption and CD spectra the presence of substantial amounts of residual aggregates was indicated for azo-bis 8 and azo-bis 10 at temperatures >90 °C.

Microscopic studies of films deposited from aggregated solutions of azo-bis 5 and azo-bis 8 aggregates indicated the presence of vesicles. Films deposited from solutions of the azo-bis 10 aggregates however, indicated the formation of fibers. Solutions of azo-bis 10 heated above 95 °C and cooled to room temperature however, resulted in the formation of vesicles. A possible explanation for this effect may be that in azo-bis 10 the strong interaction between the individual molecules, due to the longer oligomethylene spacers, could initially lead to the formation of the kinetically trapped aggregates [54–56], resulting in the formation of fibers. In solutions that are cooled from above 95 °C to room temperature under ambient conditions, the self-assembly process can be slowed down sufficiently, resulting in the formation of vesicles, which may be thermodynamically more stable. It is interesting to note that the case of the photolyzed solutions of azo-bis 8, the reverse *cis* to *trans* isomerization of the azobenzene unit resulted in a preferential formation of flat sheets and fibers. Under such conditions the *trans*-isomer, which is the only species capable of aggregating, becomes available at a very slow rate (controlled by the rate of the thermal *cis* to *trans* isomerization), which may not be conducive for the formation of vesicles. Formation of vesicles capable of trapping solvent within them can be expected to be a more spontaneous process. In contrast, when these solutions in which the thermal *cis* to *trans* isomerization had been completed, are heated and cooled to room temperature, formation of the vesicles was observed. In conclusion this work provides an understanding of the controlled thermal and photochemical transformation of organized assemblies in a series of azobenzene containing bolaamphiphiles. Further studies along these lines are expected to lead to more versatile photoresponsive vesicles which are of interest from the point of view of developing controlled release systems [13,49,50,57].

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2007.03.003.

References

[1] T. Shimizu, M. Masuda, H. Minamikawa, Chem. Rev. (Washington, DC, USA) 105 (2005) 1401–1443.
[2] J.-H. Fuhrhop, T. Wang, Chem. Rev. (Washington, DC, USA) 104 (2004) 2901–2937.
[3] I.O. Shklyarevskiy, P. Jonkheijm, P.C.M. Christianen, A.P.H.J. Schenning, E.W. Meijer, O. Henze, A.F.M. Kilbinger, W.J. Feast, A. Del Guerzo, J.-P. Desvergne, J.C. Maan, J. Am. Chem. Soc. 127 (2005) 1112–1113.
[4] H. Ringsdorf, B. Schlarb, J. Venzmer, Angew. Chem. Int. Ed. 27 (1988) 113–158.
[5] R. Auzély-Velty, T. Benvegnu, D. Plusquellec, G. Mackenzie, J.A. Haley, J.W. Goodby, Angew. Chem. Int. Ed. 37 (1998) 2511–2515.
[6] B.O. Fraser-Reid, K. Tatsuta, J. Thiem (Eds.), Glycoscience: Chemistry and Chemical Biology, vols. I–III, Springer-Verlag, Berlin, 2001.
[7] M. Masuda, V. Vill, T. Shimizu, J. Am. Chem. Soc. 122 (2000) 12327–12333.
[8] E. Soussan, A. Pasc-Banu, S. Consola, T. Labrot, E. Perez, M. Blanzat, R. Oda, C. Vidal, I. Rico-Lattes, ChemPhysChem 6 (2005) 2492–2494.
[9] F.M. Menger, J. Bian, E. Sizova, D.E. Martinson, V.A. Seredyuk, Org. Lett. 6 (2004) 261–264.
[10] S. Gerber, V.M. Garamus, G. Milkereit, V. Vill, Langmuir 21 (2005) 6707–6711.
[11] J.-M. Lehn, Supramolecular Chemistry: Concepts and Perspectives, VCH, Weinheim, 1995, pp. 139–197.
[12] G. John, M. Masuda, Y. Okada, K. Yase, T. Shimizu, Adv. Mater. (Weinheim, Ger.) 13 (2001) 715–718.
[13] D.G. Whitten, L. Chen, H.C. Geiger, J. Perlstein, X. Song, J. Phys. Chem. B 102 (1998) 10098–10111.
[14] H. Kobayashi, K. Koumoto, J.H. Jung, S. Shinkai, J. Chem. Soc., Perkin Trans. 2 (2002) 1930–1936.
[15] H.A. van Doren, E. Smits, J.M. Pestman, J.B.F.N. Engberts, R.M. Kellogg, Chem. Soc. Rev. 29 (2000) 183–199.
[16] J. Barberá, A.C. Garcés, N. Jayaraman, A. Omenat, J.L. Serrano, J.F. Stoddart, Adv. Mater. (Weinheim, Ger.) 13 (2001) 175–180.
[17] N.S.S. Kumar, S. Varghese, G. Narayan, S. Das, Angew. Chem. Int. Ed. 45 (2006) 6317–6321.
[18] J. Nithyanandhan, N. Jayaraman, R. Davis, S. Das, Chem. -Eur. J. 10 (2004) 689–698.
[19] S. Abraham, V.A. Mallia, K.V. Ratheesh, N. Tamaoki, S. Das, J. Am. Chem. Soc. 128 (2006) 7692–7698.
[20] S. Abraham, S. Paul, G. Narayan, S.K. Prasad, D.S.S. Rao, N. Jayaraman, S. Das, Adv. Funct. Mater. 15 (2005) 1579–1584.
[21] S. Yagai, T. Karatsu, A. Kitamura, Chem. -Eur. J. 11 (2005) 4054–4063.
[22] S. Yagai, T. Iwashima, K. Kishikawa, S. Nakahara, T. Karatsu, A. Kitamura, Chem. -Eur. J. 12 (2006) 3984–3994.
[23] M. Han, M. Hara, J. Am. Chem. Soc. 127 (2005) 10951–10955.
[24] J. Eastoe, A. Vesperinas, Soft Matter 1 (2005) 338–347.
[25] T. Yutaka, I. Mori, M. Kurihara, J. Mizutani, N. Tamai, T. Kawai, M. Irie, H. Nishihara, Inorg. Chem. 41 (2002) 7143–7150.
[26] D. Grebel-Koehler, D. Liu, S. De Feyter, V. Enkelmann, T. Weil, C. Engels, C. Samyn, K. Müllen, F.C. De Schryver, Macromolecules 36 (2003) 578–590.
[27] N. Berova, K. Nakanishi, in: N. Berova, K. Nakanishi, R.W. Woody (Eds.), Circular Dichroism: Principles and Applications, 2nd ed., Wiley–VCH, New York, 2000, pp. 337–382.

[28] A. Rodger, B. Nordén, Circular Dichroism and Linear Dichroism, Oxford University Press, New York, 1997.

[29] H.H. Szmant, in: S.W. Jacob, E.E. Rosenbaum, D.C. Wood (Eds.), Dimethyl Sulfoxide, vol. 1: Basic Concepts of DMSO, Marcel Dekker, New York, 1971, p. 30.

[30] S. Yagai, T. Nakajima, T. Karatsu, K. Saitow, A. Kitamura, J. Am. Chem. Soc. 126 (2004) 11500–11508.

[31] T. Kawasaki, M. Tokuhiro, N. Kimizuka, T. Kunitake, J. Am. Chem. Soc. 123 (2001) 6792–6800.

[32] M. Kasha, H.R. Rawls, M.A. El-Bayoumi, Pure Appl. Chem. 11 (1965) 371–392.

[33] X. Song, J. Perlstein, D.G. Whitten, J. Am. Chem. Soc. 119 (1997) 9144–9159.

[34] S. Yagai, T. Karatsu, A. Kitamura, Langmuir 21 (2005) 11048–11052.

[35] J.M. Kuiper, J.B.F.N. Engberts, Langmuir 20 (2004) 1152–1160.

[36] H. Xie, L. Liu, W. Wang, L. Xu, Chem. Phys. Lett. 403 (2005) 175–179.

[37] I. Kim, J.F. Rabolt, P. Stroeve, Colloids Surf. A 171 (2000) 167–174.

[38] Y. Deng, Y. Li, X. Wang, Macromolecules 39 (2006) 6590–6598.

[39] H. Asanuma, K. Shirasuka, T. Takarada, H. Kashida, M. Komiyama, J. Am. Chem. Soc. 125 (2003) 2217–2223.

[40] F. Würthner, S. Yao, U. Beginn, Angew. Chem. Int. Ed. 42 (2003) 3247–3250.

[41] A.H. Herz, Photogr. Sci. Eng. 18 (1974) 323–335.

[42] R. Iwaura, F.J.M. Hoeben, M. Masuda, A.P.H.J. Schenning, E.W. Meijer, T. Shimizu, J. Am. Chem. Soc. 128 (2006) 13298–13304.

[43] F.D. Lewis, L. Zhang, X. Liu, X. Zuo, D.M. Tiede, H. Long, G.C. Schatz, J. Am. Chem. Soc. 127 (2005) 14445–14453.

[44] J.K.M. Sanders, B.K. Hunter, Modern NMR Spectrosopy, 2nd ed., Oxford University Press, New York, 1993, p. 161.

[45] B. Escuder, M. LLusar, J.F. Miravet, J. Org. Chem. 71 (2006) 7747–7752.

[46] K.M. Tait, J.A. Parkinson, S.P. Bates, W.J. Ebenezer, A.C. Jones, J. Photochem. Photobiol. A 154 (2003) 179–188.

[47] M.I. Viseu, K. Edwards, C.S. Campos, S.M.B. Costa, Langmuir 16 (2000) 2105–2114.

[48] M. Yang, W. Wang, F. Yuan, X. Zhang, J. Li, F. Liang, B. He, B. Minch, G. Wegner, J. Am. Chem. Soc. 127 (2005) 15107–15111.

[49] D.M. Vriezema, M.C. Aragonès, J.A.A.W. Elemans, J.J.L.M. Cornelissen, A.E. Rowan, R.J.M. Nolte, Chem. Rev. (Washington, DC, USA) 105 (2005) 1445–1489.

[50] D.E. Discher, A. Eisenberg, Science (Washington, DC, USA) 297 (2002) 967–973.

[51] M. Yoon, M. Seo, C. Jeong, J.H. Jang, K.S. Jeon, Chem. Mater. 17 (2005) 6069–6079.

[52] G. John, J.H. Jung, H. Minamikawa, K. Yoshida, T. Shimizu, Chem. -Eur. J. 8 (2002) 5494–5500.

[53] N. Kameta, M. Masuda, H. Minamikawa, N.V. Goutev, J.A. Rim, J.H. Jung, T. Shimizu, Adv. Mater. (Weinheim, Ger.) 17 (2005) 2732–2736.

[54] C. Boettcher, B. Schade, J.-H. Fuhrhop, Langmuir 17 (2001) 873–877.

[55] V. Paraschiv, M. Crego-Calama, T. Ishi-i, C.J. Padberg, P. Timmerman, D.N. Reinhoudt, J. Am. Chem. Soc. 124 (2002) 7638–7639.

[56] L. Zhang, A. Eisenberg, Polym. Adv. Technol. 9 (1998) 677–699.

[57] O.V. Gerasimov, J.A. Boomer, M.M. Qualls, D.H. Thompson, Adv. Drug Delivery Rev. 38 (1999) 317–338.