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Synthesis and Characterization of Photoactive Amphiphilic Polymers

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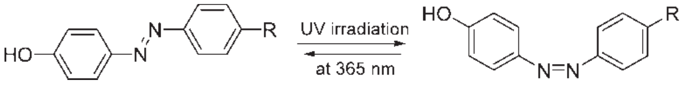
We have synthesized light sensitive nano micelles for their applications as drug delivery agents. Various azo compounds having different dipole moment values have been covalently attached to an amphiphilic pegylated co-polymer and their light sensitive behavior has been studied in both aqueous and organic media with ultra violet light to understand the light dependent supramolecular organization.

Keywords: photoactive amphiphilic polymers; azobenzene; supramolecular organization

1 Introduction

Photochemical reactions which occur in small molecules can also be induced to occur in macromolecules. Though, in macromolecular environments there are constraints which are not present on a small-molecule scale, the challenge is to apply fundamental principles to macromolecules which may coil, branch, or be chemically crosslinked increasing the order of complexity. Likewise, molecular mobility plays an important role in determining the course of photochemical behavior in polymers and is related to the size of the molecule, the flexibility of the polymer chain, and whether the polymer is in solution or in the solid state. In order to fully understand these effects, it is useful to select few azo compounds that differ in their dipole moments to study them in a macromolecular environment. Such a photochemical reaction is the *cis-trans* isomerism of an azobenzene.



Azobenzene-containing polymers have attracted considerable attention in the last decade due to their potential applications as photoactive compounds for molecular devices, information storage systems, and photochemical switching (1, 2). There are some photosensitive azobenzene and stilbene containing gemini photo surfactants which are potentially useful in a variety of applications (3–5), and show light-triggered changes in their supramolecular organization (6). We have designed and synthesized photo responsive amphiphilic polymers using a novel chemo-enzymatic methodology to study their supra-molecular organization in aqueous and organic media so that their supramolecular organization can be changed in a controlled manner. The developed methodology and light responsive micelles are envisioned to provide opportunities and applications as photosensitive nano-particles.

2 Experimental

2.1 Materials

Novozyme-435, an immobilized enzyme, was a gift from Novozymes A/S, Denmark. Anhydrous potassium carbonate, dibromoethane, acetonitrile and polyethylene glycols were purchased from Aldrich (Milwaukee, WI). Compounds **5–8** were synthesized and characterized using standard procedure (7–10). Anhydrous potassium carbonate was fused overnight at 200°C before use, whereas polyethylene glycol was dried under vacuum at 60°C for 3 h prior to use. All other chemicals and solvents were of analytical grade and were used without further purification.

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2.2 Characterization

Gel permeation chromatography (GPC) was used to determine the molecular weight and molecular weight distribution, Mw/Mn of polymers using THF as solvent and polystyrene as standard. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Instrument Inc. DPX 500 spectrometer at 500 and 125 MHz, respectively using TMS as internal standard. Light scattering data was determined by a laser light scattering photometer (Wyatt Technology DAWN Model F) equipped with a 632 nm He-Ne laser as the light source.

2.3 General Method For Attachment of Dibromoethane to Azo Compounds 1–4

Compounds **1–4** (1 equivalent) and dibromoethane (4 equivalents) were dissolved in dry acetonitrile and to the resultant solution was added 1.5 equivalents of anhydrous potassium carbonate. The reaction mixture was refluxed at 70°C and progress of the reaction was monitored by the disappearance of compound **1–4** on TLC using 5% methanol/chloroform. After completion, the reaction was quenched by filtering off potassium carbonate by simple filtration and filtrate so obtained was concentrated on a rotavapor and properly washed with hexane to remove the excess of dibromoethane to obtain the products **5–8** (7–10).

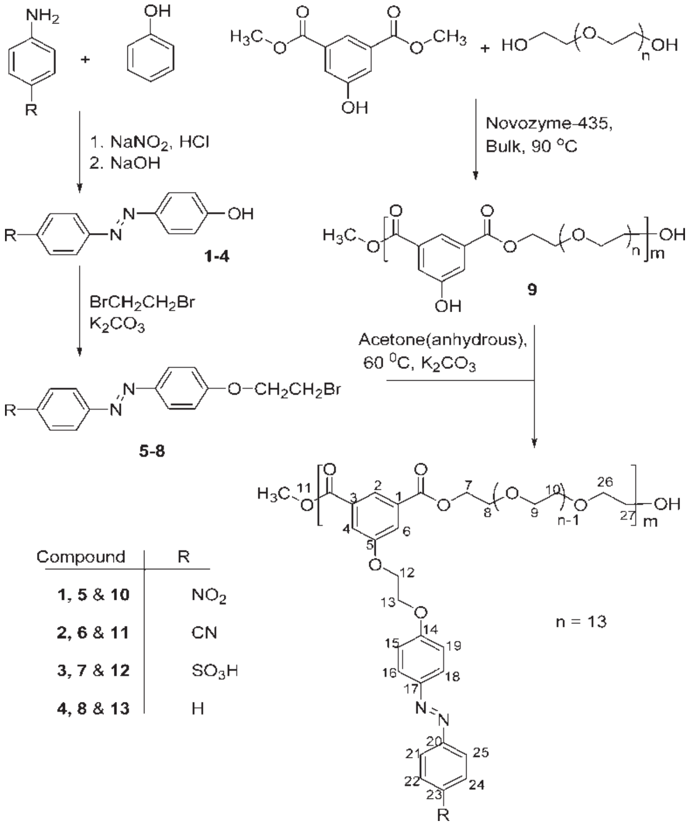
2.4 Synthesis and Characterization of α-Bromo-ω-(4-sulphonylazobenzene-4′-oxy)ethane (7)

α-Bromo-ω-(4-sulphonylazobenzene-4′oxy)ethane (**7**) was prepared by taking compound **3** (2.78 g, 1.0 mmol), dibromoethane (7.52 g, 4.0 mmol), potassium carbonate (2.7 g, 1.5 mmol) in 200 ml acetonitrile.

^{1}H-NMR (δ_H CDCl$_3$, 500 MHz): 3.73 (t, 2H, CH_2Br), 4.46 (t, 3H, OCH_2), 7.09 (d, 2H), 7.49 (dd, 1H), 8.00 (d, 2H), 8.15 (d, 1H), 8.72 (d, 1H), 9.20 (d, 1H). **^{13}C-NMR (δc CDCl$_3$, 125 MHz):** 29.1 (CH$_2$Br), 68.5 (OCH$_2$), 115.4 (CH × 2), 124.4 (CH), 125.6 (CH × 2), 127.4 (CH), 147.3 (CH), 147.8 (q), 148.1 (q), 148.4 (q), 151.4 (CH), 161.5 (q).

2.5 General Method for Alkylation

Equimolar quantities of the polymer, poly [(polyoxyethylene-600)-5-hydroxyisophthaloyl] (**9**) and the azo compound **5–8** were dissolved in anhydrous acetone, followed by the addition of 1.5 equivalent of anhydrous potassium carbonate. The reaction mixture was refluxed and progress of the reaction was monitored by TLC using 5% methanol in chloroform. After completion, the potassium carbonate was removed by filtration and the solvent was removed under vacuum to give the product, which was further dialyzed with 8,000 molecular weight cut off membrane.



Compound	R
1, 5 & 10	NO_2
2, 6 & 11	CN
3, 7 & 12	SO_3H
4, 8 & 13	H

Sch. 1. Synthesis of amphiphilic polymers **10–13**.

Compound 10 was prepared by taking compound **5** (0.35 g, 0.10 mmol), polymer **9** (0.81 g, 0.10 mmol) and potassium carbonate (0.20 g, 0.15 mmol) in 80 ml acetone (Scheme 1).

^{1}H-NMR Data (δ_H CDCl$_3$, 500 MHz): 3.64–3.70 (brs, methylene PEG protons on C-9 and C-10), 3.85 (s, 2H, H-8), 3.90 (s, 3H, H-11), 4.44–4.51 (brs, 6H, H-7, 12 and 13), 7.10 (d, 2H, H-15 and 19), 7.76 (s, 1H, H-2), 7.85 (s, 2H, H-4 and 6), 7.99 (d, 4H), 8.38 (d, 2H).

^{13}C NMR Data (δc CDCl$_3$, 125 MHz): 52.9 (-OCH$_3$ end group), 62.0 (C-27 end group), 64.6 (CH$_2$), 67.2 (CH$_2$), 67.3 (CH$_2$), 69.5 (CH$_2$), 70.9 (repeating PEG unit carbons), 72.9 (C-26 of end group), 115.5 (CH × 2), 120.5 (CH × 2), 123.6 (CH × 2), 124.0 (CH), 125.1 (CH × 2), 126.1 (CH × 2), 132.3 (q × 2), 147.6 (q), 148.7 (q), 156.4 (q), 158.9 (q), 162.5 (q), 165.8 (>CO), 166.3 (-COOMe end group).

Compound 11 was prepared by taking compound **6** (0.330 g, 0.10 mmol), polymer **9** (0.810 gm, 0.10 mmol) and potassium carbonate (0.20 g, 0.15 mmol) in 80 ml acetone.

^{1}H-NMR Data (δ_H CDCl$_3$, 500 MHz): 3.64–3.70 (brs, methylene PEG protons H-9 and 10), 3.81 (s, 2H, H-8), 3.90 (s, 3H, H-11), 4.45–4.51 (brs, 6H, H-7, 12, and 13), 7.10 (d, 2H, H-15 and 19), 7.77 (s, 1H, H-2), 7.84 (s, 2H, H-4 and 6), 7.93 (d, 4H), 8.33 (s, 2H).

^{13}C-NMR Data (δc CDCl$_3$, 125 MHz): 52.9 (-OCH$_3$ end group), 61.8 (*C*-27 end group), 64.9 (*C*H$_2$), 67.3 (*C*H$_2$ × 2), 69.5 (*C*H$_2$), 70.9 (repeating PEG unit carbons), 72.9 (*C*-26 end group), 114.1 (q), 116.7 (*C*H × 2), 119.0 (q), 122.2 (*C*H × 2), 124.5 (*C*H × 2), 124.9 (*C*H), 127.2 (*C*H × 2), 132.3 (q × 2), 134.9 (*C*H × 2), 147.5 (q), 155.2 (q), 158.9 (q), 162.5 (q), 165.8 (>*C*O), 166.3 (-*C*OOMe end group).

Compound 12 was prepared by taking compound **7** (0.385 gm, 0.10 mmol), polymer **9** (0.810 g, 0.10 mmol) and potassium carbonate (0.20 gm, 0.15 mmol) in 80 ml acetone.

^{1}H-NMR Data (δ_H CDCl$_3$, 500 MHz): 3.62–3.70 (brs, methylene PEG protons *H*-9 and 10), 3.85 (s, 2H, *H*-8), 3.90 (s, 3H, *H*-11), 4.46–4.49 (brs, 6H, *H*-7, 12 and 13), 7.07 (d, 2H, *H*-15 and 19), 7.77 (s, 1H, *H*-2), 7.87 (s, 2H, *H*-4 and 6), 7.99 (dd, 2H), 8.37 (bs, 2H), 8.74 (d, 1H), 8.32 (s, 1H), 9.21 (s, 1H).

^{13}C-NMR Data (δc CDCl$_3$, 125 MHz): 52.9 (-OCH$_3$ end group), 61.8 (*C*-27 end group), 64.7 (*C*H$_2$), 67.1 (*C*H$_2$), 67.4 (*C*H$_2$), 69.5 (*C*H$_2$), 70.9 (repeating PEG unit carbons), 71.0 (*C*-26 end group), 115.4 (*C*H × 2), 120.5 (*C*H × 2), 121.7 (*C*H), 124.4 (*C*H), 125.5 (*C*H × 2), 127.3 (*C*H), 132.3 (q × 2), 147.5 (*C*H), 147.6 (q), 148.3 (q), 148.4 (q), 151.5 (*C*H), 158.9 (q), 161.9 (q), 165.9 (>*C*O), 166.25 (-*C*OOMe end group).

Compound 13 was prepared by taking compound **8** (0.350 g, 0.10 mmol), polymer **9** (0.810 gm, 0.10 mmol) and potassium carbonate (0.20 g, 0.15 mmol) in 80 ml acetone.

^{1}H-NMR Data (δ_H CDCl$_3$, 500 MHz): 3.64–3.70 (brs, methylene PEG protons *H*-9 and 10), 3.85 (s, 2H, *H*-8), 3.90 (s, 3H, *H*-11), 4.46–4.49 (brs, 6H, *H*-7, 12 and 13), 7.07 (d, 2H, *H*-15, and 19), 7.44 (m, 1H, *H*-23), 7.49 (t, 2H, *H*-2), 7.85 (s, 2H, *H*-4, and 6), 7.99 (d, 4H), 8.38 (d, 2H).

^{13}C-NMR Data (δc CDCl$_3$, 125 MHz): 52.8 (-OCH$_3$ end group), 61.9 (*C*-27 end group), 64.9 (*C*-26 end group), 67.1 (*C*H$_2$), 67.6 (*C*H$_2$), 69.5 (*C*H$_2$), 71.1 (repeating PEG unit carbons), 72.9 (*C*H$_2$), 115.30 (*C*H × 2), 120.7 (*C*H × 2), 123.1 (*C*H × 2), 124.1 (*C*H), 125.14 (*C*H × 2), 129.3 (*C*H × 2), 131.1 (*C*H), 132.3 (q × 2), 147.7 (q), 153.1 (q), 159.0 (q), 161.3 (q), 165.8 (>*C*O), 166.3 (-*C*OOMe end group).

3 Results and Discussion

The polymers **10–13** as shown in Scheme 1 were synthesized by alkylation of phenolic hydroxyl of the polymer poly[(polyoxyethylene-600)-5 hydroxyisophthaloyl] (**9**) with compounds **5–8** as an alkylating agent. The polymer **9** was synthesized by *Candida antarctica* lipase B (Novozyme-435) catalyzed condensation polymerization of dimethyl 5-hydroxyisophthalate with polyethylene glycol (10–12). The alkylating agents **5–8** were prepared by diazotization of aniline derivatives with phenol, followed by the alkylation with dibromoethane (13). The amphiphilic polymers **10–13** were characterized by their UV, ^{1}H-NMR and ^{13}C-NMR spectra. The UV spectra of polymers **10–13** showed two absorption maxima at 311 and 365 nm corresponding to isophthalate moiety and azo group, indicating the presence of both types of chromophores. The ^{1}H-NMR spectra of polymers **10–13** also showed signals in the downfield region for the presence of aromatic protons of linker and pendent side chain. The alkylation of phenolic hydroxyl group of **9** by compounds **5–8** was further confirmed by the disappearance of the signal at δ 28.9–29.3 for CH$_2$Br and appearance of new signal in their ^{13}C-NMR spectra at δ 67.3–67.6 due to the formation of ether bond (OCH$_2$) in polymers **10–13**. We have carried out UV and light scattering experiments to study the light dependent behavior of these newly synthesized polymers. In order to do that, the photochemical and thermal isomerization has been studied in water, methanol and chloroform by irradiating the samples at 365 nm by UV lamp, using UV spectroscopy. The UV spectrum was recorded over different time intervals until photo stationary state reached. Upon UV irradiation, the intensity of the band at 365 nm decreased and the intensity of transition band at 452 nm increased gradually. The spectrum clearly showed the *trans* to *cis* isomerization of the azo group. By keeping the sample in dark, the *cis* form slowly isomerizes to *trans* form and the spectra gradually moved towards the original curve. Similar spectrum variation was observed for all the polymeric samples **10–13**, except the variation in the rate of conversion (*trans* to *cis* & *cis* to *trans*) of isomerization. After careful analysis, it was observed that the presence of electron withdrawing group at the C-23 position is responsible for rate of conversion. In the case of polymer **10**, there was no complete conversion from *trans* to *cis* band (Figure 1) even if we irradiate the sample up to

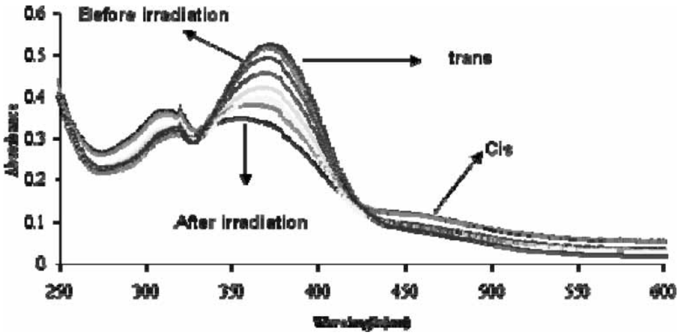


Fig. 1. UV Spectrum of polymer **10** in CHCl$_3$ shows the transition from *trans* to *cis* isomer after one minute and then instantly starts reverting back to the *trans* isomer and completely converts to *trans* from in 30 min.

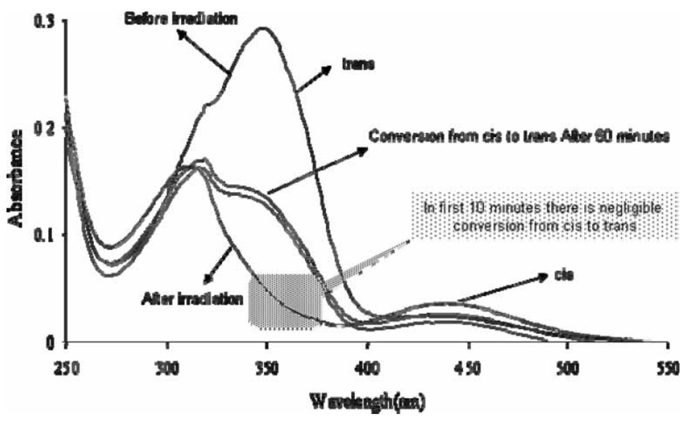


Fig. 2. UV Spectrum of polymer **11** in $CHCl_3$ shows the transition from *trans* to *cis* isomer after one minute and then reverts back to partially *trans* isomer within 60 min.

one hour, where as in the case of compounds **11** and **12**, we observed complete conversion of *trans* to *cis* band **(**Figures 2 and 3**)** just after irradiating the sample for few seconds. Whereas the transition from *cis* to *trans* form is reversible, i.e., polymer **10** completely isomerized to *trans* form after 30 min and compounds **11** and **12** did not. The rate of *cis* to *trans* isomerization was slower in polymer **11** then it was in **12** because the CN group present in polymer **11** is a stronger electron withdrawing group then the SO_3H group present in compound **12**. Identical isomerization studies in methanol showed that the rate of isomerization from *trans* to *cis* was the same, but the conversion from *cis* to *trans* was much slower with respect to the conversion in chloroform. Whereas, in aqueous medium, there wasn't any isomerization except the quenching of *trans* form after irradiating the solution. To examine the effect of solvents on their isomerization, we studied their self assembly in different solvents by using static and dynamic light scattering instruments.

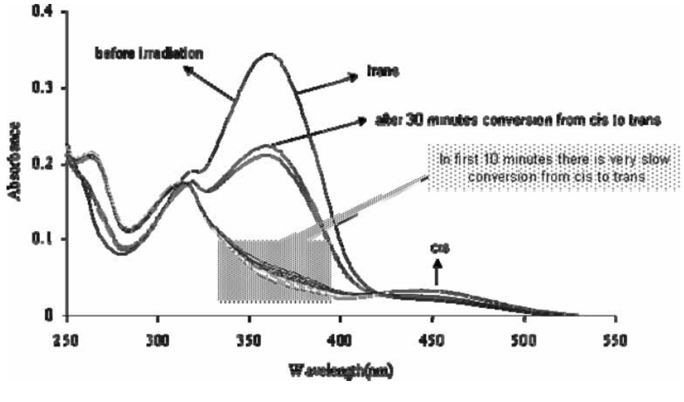


Fig. 3. UV Spectrum of polymer **12** in $CHCl_3$ shows the complete transition from *trans* to *cis* isomer after one minute and then shows isomerization to *trans* form but not able to achieve the complete *trans* form.

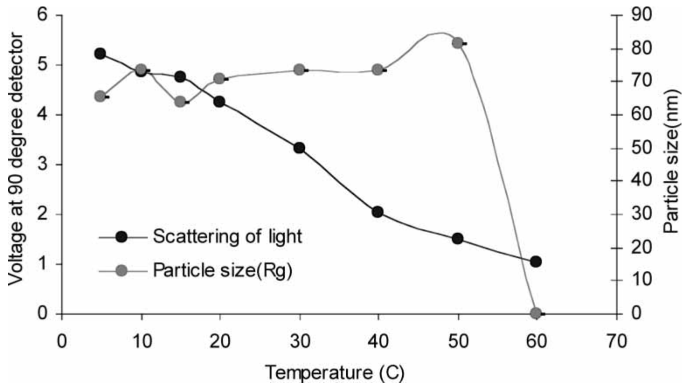


Fig. 4. Change in radius of gyration (Rg) and intensity of scattered light by raising the temperature of aqueous solution of polymer **10**.

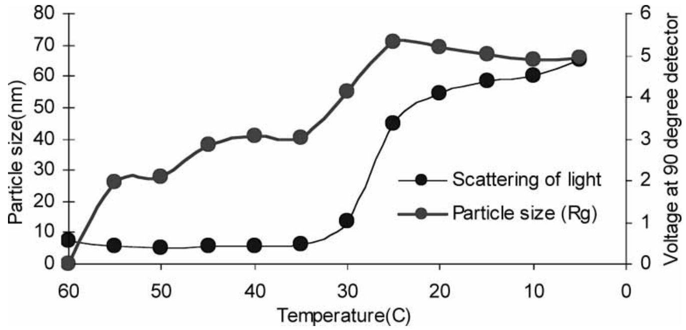


Fig. 5. Change in radius of gyration (Rg) and intensity of scattered light on cooling the aqueous solution of polymer **10**.

The studies were continued to examine self aggregation of polymers **10–13** in aqueous medium and, in that regard, we prepared the solution of polymer **10** at different concentrations in different solvents (Figures 4 and 5), and attempted to measure the critical micelle concentration (CMC) of the polymer by static light scattering. During this measurement, we observed that aggregation initiates at very low concentration (0.005 mg/ml) in aqueous solution. They form nanospheres which have the radius of gyration 50–70 nm, whereas these polymers did not show any aggregation in organic solvents. To further examine the effect of irradiation, we did not observe any change in their supramolecular organization. About the stability and effect of temperature on their isomerization, we monitored the particle size, i.e., radius of gyration with respect to scattering. By heating the polymeric aqueous solution of polymer **10** up to 60°C we observed complete disruption of nanospheres suddenly at 60°C (Figure's 4 and 5) with gradual loss of scattering, whereas on cooling the same sample we observed a very sharp transition at 25°C. By all these aggregation studies, we would like to conclude that because of high dipole moments in polar solvents, these polymers showed the rigidity, that is why the transition from *cis* to *trans* was slow. It has also been observed that aggregation properties were not affected by exposing the solutions to UV light.

4 Conclusions

Four novel azo benzene containing amphiphilic polymers **10–13** have been successfully designed and synthesized and were fully characterized by their detailed spectroscopic studies. All these newly synthesized polymers obtained were found to be water soluble and have been examined for supramolecular organization in aqueous and organic media by both static and dynamic light scattering. The self-assembly of amphiphilic polymers in aqueous media showed the formation of nanomicelles both by static (50–70 nm) and dynamic (60 nm) light scattering. Their aggregation and isomerization behavior in different solvents indicated the rigidity in aqueous solution and no change in their supramolecular organization was noticed after irradiating the solution in UV light.

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