Polym. Bull. (2010) 65:69–81
DOI 10.1007/s00289-010-0247-4

ORIGINAL PAPER

Photosensitive micelles based on polysiloxanes containing azobenzene moieties

Ioana Moleavin · Silvia Grama · Irina Cârlescu · Dan Scutaru · Nicolae Hurduc

Received: 17 November 2009 / Revised: 2 January 2010 / Accepted: 5 January 2010 /

Abstract Photosensitive micelles based on amphiphilic azo-polysiloxanes were obtained and characterized. The amphiphilic polymers were synthesized in a two-step reaction, starting from a polysiloxane containing chlorobenzyl groups in the side chain. In the first step, the polysiloxane was modified with azo-aromatic groups (35–45% substitution degree) and in the second step the unreacted chlorobenzyl groups were quaternized, using different tertiary amines. The structure of the polysiloxanes and their aggregation/disaggregation capacity were evaluated by 1H-NMR, DSC, fluorescence and UV–VIS spectroscopy, dynamic light scattering and transmission electron microscopy. All the amphiphilic polysiloxanes are capable of generating micelles, the critical concentration of the aggregation values being situated in the range 10^{-3}–10^{-2} g/L. As a function of the ternary amine structure used in the quarterisation reaction, the micellar aggregation process is different, individual micelles or micellar clusters being obtained. The clusters' dimension cannot be controlled, the polydispersity index having high values. The disaggregation processes of the micelles under UV irradiation reveal that the polymer chemical structure influences the aggregates stability. A total micelles disaggregation was obtained for the polysiloxane modified with azophenol and amine containing a long hydrocarbon segment. In the other cases, only a partially disaggregation process takes place.

Keywords Photosensitive micelles · Azobenzene · Polysiloxanes · Amphiphilic polymers

I. Moleavin · S. Grama · I. Cârlescu · D. Scutaru · N. Hurduc (✉)
Department of Natural and Synthetic Polymers, "Gheorghe Asachi" Technical University Iasi,
Bd. Mangeron 71, 700050 Iasi, Romania
e-mail: nhurduc@ch.tuiasi.ro

Introduction

Controlled drug delivery field is one of the most attractive and challenging area in biological sciences. Among the variety of reported candidates, polymeric systems based on non-covalent interactions are expected to present a high interest for biology, due to the possibility to adjust and control their properties at the molecular level. Taking advantage of the macromolecular partner functionality, a large number of controlled delivery systems like 3D physical or chemical networks, micelles, biodegradable polymers, or external stimuli sensitive materials have been successfully developed [1–5]. Different polymeric micelles and vesicles have emerged as delivery systems due to their higher stability, specificity, or blood circulation stability toward liposomes. These advantages of the polymeric micelles and vesicles can be combined with stimuli-responsive properties (temperature, light, pH, and oxidation/reduction conditions etc.) that can act as triggers in the aggregation/disaggregation process [6–8]. Azobenzene molecules have attracted wide interest since they show photo-responsive property, based on the UV *trans–cis* isomerization capacity. As a function of the polymeric architecture, the material response can be concretized as phase transition [9], surface relief grating [10–12], or film contraction [13]. Polymers with photo-switching properties can be used in optical data storage, sensors, and artificial muscles [14–16]. Recent research has shown that, micelles with photo-responsive self assembly properties could be obtained by inclosing of ionisable groups in the structural units of the azopolymers [17–19].

In some previous studies, we evidenced the aggregation capacity of the amphiphilic azo-polysiloxanes that are capable to generate micelles [20]. The degree of novelty of these systems is the particular architecture, characterized by the statistical connection on the same polysiloxanic main-chain both of hydrophilic (quaternary ammonium groups) and hydrophobic (azobenzene) side groups. A possible explanation of the micellar aggregation capacity can be the flexibility of the polysiloxane main-chain that permits the arrangement of the hydrophilic and the hydrophobic groups on both sides of the polymeric chain generating structures similar to tectons. The aim of the present article is the study of the aggregation/disaggregation capacity of UV light sensitive micelles based on amphiphilic azo-polysiloxanes. The photosensitive behavior of micelles presents a potential interest in the field of the drugs delivery systems. In this context, the presence of a crown ether group connected to the azobenzenic hydrophobic moiety can induce to the polymer the capacity to generate vesicles, due to the specific architecture that presents three different segments: two hydrophilic ones (quaternary ammonium groups and crown ether) and a hydrophobic core (formed by the azo-groups and the polysiloxanic chain). The chemical structure and the aggregation capacity of the polysiloxanes were evaluated by ^{1}H-NMR, DSC, fluorescence, and UV–VIS spectroscopy, dynamic light scattering (DLS), and transmission electron microscopy (TEM).

Experimental

Materials

Except the 4′-hydroxyphenylazo-benzo-15-crown-5 ether (AzBCE), all the chemicals were purchased from Aldrich and used without supplementary purification.

4′-Hydroxyphenylazo-benzo-15-crown-5 ether has been obtained by diazotization of 4′-aminobenzo-15-crown-5-ether and then coupling of diazonium salt to phenol, by adapting literature data [21].

Diazotization

4′-Aminobenzo-15-crown-5-ether (0.5 g, 1.765 mmol) was dissolved to a water solution (10 ml) of HCl 32% (0.44 ml). After cooling in an ice bath, $NaNO_2$ (0.135 g, 1.94 mmol) dissolved in 2 ml water was added dropwise.

Coupling

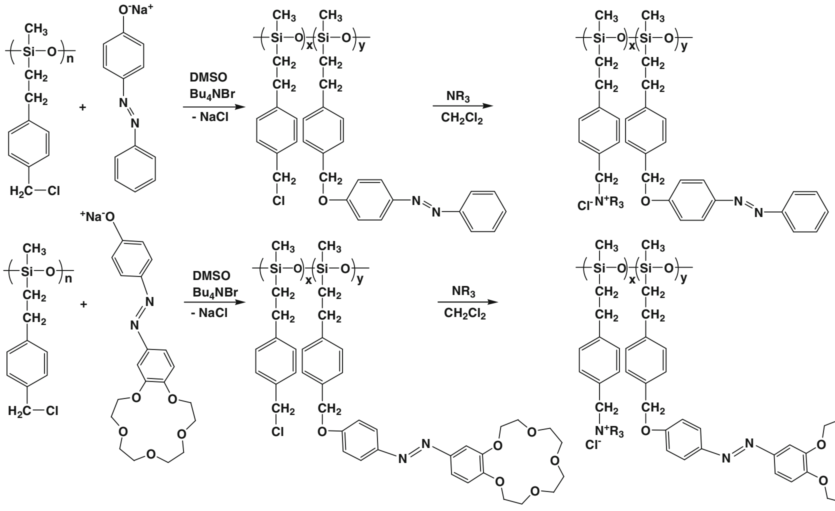
The diazonium salt was added dropwise over a solution consisting of water (14 ml), NaOH (0.2 g), Na_2CO_3 (2 g), and phenol (0.35 g, 2.12 mmol), with stirring and cooling to 0 °C. The resulted yellow-orange suspension was stirred below 0 °C for 2 h, filtered, washed with water, and dried. Yield: 0.65 g ($\eta = 95\%$).

^{1}H-NMR (DMSO; δ ppm): 3.59–3.65 (m, 8H, –O–CH_2–CH_2–O); 3.78–3.83 (m, 4H); 4.41–4.18 (m, 4H); 6.91 (d, 2H ArH); 7.12 (d, 1H ArH), 7.42 (d, 1H, ArH); 7.50 (dd, 1H, ArH); 7.75 (d, 2H, ArH).

^{13}C-NMR (DMSO; δ ppm): 67, 68, 69, 104, 112, 116, 118, 124, 128, 144, 146, 148, 151, 157, 160.

General procedure

The investigated polymers were obtained in a two-step reaction, starting from a polysiloxane containing chlorobenzyl side groups. In the first step, the polysiloxane was modified [22, 23] with 4-(phenyl-azo)-phenol (35–45% substitution degree) and in the second step the unreacted chlorobenzyl groups were quaternized using different tertiary amines (Scheme 1). In a typical reaction, 0.3 g of polysiloxane was dissolved in 6 mL DMSO and mixed with the corresponding amount (based on the chloromethyl groups content) of sodium salt of 4-(phenyl-azo)-phenol and 0.1 g tetrabutyl ammonium hydrogen sulfate. The mixture was introduced in a flask and heated for 5 h at 90 °C. The polymer was precipitated in methanol, washed 5–6 times with methanol (to eliminate the unreacted products), filtered, and dried under vacuum. In the second step, 0.5 g azo-polysiloxane was dissolved in 3 mL CH_2Cl_2 under stirring; an equivalent quantity of tertiary amine (the final value of the total substitution degree was below 95% to eliminate the removing step of the unreacted amine) was added and the reaction mixture was heated for 24 h at 30 °C. The methylene chloride was removed by evaporation and the final product was dried under vacuum at 40 °C.



Scheme 1 Synthesis reaction scheme of the amphiphilic azo-polysiloxanes

Instruments

The polymers were characterized by ^{1}H-NMR, GPC, DSC, UV spectroscopy, dynamic light scattering (DLS), and TEM microscopy. The ^{1}H-NMR spectra were recorded on a Brucker 400 MHz apparatus. DSC thermograms were recorded on a Mettler DSC12E calorimeter with a heating/cooling rate of 10 K/min. The polymer photochromic behavior was investigated in $CHCl_3$ solution using a UV lamp source (100 W) equipped with 350 nm filter. In order to evaluate the amphiphilic polysiloxanes' aggregation capacity, the classical method using pyrene fluorescence spectroscopy was used [20]. In order to calculate the critical concentration of aggregation (CCA) value, the first (named I_1) and the third (named I_3) absorption peaks corresponding to the fluorescence emission spectrum of pyrene were used. In aqueous solution, the I_1/I_3 ratio value corresponding to the free pyrene (not incorporated in the micelles) is situated around 1.70–1.75. For concentrations lower than 10^{-3} g/L, no aggregation process was evidenced, the I_1/I_3 ratio being around 1.7. By increasing the azo-polysiloxane concentration in the aqueous solution, the pyrene was progressively incorporated in the hydrophobic core of the aggregates that begin to form, the result being reflected by the decreasing of the I_1/I_3 ratio value. This modification is not sudden as in the case of low-molecular amphiphiles, the CCA values being estimated as the first inflexion point of the curves.

The micelles' morphology was studied using DLS and TEM methods. The micelles were prepared using the co-solvent method that supposes dissolving the polymer in THF, followed by the addition of water. The DLS experiments were made using an ALV-5000/E apparatus equipped with a He–Ne laser source (JDS Uniphase, $\lambda = 633$ nm), the auto-correlation function being automatically calculated. The TEM microscopy studies were performed using a Philip Morgagni 268 microscope. The samples were negatively stained using a 2% uranyl acetate solution and deposed on a carbon network covered with copper.

Results and discussion

In order to modify the polysiloxane, two types of azo-aromatic compounds were used: 4-hydroxyazobenzene and 4′-hydroxyphenylazo-benzo-15-crown-5-ether (Scheme 1). In the second step, the unreacted chlorobenzyl groups were quaternized using different tertiary amines. Some characteristics of the synthesized polymers are presented in Table 1.

The polymers' molecular weights (M_n) were calculated using ^{1}H-NMR spectra, by taking into account the substitution degree (the starting polysiloxane containing chlorobenzyl groups has for all the samples a molecular weight value M_n = 4,800–5,000). The substitution degree was evaluated based on the signals corresponding to the methylenic chlorobenzyl (4.5 ppm) and $-C_6H_4-CH_2-O-C_6H_4-$ (5.0 ppm) signals. Due to the fact that both methylenic groups ($-C_6H_4-CH_2-O-C_6H_4-$ and $-C_6H_4-CH_2-N^+-$) present similar chemical shifts (5 ppm), it is compulsory to calculate the substitution degree after the first substitution step (with azo-groups). As an example, Fig. 1 presents the ^{1}H-NMR spectra corresponding to the Sample 1 and Sample 2, respectively.

First of all, the photochromic behaviors of the azo-polysiloxanes in solution ($CHCl_3$) were evaluated. The photochromic behavior was investigated to establish the minimum UV irradiation time, corresponding to the maximum conversion degree on *cis*-isomer (in order to control the disaggregation process). As one can see in Fig. 2, in the case of the Sample 1 there are necessary only 20 s of irradiation to obtain the maximum content (82%) in *cis*-isomer.

Except Sample 6, the other azo-polysiloxanes containing quaternary ammonium groups have similar behavior concerning the photochromic response, 20–30 s of UV irradiation being sufficient to obtain the maximum conversion degree in *cis*-isomer. The relative lower values of *cis*-isomer content after UV irradiation, corresponding to the Samples 2 and 6, are probably the result of some specific main-chain conformations, which hinder the azo-groups in the isomerization process.

Table 1 Some characteristics of the synthesized polymers

Sample no.	Azobenzene content (%)	Azo-crown-ether content (%)	Ternary amine type	Quaternary ammonium groups content (%)	M_n	T_g (°C)	CAC (g/L)
1	38	–	–	–	6,950	7	–
2	39	–	DMDA	35	8,900	0	6×10^{-3}
3	32	–	TEA	35	7,550	−9	2×10^{-3}
4	33	–	TBA	38	8,300	−6	1×10^{-2}
5	–	45	DMTA	39	11,600	25	4×10^{-3}
6	–	45	TBA	37	10,900	22	8×10^{-3}

TEA triethylamine; *TBA* tributhylamine; *DMDA* dimethyldodecylamine; *DMTA* dimethyltetradecylamine

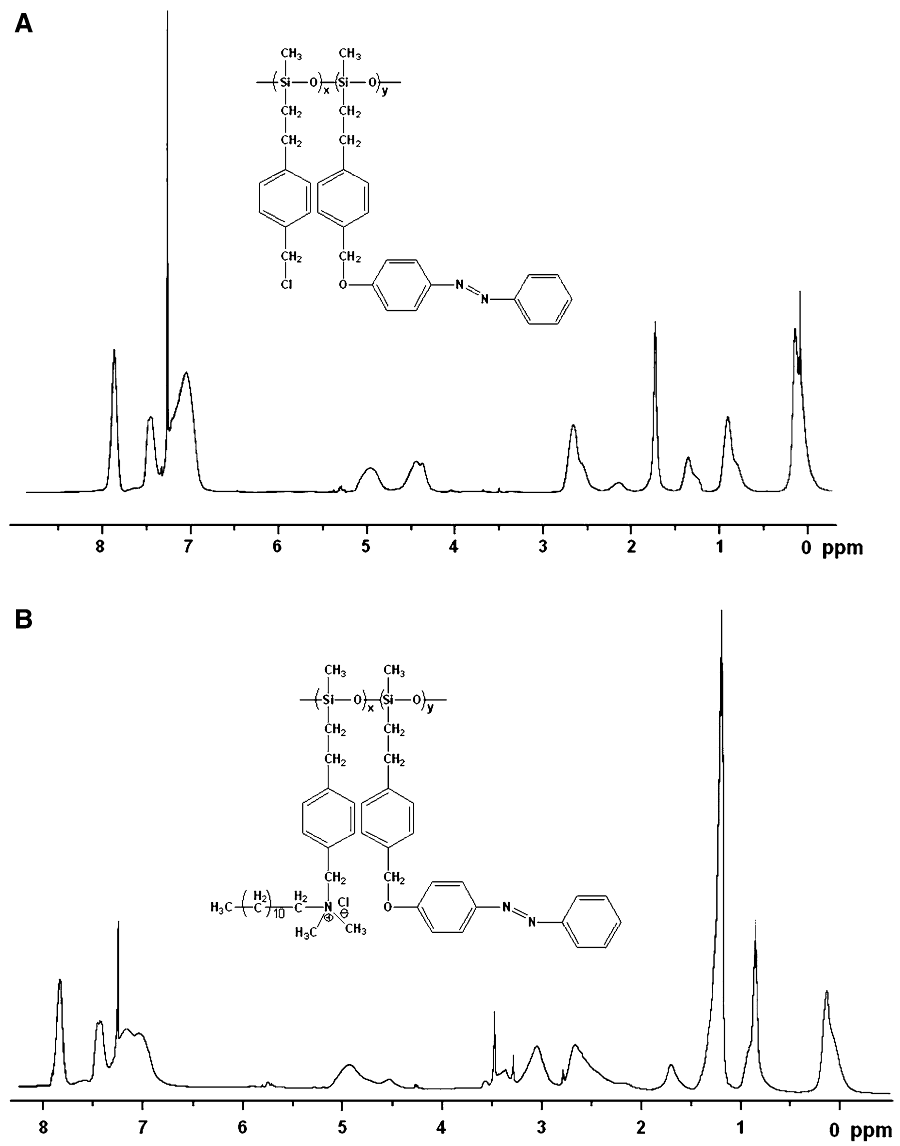


Fig. 1 ^{1}H-NMR spectra corresponding to the Sample 1 (**a**) and Sample 2 (**b**)

This assumption is based on some studies developed now in our group on azo-polysiloxanes having different ratios between the hydrophilic and hydrophobic segments [24].

Another important parameter concerning the aggregation/disaggregation process is the relaxation time of the azo-moieties (from *cis*- to *trans*-configuration) in the presence of natural visible light. The azo-polysiloxanes modified with quaternary ammonium groups present a similar behavior and need 5–6 min for a complete

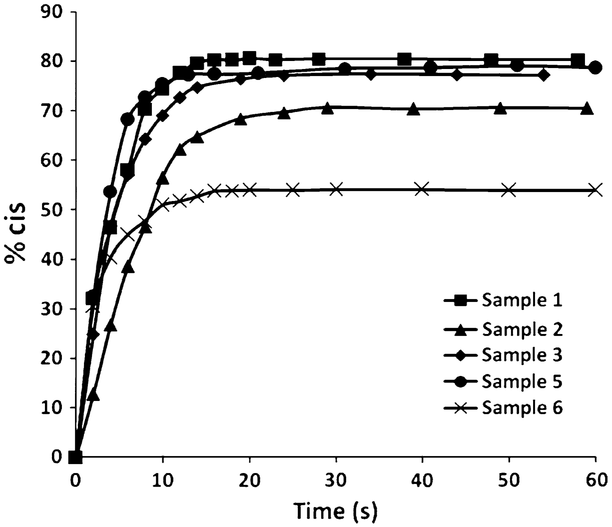


Fig. 2 Photoisomerization kinetic curves in solution corresponding to the Samples 1, 2, 3, 5, and 6

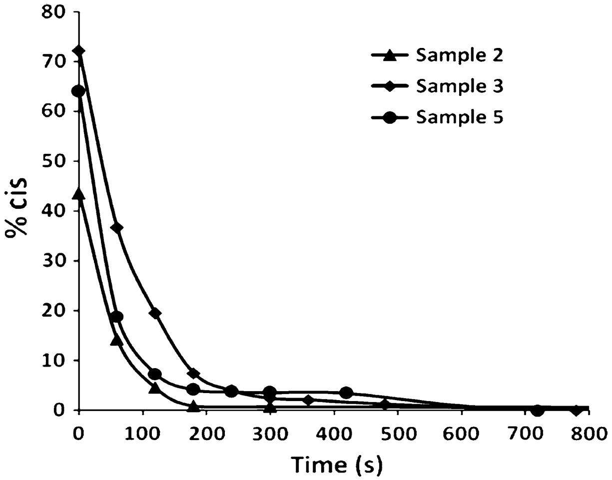


Fig. 3 The relaxation process of azo-groups in the presence of natural visible light

relaxation (Fig. 3). This means that after UV irradiation, in the presence of natural light, the re-aggregation process of micelles needs more than 5 min. This aspect can be important in the controlled delivery processes.

The next step of the study was to verify if the amphyphilic azo-polysiloxanes are capable to generate micelles and to evaluate their critical concentration of aggregation (CCA) values. Typical examples concerning polymers' aggregation behavior and estimation of the CCA value are presented in Fig. 4. The CCA values

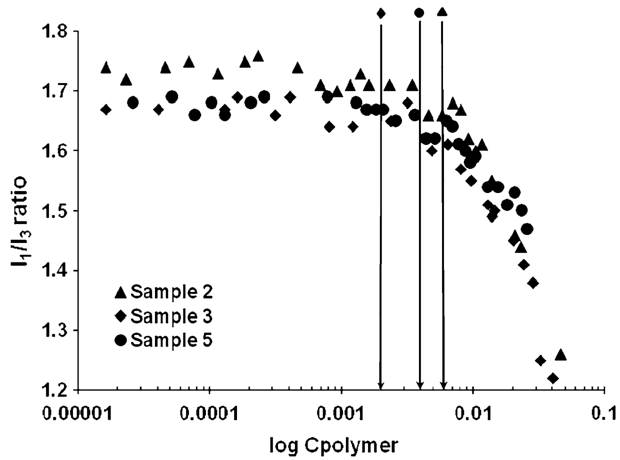


Fig. 4 Plot of the I_1/I_3 ratio as a function of the azo-polysiloxane concentration corresponding to the Samples 2, 3, and 5

were estimated as the first inflexion point from the curves that represent the plot of the I_1/I_3 ratio as a function of the polymer concentration.

The first observation that can be made is that the critical values do not suffer important modifications as a function of the chemical structure (Table 1). The relatively low CCA values can be explained by the presence in the side-chain of the azobenzenic hydrophobic groups, with a high aggregation tendency (H-type or J-type) [25–27].

The DLS and TEM analysis reflect the presence of the aggregates, as a function of the polymer concentration, heterogeneous or homogenous populations being present.

Figure 5 presents the distribution of the micellar populations corresponding to concentrations of 0.01 and 0.1 g/L. At a low concentration, three different populations containing aggregates with 9, 40, and 200 nm as average diameters were identified. The smallest diameter values (9 nm) correspond probably to a primary form of aggregation, that suppose the association of only few macromolecular chains. Preliminary molecular modeling studies, effectuated using Materials Studio software [28] showed that an azo-polysiloxanic single chain, having similar structural characteristic and polymerization degree (Fig. 6) has a diameter of approximately 3–4 nm [24].

By increasing the polymer concentration, two different populations having the diameter average values of 10 and 200 nm could be noticed. It must be underlined the high value of the polydispersity index, in the case of the population with 200 nm diameter.

The TEM studies clarified the DLS results concerning the high polydispersity index in the case of the population with 200 nm diameter. At low concentration values (0.01 g/L), one can observe both individual spherical micelles (20–30 nm) and associates of 2–4 micelles (Fig. 7a). In the case of higher concentration (0.1 g/L),

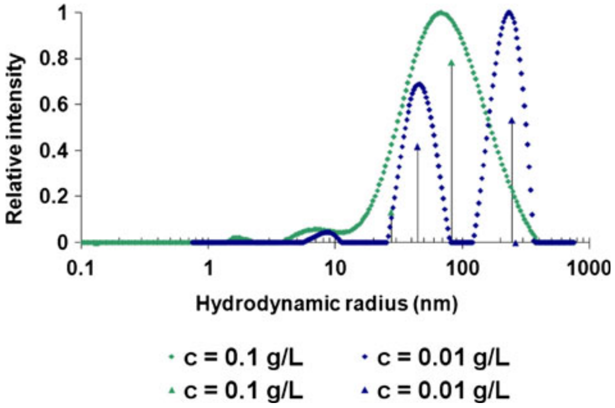


Fig. 5 Relative scattered intensity versus hydrodynamic radius corresponding to Sample 2

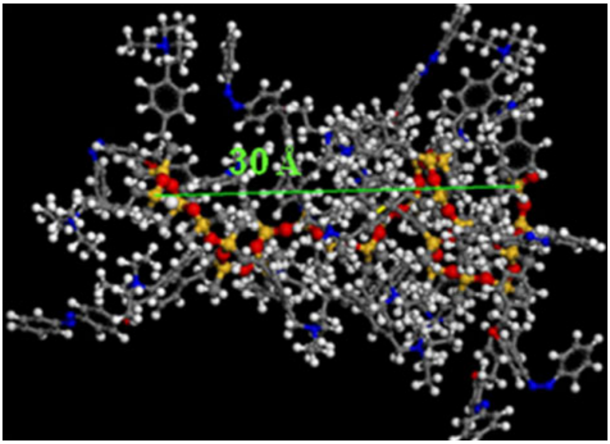


Fig. 6 Minimum energy conformation of an azopolysiloxane amphiphilic chain (having similar composition with Sample 3)

the inter-micellar association process is predominantly leading to the cluster formation (Fig. 7b).

The chemical structure of the amine has a strong influence on the aggregation mechanism. If the amine contains short hydrocarbon segments, no association between micelles was observed. For example, in the case of Sample 3 the DLS curves reflect the presence of aggregates with both 4–5 nm and 60 nm diameters (Fig. 8). As in the case of the Sample 2, the first populations (4–5 nm diameter) correspond to primary aggregation forms. The second population is mono-disperse and shows micellar structures with 60 nm diameter. Similar results concerning the presence of the individual micelles and not inter-micellar aggregation were obtained in the case of Sample 4.

This behavior suggests that only the presence of a long hydrocarbon chain (ex. dodecyl) in the amine structure imposes the apparition of the clusters. The influence

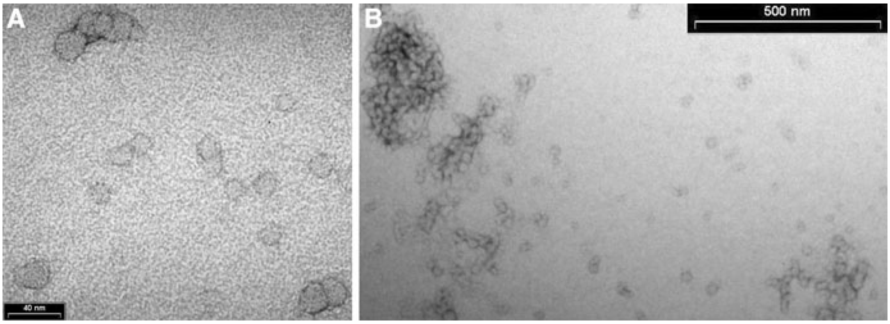


Fig. 7 TEM images of Sample 2 reflecting different populations type of micelles: individual micelles (**a**) and clusters (**b**)

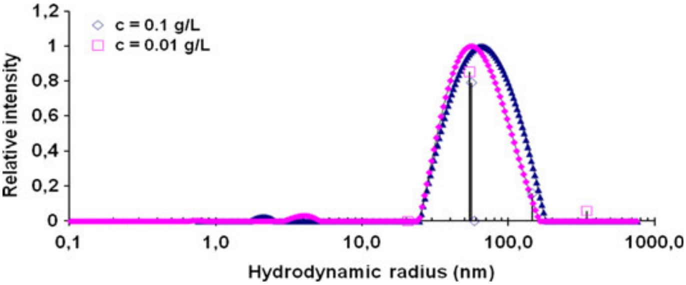


Fig. 8 Relative scattered intensity versus hydrodynamic radius corresponding to the Sample 3

of the long hydrocarbon chains in the amine can be observed too in the case of polysiloxanes substituted with azo-crown ether groups (Samples 5 and 6). Figure 9 reveals the presence of clusters with diameters around 100 nm. However, in the case of the Sample 5 a different morphology of the clusters was identified, cylindrical aggregation forms being present.

The micelles' disaggregation process was studied by fluorescence spectroscopy using pyrene as marker. If the micelles are present in the water, the pyrene will be incorporated inside them and the ratio I_1/I_3 will have values situated around 1.4. After the disaggregation of micelles, pyrene will be liberated in water, and the I_1/I_3 ratio will increase until 1.70–1.72. The azo-polymers were dissolved in water at concentrations above the CCA values and the micelles were UV irradiated for 15 or 30 min (Table 2).

The best results concerning the disaggregation process were obtained for the Sample 2 when the I_1/I_3 ratio increases after 30 min of irradiation from 1.40 to 1.72 (the value that correspond to the free pyrene in solution). This suggests that the process of micelles' disaggregation is complete and the pyrene was delivered in solution. In the other cases, the disaggregation process is only partial, the final value corresponding to I_1/I_3 ratio being situated in the range of 1.53–1.63.

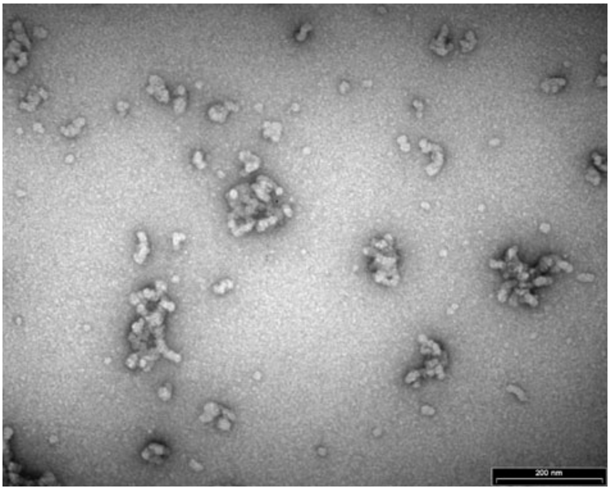


Fig. 9 TEM image of micellar clusters corresponding to Sample 5 (0.01 g/L)

Table 2 Micelles' disaggregation under UV irradiation

	Polymer concentration (g/L)	I_1/I_3 ratio		
		Non-irradiated	15 min irradiation	30 min irradiation
Sample 2	2.3×10^{-2}	1.40	1.66	1.72
Sample 3	2.8×10^{-2}	1.45	1.51	1.54
Sample 5	2.6×10^{-2}	1.43	1.50	1.53
Sample 6	1.5×10^{-2}	1.45	1.59	1.63

Conclusions

Amphiphilic azo-polysiloxanes containing quaternary ammonium groups were synthesized and characterized. The photochromic studies evidenced that only 20–30 s of UV irradiation are necessary to obtain the maximum *cis*-isomer content. All the amphiphilic polysiloxanes are capable to generate micelles, the CCA values being situated within the 10^{-3}–10^{-2} g/L range. Concerning the aggregates' morphology, different situations were identified as a function of the concentration and the amine structure. At low concentration of the polymer in water, individual micelles and primary aggregates containing only few macromolecular chains were identified. As a function of the ternary amine structure used in the quarterization reaction, the micellar aggregation process leads to formation of individual micelles or micellar clusters. If the amine contains short hydrocarbon segments, individual micelles can be obtained. If the amine contains a long hydrocarbon segment, a primary micellar association process takes place, followed by the formation of the multi-micellar clusters. The clusters'dimension cannot be controlled, the polydispersity index having high values. The disaggregation process of the micelles under

UV irradiation and the influence of the polymer chemical structure on the aggregates' stability were investigated. A total disaggregation process was obtained for the polysiloxane modified with azophenol and amines containing a long hydrocarbon chain. In the other cases, only a partial micelles' disaggregation process takes place.

Acknowledgments The authors want to express their gratitude to Roumanian Ministry of Education Research and Innovation, for partial financial support of this research (CNCSIS Idei Grant-356/2008). The authors thank to Dr. Ramona Enea for the DLS analysis.

References

1. Martina M, Hutmacher D (2007) Biodegradable polymers applied in tissue engineering research: a review. Polym Int 56:145–157. doi:10.1002/pi.2108
2. Jiang J, Tong X, Zhao Y (2005) A new design for light-breakable polymer micelles. J Am Chem Soc 127:8290–8291. doi:10.1021/ja0521019
3. Burke S, Barrett C (2004) Controlling the physicochemical properties of weak polyelectrolyte multilayer films through acid/base equilibria. Pure Appl Chem 76:1387–1398. doi:10.1351/pac200476071387
4. Chien H-W, Chang T-Y, Tsai W-B (2009) Spatial control of cellular adhesion using photo-cross-linked micropatterned polyelectrolyte multilayer films. Biomaterials 30:2209–2218. doi:10.1016/j.biomaterials.2008.12.060
5. Khandare J, Minko T (2006) Polymer–drug conjugates: Progress in polymeric prodrugs. Prog Polym Sci 31:359–397. doi:10.1016/j.progpolymsci.2005.09.004
6. Rijcken CJF, Soga O, Hennink WE, van Nostrum CF (2007) Triggered destabilisation of polymeric micelles and vesicles by changing polymers polarity: an attractive tool for drug delivery. J Con Rel 120:131–148. doi:10.1016/j.jconrel.2007.03.023
7. Duan Q, Miura Y, Narumi A, Shen X, Sato S-I, Satoh T, Kakuchi T (2006) Synthesis and thermoresponsive property of end functionalized poly(N-isopropyl acrylamide) with pyrenyl group. J Polym Sci Part A: Polym Chem 44:1117–1124. doi:10.1002/pola.21208
8. Einaga Y, Sato O, Iyoda T, Fujishima A, Hashimoto K (1999) Photofunctional vesicles containing prussian blue and azobenzene. J Am Chem Soc 121:3745–3750. doi:10.1021/ja9824501
9. Ikeda T, Horiuchi S, Karanjit DB, Kurihara S, Tazuke S (1990) Photochemically induced isothermal phase transition in polymer liquid crystals with mesogenic phenyl benzoate side chains 1 Calorimetric studies and order parameters. Macromolecules 23:36–42. doi:10.1021/ma00203a008
10. Rochon P, Batalla E, Natansohn A (1995) Optically induced surface gratings on azoaromatic polymers films. Appl Phys Lett 66:136–138. doi:10.1063/1.113541
11. Kim DY, Tripathy SK, Li L, Kumar J (1995) Laser-induced holographic surface relief gratings on nonlinear optical polymer films. Appl Phys Lett 66:1166–1168. doi:10.1063/1.113845
12. Sava I, Resmerita A-M, Lisa G, Damian V, Hurduc N (2008) Synthesis and photochromic behavior of new polyimides containing azobenzene side groups. Polymer 49:1475–1482. doi:10.1016/j.polymer.2008.02.004
13. Yu YL, Nakano M, Ikeda T (2003) Photomechanics: directed bending of a polymer film by light. Nature 425:145–146. doi:10.1038/425145a
14. Li M-H, Keller P (2006) Artificial muscles based on liquid crystal elastomers. Phil Trans R Soc A 364:2763–2777. doi:10.1098/rsta.2006.1853
15. Egawa Y, Gotoha R, Niinaa S, Anzai J (2007) Ortho-azo substituted phenylboronic acids for colorimetric sugar sensors. Bioorg Med Chem Lett 17:3789–3792. doi:10.1016/j.bmcl.2007.02.073
16. Egami C, Kawata Y, Aoshima Y, Alasfar S, Sugihara O, Fujimura H, Okamoto N (2000) Two-stage optical data storage in azo polymers. Jpn J Appl Phys 39:1558–1561. doi:10.1143/JJAP.39.1558
17. Onaca O, Enea R, Hughes DW, Meier W (2008) Stimuli-responsive polymersomes as nanocarriers for drug and gene delivery. Macromol Biosci 9:129–139. doi:10.1002/mabi.200800248
18. Yoshida E, Ohta M (2005) Preparation of light-stable micelles with azo dyes from a nonamphiphilic random block copolymer. Colloid Polym Sci 283:872–879. doi:10.1007/s00396-004-1229-6

19. Deng Y, Li Y, Wang X (2006) Colloidal sphere formation, H-aggregation, and photoresponsive properties of an amphiphilic random copolymer bearing branched azo side chains. Macromolecules 39:6590–6598. doi:10.1021/ma061335p
20. Hurduc N, Enea R, Rezmerita AM, Moleavin I, Cristea M, Scutaru D (2008) Modified azo-polysiloxanes for complex photo-sensible supramolecular systems. In: Ganachaud F, Boileau S, Boury B (eds) Silicon based polymers. Springer, Netherlands, pp 65–84. doi:10.1007/978-1-4020-8528-4_6
21. Ardeleanu R, Airinei A, Sacarescu G, Sacarescu L (2002) Photosensitive crown ether-siloxane copolymers bearing azobenzene chromophores. Eur Pol J 38:2265–2270. doi:10.1016/S0014-3057(02)00128-3
22. Kazmierski K, Hurduc N, Sauvet G, Chojnowski J (2004) Polysiloxanes with chlorobenzyl groups as precursors of new organic-silicone materials. J Polym Sci Part A Polym Chem 42:1682–1692. doi:10.1002/pola.11066
23. Hurduc N, Enea R, Scutaru D, Sacarescu L, Donose BC, Nguyen AV (2007) Nucleobases modified azo-polysiloxanes, materials with potential application in biomolecules nanomanipulation. J Polym Sci Part A Polym Chem 45:4240–4248. doi:10.1002/pola.22165
24. Epure L, Moleavin I, N. Hurduc—paper in preparation
25. Kalyanasundaram K, Thomas JK (1977) Environmental effects on vibronic band intensities in pyrene monomer fluorescence and their application in studies of micellar systems. J Am Chem Soc 99:2039–2044. doi:10.1021/ja00449a004
26. Kuiper JM, Engberts JB (2004) H-aggregation of azobenzene-substituted amphiphiles in vesicular membranes. Langmuir 20:1152–1160. doi:10.1021/la0358724
27. Enea R, Resmerita A-M, Petraru L, Grigoras C, Hurduc N, Simionescu CI (2007) Synthesis and photochromic behaviour of some azo-polysiloxanes modified with nucleobases or donor-acceptor groups. Central Eur J Chem 5:981–995. doi:10.2478/s11532-007-0042-8
28. Materials Studio 4.0., Accelrys Software, Inc., San Diego (licensed to Nicolae Hurduc)