Cent. Eur. J. Chem. • 9(6) • 2011 • 1117-1125
DOI: 10.2478/s11532-011-0102-y

VERSITA

Central European Journal of **Chemistry**

Amphiphilic azopolymers capable to generate photo-sensitive micelles

Research Article

Ioana Moleavin[1], Constanta Ibanescu[1, 2], Anca Hodorog-Rusu[1], Ecaterina Peptu[1], Florica Doroftei[2], Nicolae Hurduc[1*]

[1]*«Gheorghe Asachi» Technical University of Iasi, Department of Natural and Synthetic Polymers, 700050-Iasi, Romania*

[2]*Department of Physical Chemistry of Polymers, «Petru Poni» Institute of Macromolecular Chemistry, 700487 Iasi, Romania*

Received 6 April 2011; Accepted 14 August 2011

Abstract: Amphiphilic macromolecular micelles are advantageous for drug delivery applications due to the decrease of side-effects, ease of screening drugs against degradation, long-term stability, targeted delivery and control of the amount of the released drug. A series of amphiphilic azo-polymers having a flexible or rigid main-chain were synthesized and characterized. The presence of chlorobenzyl side-groups allowed both the easy bonding of photo-sensitive or hydrophilic groups and good control of the degree of substitution. The chemical structure was confirmed by ^{1}H-NMR. The critical concentration of aggregation (CCA) was calculated using the fluorescence emission spectrum of pyrene. The interest was focused on a preliminary study concerning the disaggregation capacity of micelles under UV irradiation. The presence of micellar aggregates was confirmed by DLS and SEM and different organization of the amphiphilic polymers was evidenced depending on polymers concentration and polymers structure. In low polymer concentrations in water predominantly globular aggregates were formed. The increase in concentration increased the polydispersity index due to the fusion of micelles and formation of associates of globular aggregates, inter-micellar associates (clusters) and vesicles.

Keywords: *Azobenzene • Amphiphilic polymers • Photo-sensitive polymers • Micelles*

1. Introduction

Since 1960, polymeric micelles have attracted researchers' attention as drug carriers due to their tunable properties and pharmacological characteristics [1]. Kataoka's research group [2] has intensively studied the potential of macromolecular micelles as drug carriers. The solubility of the active component in the hydrophobic core and the capacity to target it to the right place [3,4] make the micelles very attractive for potential use in drug delivery systems. Amphiphilic macromolecular micelles are particularly advantageous for such applications because of the reduction of side-effects incidence, ease of screening of drugs against degradation, long-term stability, targeted delivery and control of the amount of the released drug. Light stimuli sensitive amphiphilic systems are able to deliver the encapsulated drug at the right moment and at a precise site under the action of UV, Vis or near infra-red (NIR) light which represent a suitable choice when other stimuli are not available. Due to the deeper penetration in the tissue and minimal effects on healthy cells, NIR light has used become more and more in biomedical applications [5,6].

For drug delivery systems, non-destructive mechanisms can be used involving light exposure of photo-active groups. Under irradiation, the photo-sensitive groups present reversible geometrical modifications changing the hydrophilic-hydrophobic equilibrium and thus inducing the disaggregation process of the micellar system. Azo-benzene groups with dipole moment modifications can be considered for such applications [5,7] as well as isomerizable or photo-dimerizable cynamoil groups producing more hydrophilic species, and thriphenylmethane leucohydroxide able to generate electric charges or spiro-benzopyran able to generate amphionic species (zwitterions) [6].

* *E-mail: nhurduc@ch.tuiasi.ro*

Azo-benzene, as well as its derivatives, undergoes a reversible photoinduced *trans–cis* isomerization between the thermodynamically more stable *trans* isomer and the metastable *cis* one. Differences between the two isomers are obvious both in UV absorption spectra and physical properties (*i.e.*, *cis* isomer is known to be more hydrophilic than *trans* isomer) [8]. The photo-induced isomerization process and thermal *cis-trans* relaxation were used to investigate supramolecular organization and molecular characteristics of systems, with azobenzene acting as a sensor (free-volume and solid phase polymer stiffness estimation) [9]. Questions arose in polymer chemistry regarding the photochemistry of macromolecular chains having covalently-bonded chromophores either in the side-chain or in the backbone [10-17]. It is very important to elucidate the influence of the polymeric chain on the photoisomerization process of azo-groups. In the meantime changes induced in the polymer matrix by photoisomerization processes may be very important for different specific applications.

Self-assembly of polymers is a process of great interest due to the large field of applications opened. Generally, polymers characterized by associative properties in solution include both hydrophilic and hydrophobic chains in the same macromolecule. In a polar environment hydrophobic segments of such a polymer associate over a critical concentration value (CCA = critical concentration of aggregation) to have a minimum contact surface with the polar surroundings. The hydrophilic part of the macromolecule acts as a stabilizing interface between the hydrophobic aggregate (micelle) and the polar environment. Usually the hydrophobic part of the macromolecule is a hydrocarbon chain. Only a few studies referred to silicon chains of poly(dimethyl siloxane) (PDMS) type as hydrophobic part in such systems. PDMS is simultaneously highly hydrophobic and oleophobic due to high chain flexibility and low cohesion energy. Moreover, PDMS has a low glass transition temperature (Tg), below -125°C. As a consequence, if the azo groups are connected to a polysiloxanic chain and undergo *cis-trans* isomerization under UV irradiation, this process will affect the geometry of the whole macromolecular chain. Therefore, a reorganization process at supramolecular level occurs and its intensity will be influenced by the chemical structure of azo-groups, the total substitution degree and the ratio of the hydrophilic to hydrophobic segments. If the polymeric main chain is rigid a different situation will appear at supramolecular level as a result of the lower mobility of the hydrophilic and hydrophobic segments. The combination between amphiphilic properties and the capacity to respond to light stimuli makes it possible to obtain photosensitive micelles [18-20] susceptible to be used as drug delivery systems.

The aim of the present work is to study the photoisomerization phenomena of UV light sensitive systems based on amphiphilic azo-polymers and the aggregation/disaggregation phenomena in the synthesised polymers. Different polymeric backbones having a flexible (polysiloxane) or a rigid (PCMS) character were used. The critical aggregation concentrations were evaluated using the classical method based on the fluorescence properties of the pyrene.

2. Experimental procedure

The photoisomerization properties were evaluated using UV/VIS spectroscopy in solution. Dilute polymer solutions in chloroform have been used to study the photoisomerization phenomena in the liquid state. Irradiation of the solutions or films was carried out at 365 nm with a 100 W mercury lamp (Bioblock model, irradiance of 7 mW cm^{-2} at 30 cm from the filter). During the irradiation, the polymeric film was exposed to a compressed air stream in order to maintain constant the temperature at 22°C.

The *cis*-isomer content was calculated from UV/VIS spectra taking into consideration the maximum absorption of the *trans*-isomer situated at 345 nm for azobenzene or 367 nm for crown-ether. To obtain 100% *trans*- isomer the samples were stored in the dark (48 hours) before the measurements. The maximum absorption value obtained in the first measurement before UV irradiation is considered to correspond to 100% *trans*-isomer.

The solution was exposed to the visible light to evaluate the *cis-trans* relaxation process, after establishment of the photoisomerization equilibrium (maximum value of the *cis*-isomer content); the diminution of the *cis*-isomer content as a function of the exposure time being calculated based on UV-VIS spectra.

The classical method using pyrene fluorescence spectroscopy was used to evaluate the amphiphilic azo-polymers aggregation capacity [20]. 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 [22]. 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^{-1}, no aggregation process was evidenced, the I1/I3 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. Pyrene was also used for CCA determination of amphiphilic polysiloxanes [1,18-26].

DLS measurements were performed on samples prepared according to the co-solvent method as follows: a well established amount of polymer (10 mg) was dissolved in 1 mL organic solvent (THF) and then added drop-by-drop in 9 mL of water. The final solution concentration was 1 mg/mL. The samples were kept under magnetic stirring for 7-8 hours at room temperature (22ºC).

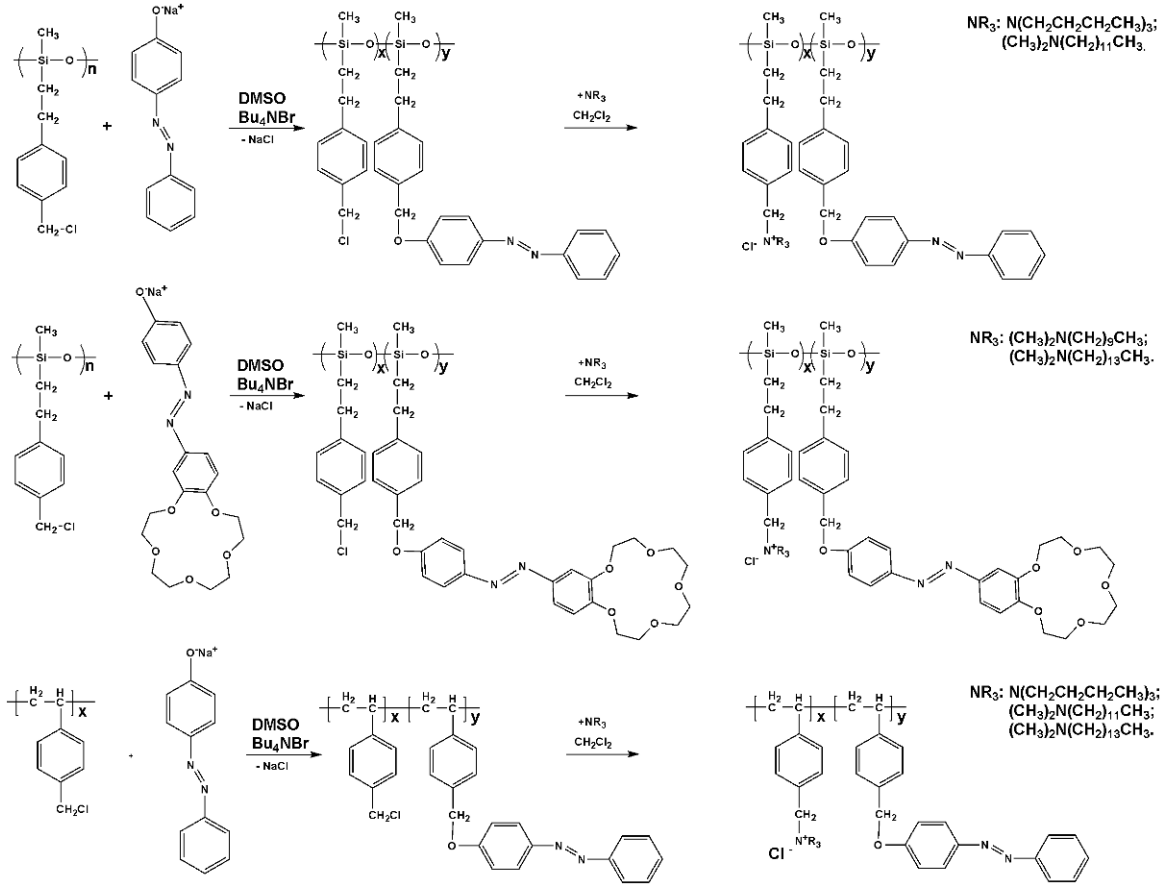
2.1. Materials

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 in two steps by diazotation of 4'-aminobenzo-15-crown-5-ether and than coupling of diazonium salt to phenol, as mentioned in a previous paper [27].

The investigated polymers were based either on a flexible polysiloxane backbone or on a rigid poly(chloromethyl)styrene backbone; both types of polymers had chlorobenzyl side-groups. The polymers were obtained in a two-step reaction. In the first step, the polymer was modified [28,29] with 4-(phenyl-azo)-phenol (35-45% substitution degree) or azo-crown-ether (45-60% substitution degree) and in the second step the unreacted chlorobenzyl groups were quaternized using different tertiary amines (Scheme 1). Details concerning the synthesis procedure were previously reported [27]

2.2. Instruments

The polymers were characterized by 1H-NMR, GPC, DSC, UV and fluorescence spectroscopy, dynamic light scattering (DLS) and scanning electron microscopy (SEM). The ^{1}H-NMR spectra were recorded on a Brucker Avance DRX 400 MHz spectrometer. DSC analyses were carried out on a Mettler Toledo DSC-1 Star System with a heating/cooling rate of 10 K min^{-1}, between -50ºC



Scheme 1. Reaction scheme for polymers synthesis.

Table 1. Characteristics of the synthesized polymers.

Spl. no.	Polymeric main chain	Azobz. content (%)	Azo-crown-ether content (%)	Ternary amine type	Quaternary ammonium groups content (%)	M_n	T_g (°C)	CCA (mg L^{-1})
1	Polysiloxane main chain	99	-	-	-	9.200	31	-
2		45	-	TBA	36	8.800	-1	3×10^{-3}
3		62	-	DMDoDA	25	9.050	0	6×10^{-3}
4		-	45	DMTDA	39	11.600	6	4×10^{-3}
5		-	45	DMDA	15	9.950	15	5×10^{-3}
6	PCMS main chain	56	-	DMDoDA	30	7.750	95	5×10^{-3}
7		35	-	DMTDA	20	6.500	93	6×10^{-3}
8		40	-	TBA	10	5.950	91	5×10^{-3}

Tg - glass transition temperature; CCA - critical concentration of aggregation

and 100ºC. DLS measurements were performed on a SAPD-700 goniometer. SEM studies were performed on a Quanta 200 (Fei) microscope. The samples were fixed on a copper support and covered with gold.

2.3. Polymers synthesis

The amphiphilic polymers were obtained in a two step process: in the first step the polymeric backbones are modified with azo-benzene (or azo-crown-ether) groups by a nucleophilic substitution reaction. In the second step the unreacted chlorobenzyl groups were quaternized using different tertiary amines (Scheme 1).

3. Results and discussion

Two types of polymers having different flexibilities were used in our study: a flexible main-chain with a polysiloxanic structure containing chlorobenzyl side-groups and a rigid backbone based on poly(chloromethyl)styrene. The presence of chlorobenzyl side-groups allowed both the easy bonding of photo-sensitive or hydrophilic groups and a good control of the substitution degree. The synthesized polymers have a specific architecture involving random tethering of both hydrophilic and hydrophobic segments on the same main chain. The characteristics of the obtained polymers are presented in Table 1.

The chemical structure was confirmed by ^{1}H-NMR. As one can see in Fig. 1, all the expected NMR signals are present: 0.23 ppm (**CH_3**-Si-); 0.98 ppm (-Si-**CH_2**-CH_2-, β-isomer); 1.45 ppm [-Si-CH-(**CH_3**), α-isomer]; 2.21 ppm [-Si-**CH-**(CH_3), α-isomer]; 2.74 ppm (-Si-CH_2-**CH_2**-, β-isomer); 4.57 ppm (-**CH_2**Cl); 4.9 ppm (-**CH_2**-O-azobenzene); 7.23 ppm (-CH_2-O-**C_6H_4**-); 7.90 ppm, 7.45 ppm and 6.90 ppm (azobenzenic protons). Details concerning the presence of α and β isomers in polysiloxane were previously explained [30]. The polymers' molecular weights (Mn) were also calculated using ^{1}H-NMR spectra, taking into account the starting polymerization degree of the polysiloxane (the polysiloxane containing chlorobenzyl groups has for all the samples a molecular weight value Mn = 5,000 – 5,200) or poly(chloromethyl)styrene (Mn = 3,600 – 3,800). The substitution degree was evaluated based on the signals corresponding to the methylenic chlorobenzyl (4.5 ppm) before the reaction and –C_6H_4-CH_2-O-C_6H_4- (5.0 ppm) signals after the azo-groups connection. Due to the fact that both methylenic groups (φ-CH_2-O-φ- and -φ-CH_2-N^+-) present similar chemical shifts (5 ppm), it is compulsory to calculate the substitution degree after the first reaction step (polymer containing only azo groups). As an example, Fig. 1 presents the ^{1}H-NMR spectra corresponding to the Sample 2 before (A) and after (B) the quarterisation reaction.

The photoisomerization behavior of the synthesized polymers is important to evaluate the polymer response to UV irradiation and the maximum content of *cis*-isomer that can be obtained. The studies were carried out in solution ($CHCl_3$) to evaluate the kinetics of isomerization under UV light. For each sample UV spectra were recorded to identify the wave length (λ_{max}) of maximum absorbance (A_{max}). Azobenzene group exhibit maximum absorbance for λ = 345 nm while azo-crown-ether group has maximum absorbance at λ = 367 nm (Fig. 2).

Except for Sample 2, the others azo-polysiloxanes containing quaternary ammonium groups have similar behaviour concerning the photochromic response, 10 to 15 seconds of UV irradiation being sufficient to obtain the maximum conversion degree in *cis*-isomer (around 80%) as one can see in Fig. 3. The relative lower value of *cis*-isomer content after UV irradiation (70%), corresponding to the Sample 2, are probably the result of some specific main-chain conformations, hindering the azo-groups in the isomerization process.

The relaxation phenomena of the azo-moieties (from *cis*- to *trans*-configuration) in the presence of natural visible light take on 150-200 s for all samples

excepting sample 2 (Fig. 4). The incomplete relaxation of sample 2 and step-wise relaxation of the sample 5 lead for a different mechanism of relaxation for samples with flexible polysiloxane chain. Sample 6 with a more rigid poly(chloromethyl)styrene backbone has a very short relaxation period (50 seconds) and less residual groups stable in *cis* configuration. These behaviours account for the important conformational modifications induced by UV light in the amphiphilic azo-polysiloxanes with very flexible backbones, phenomenon allowing the development of different intra-molecular aggregation/disaggregation processes with direct consequences on the steric shielding of side-chain groups.

The next step in our study was focused on testing the aggregation/disaggregation capacity of the synthesized polymers. For this purpose the fluorescence spectroscopy was used. Typical examples concerning polymers' aggregation behavior and estimation of the *CCA* value are presented in Fig. 5. The critical aggregation concentration (CCA) values 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 *CCA* values for the synthesized amphiphilic polymers are given in Table 1. For all samples these values are situated in a low ranging from 3×10^{-3} to 6×10^{-3} mg mL^{-1} regardless the

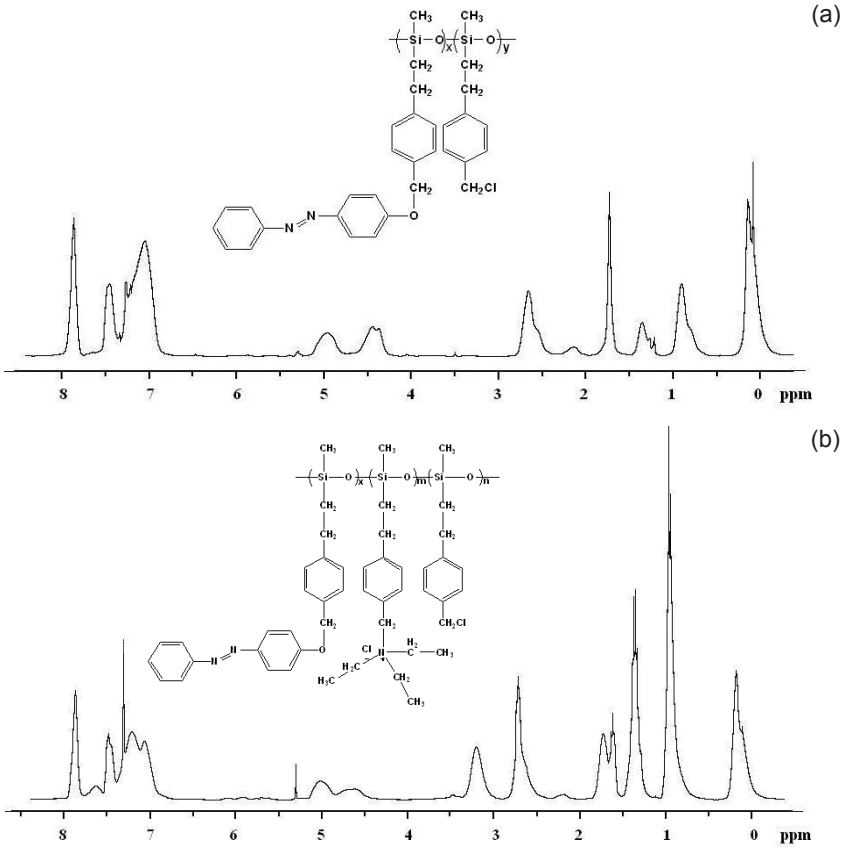


Figure 1. ^{1}H-RMN spectra for sample 2: (a) before and (b) after quarterisation reaction.

Table 2. UV irradiation behaviour of the azopolymeric micelles.

Sample	Solution concentration (mg mL^{-1})	Ratio I_1/I_3		
		Un-irradiated solution	Irradiated solution, 15 min	Irradiated solution, 30 min
2	2.7×10^{-2}	1.36	1.53	1.53
3	2.3×10^{-2}	1.38	1.70	1.72
4	2.6×10^{-2}	1.48	1.50	1.53
5	3.6×10^{-2}	1.36	1.39	1.37
6	2.9×10^{-2}	1.40	1.69	1.70
7	2.9×10^{-2}	1.30	1.51	1.50
8	1.7×10^{-2}	1.40	1.46	1.44

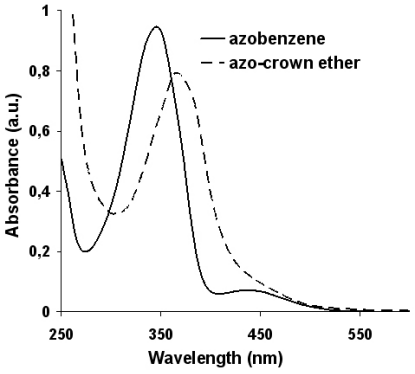


Figure 2. UV spectra in solution (chloroform) for modified polysiloxanes.

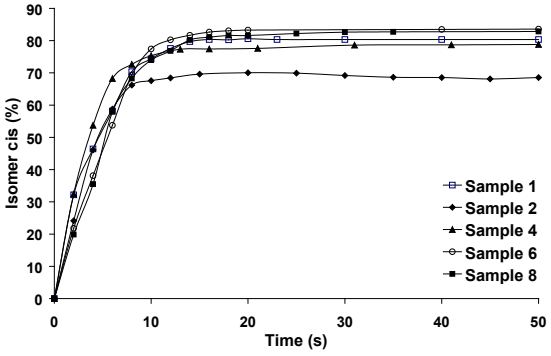


Figure 3. Photoisomerization kinetic curves in solution (chloroform) corresponding to the Samples 1, 2, 4, 6 and 8.

chemical structure and the ratio hydrophobic/hydrophilic of the base polymer. In the case of the amphiphilic polymers the decreasing rate of the value corresponding to I_1/I_3 ratio is not so clearly defined as in the case of the amphiphilic small molecules. For this reason, the CCA value has a certain approximation degree. 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.

One of the main objectives of the present work was a preliminary study concerning the disaggregation capacity of micelles under UV irradiation. In principle the disaggregation of micelles is a consequence of *trans-cis* photoisomerization process of the side-chain azobenzene groups under UV irradiation. For some values of the hydrophobic/hydrophilic ratio in the amphiphilic system, changes in the azobenzene dipole moment due to *cis-trans* photoisomerization can generate partial or total micellar disaggregation. The behavior of amphiphilic polymeric system under UV irradiation was studied with classical fluorescence spectroscopy method. When the micellar aggregates are formed the pyrene is immobilized inside them and the I_1/I_3 ratio decreases to values around 1.4. After UV irradiation of the polymeric solutions the disaggregation of micelles takes place and the encapsulated pyrene is released. As a consequence the I_1/I_3 ratio increases up to values close to 1.7 characteristic for the I_1/I_3 ratio in water (Table 2).

As can be seen from Table 2, in the case of Sample 2, only an incomplete disaggregation process takes place, the pyrene being partial delivered (the ratio I_1/I_3 after irradiation is only 1.53 and not 1.70). The incomplete delivery of the pyrene could be also possible due to π-π interactions developed between azo-groups and pyrene. Supplementary experiments are necessary to clarify this aspect. By increasing the azobenzene content (Sample 3) the disaggregation process is complete. In the case of azo-crown-ether substituent, only a very low stage of the disaggregation process can be obtained. For the rigid main-chain azo-polymers the disaggregation process is also influenced by the azo-groups content, the higher concentration corresponding to the total disaggregation process (Sample 6).

The presence of micellar aggregates is confirmed by DLS and SEM and different organization of the amphiphilic polymers is evidenced depending on polymers concentration and polymers structure. The DLS curves for two solutions of sample 2 polymer of different concentrations (0.1 and 1 mg mL^{-1}) are presented in Fig. 6.

At low concentration (0.1 mg mL^{-1}) two different populations containing aggregates with 20 and 40 nm as average diameters were identified. The presence of two populations can be explained by a secondary inter-micellar aggregation process. This assumption is supported by the results corresponding to the second concentration. At 1 mg mL^{-1} concentration, the diameter average values increased up to a mean value of 230 nm. It must be underlined the high value of the polydispersity index.

Sample 3 presents a similar profile for DLS curves (Fig. 7), but the shape of the curves is much more influenced by the concentration of solutions, reflecting different types of organization of the micellar system. For concentrations close to *CCA* (0.1 mg mL^{-1}) the DLS curve reflected the presence of an individual micelle with an average diameter of 23 nm. For a concentration of 0.5 mg mL^{-1} an increase in the average diameter of micelles was noticed up to 340 nm. The polydispersity index is probably high due to the presence of individual micelles together with micellar associates and vesicles.

SEM images for the sample 3 for a 0.1 mg mL^{-1} concentration (Fig. 8) clariffied the DLS results [25] confirming the high system polydispersity and the presence of both high and small size aggregates in solution.

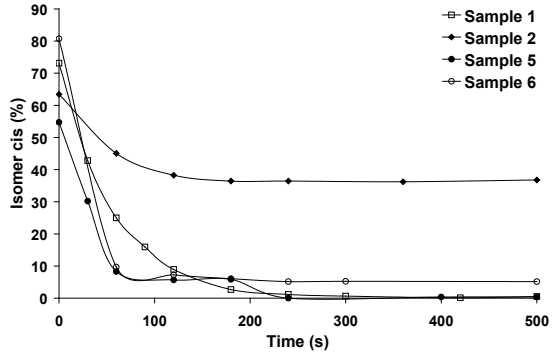


Figure 4. The relaxation process of azo-groups in solution (chloroform) in the presence of natural visible light.

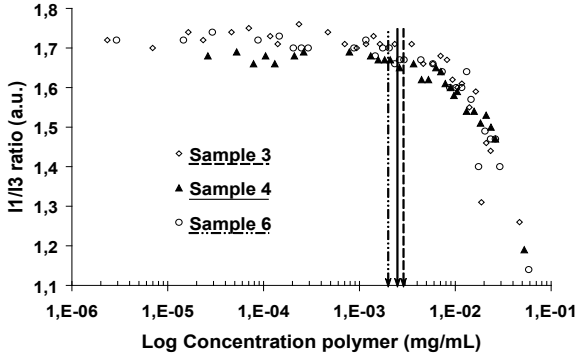


Figure 5. Plot of the I_1/I_3 ratio as a function of azo-polysiloxane concentration corresponding to the samples 3, 4 and 6.

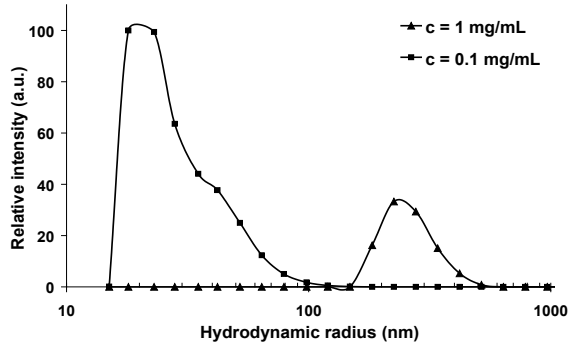


Figure 6. Relative scattered intensity vs. hydrodynamic radius corresponding to Sample 2.

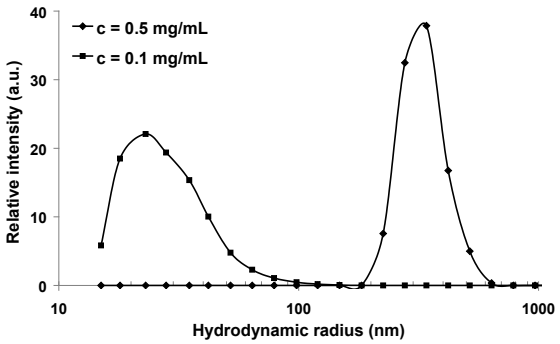


Figure 7. DLS curves for a polysiloxane modified with 62% azo groups and 25% dimethyl-dodecylamine (Sample 3).

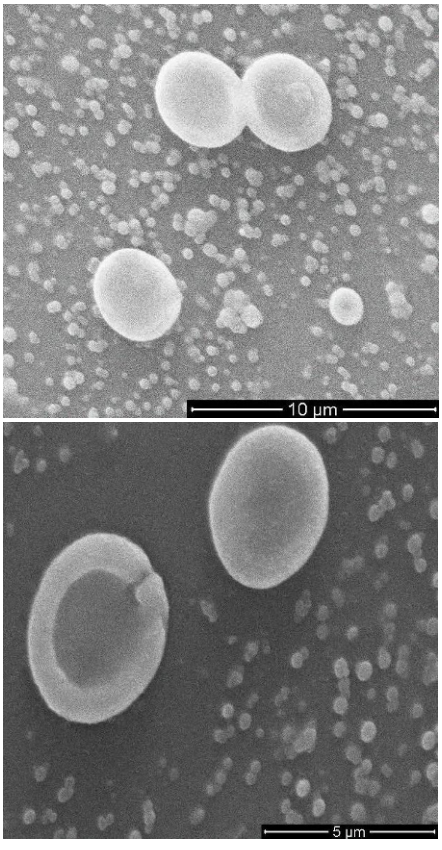


Figure 8. SEM images of 3 sample (0.1 mg mL^{-1}).

Beside the inter-micellar aggregates, discotic aggregates could be evidenced, with a 1-2 µm diameter. Discotic aggregates could be formed by the fusion of micelles. The problem is if the fusion process can be controlled or it is random. To elucidate this problem supplementary study will be needed.

DLS studies were also performed for polysiloxanes functionalized with crown-ethers and quaternary ammonium groups for two different concentrations 0.1 mg mL^{-1} and 0.5 mg mL^{-1} respectively. For both cases only one population was observed. For the diluted solution the presence of micelles with an average diameter of 25 nm was observed. Increasing concentration only inter-micellar aggregates were present with diameters situated between 200 and 800 nm (Fig. 9).

The high polydispersity index is confirmed by SEM where the formation of globular structures and aggregates of the micelles can be observed (Fig. 10).

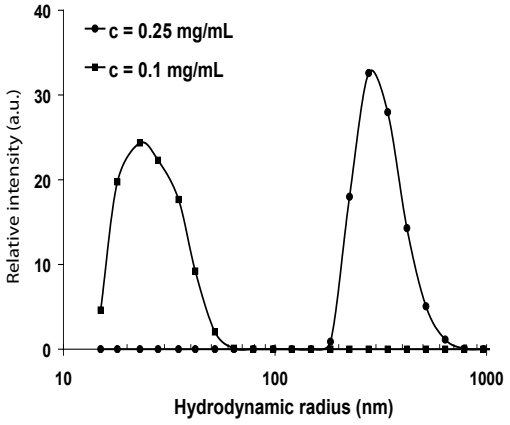


Figure 9. DLS curves for the sample 4 (0.1 mg mL^{-1} and 0.5 mg mL^{-1})

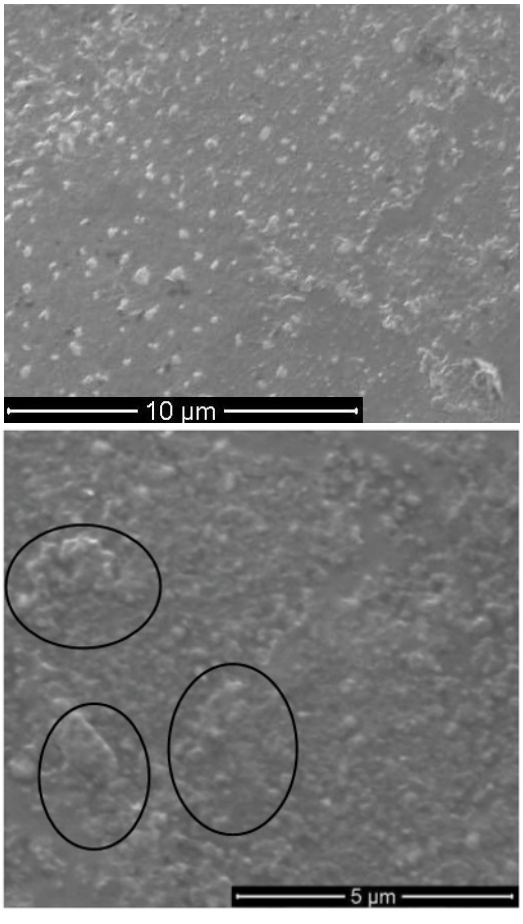


Figure 10. SEM images of a polysiloxane modified with 45% azo-crown-ether and 15% dimethyl-dodecyl amine (sample 5) at a concentration of (0.01 mg mL^{-1})

For the amphiphilic polymers with a poly (chloromethyl)styrene backbone (sample 6) only well defined individual micelles are evidenced in the SEM images for low concentrations (0.01 mg mL^{-1})

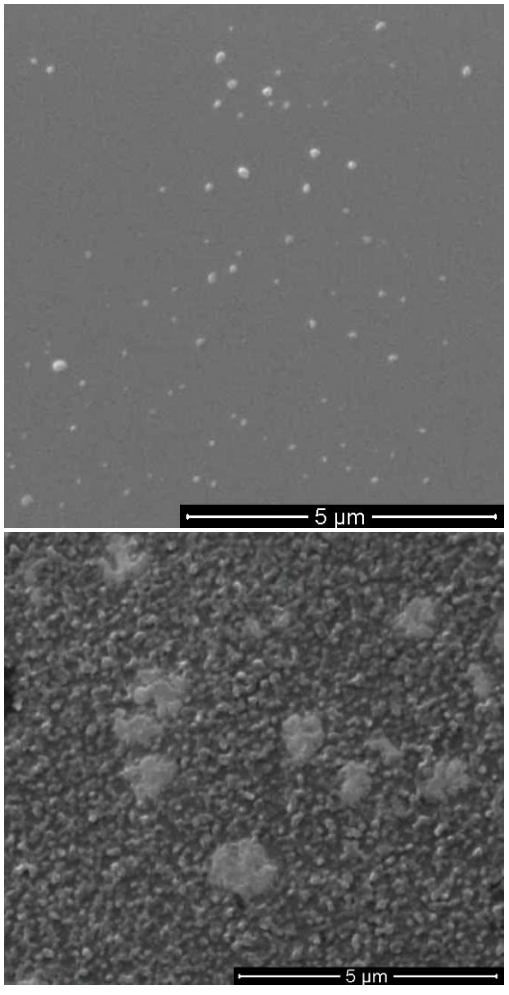


Figure 11. SEM images of the sample 6 at a concentration of 0.01 mg mL^{-1} (A) and 0.5 mg mL^{-1} (B).

(Fig. 11). Increasing the solution concentration to 0.5 mg mL^{-1} smaller or bigger aggregates are formed and the polydispersity index has increased.

4. Conclusions

A series of amphiphilic azo-polymers having a flexible or rigid main-chain were synthesized and characterized. The photoisomerization phenomena were studied under UV irradiation. For all the analyzed samples a maximum concentration in *cis*-azo groups (80%) was obtained after only 10 – 15 seconds of UV irradiation. The only exception was sample 2 for which the maximum isomerization degree has lower values, probably due to conformational reasons. Preliminary studies of the aggregation/disaggregation processes were made and the CCA was determined using the fluorescence spectroscopy. The CCA values were between 3×10^{-3}

and 6×10^{-3} mg mL^{-1} as a function of the chemical structure and the hydrophilic/hydrophobic ratio. For low polymer concentrations in water predominantly globular aggregates were formed. The increase in concentration increased the polydispersity index due to the fusion of micelles and formation of associates of globular aggregates, inter-micellar associates (clusters) and vesicles. Regarding the disaggregation process of micelles under UV irradiation it was noticed that for content in azobenzene higher than 50% a large amount of pyrene was entrapped inside micelles and totally released after only 15 minutes of UV irradiation. This observation is valuable both for flexible or rigid main-chains.

Acknowledgements

The authors want to thank to ANCS for financial support of this research (Grant 01CEA/2010).

References

[1] M.F. Francis, M. Cristea, F.M. Winnik, Pure Appl. Chem. 76, 1321 (2004)
[2] L. Prati , M. Rossi, S. Cammas-Marion, T. Okano, K. Kataoka, Colloid Surface B: Biointerfaces 16, 207 (1999)
[3] M. Adams, A. Lavasanifar, G.S. Kwon, J. Pharm. Sci. 92, 1343 (2003)
[4] R. Haag, Angew. Chem. Int. Ed. 43, 278 (2004)
[5] P. Rigler, W. Meier, J. Am. Chem. Soc. 128, 367 (2005)
[6] C.J.F. Rijcken, O. Soga, W.E. Hennink, C.F. van Nostrum, J. Controlled Release 120, 131 (2007)
[7] J. Jiang, X. Tong, Y. Zhao, J. Am. Chem. Soc. 127, 8290 (2005)
[8] C.T. Lee, K.A. Smith, T.A. Hatton, Macromolecules 37, 5397 (2004)
[9] B. Dunn, J.I. Zink, Chem. Mater. 9, 2280 (1997)
[10] E. Yoshida, M. Otha, Colloid Polym. Sci. 285, 431 (2007)
[11] G. Sudesh Kumar, D.C Neckers, Chem. Rev. 89, 1915 (1989)
[12] Y. Zong, K. Tawa, B. Menges, J. Ruhe, W. Knoll, Langmuir 21, 7036 (2005)
[13] M. Irie, W. Schnabel, Macromolecules 14, 1246 (1981)
[14] N. Ma, Y. Wang, Z. Wang, X. Zhang, Langmuir 22, 3906 (2006)
[15] A. Sobolewska, A. Miniewicz, D. Sek, Cent. Eur. J. Chem. 4, 266 (2006)
[16] Y. Deng, N. Li, Y. He, X. Wang, Macromolecules 40, 6669 (2007)
[17] S. Bai, Y. Zhao, Macromolecules 34, 9032 (2001)
[18] D. Wang, J. Liu, G. Ye, X. Wang, Polymer 50, 418 (2009)
[19] W. Su, Y. Luo, Q. Yan, S. Wu, K. Han, Q. Zhang, Y. Gu, Y. Li, Macromol. Rapid Commun. 28, 1251 (2007)
[20] H. Yu, A. Shishido, T. Ikeda, T. Iyoda, Macromol. Rapid Commun. 26, 1594 (2005)
[21] Y. Lin, P. Alexandridis, J. Phys. Chem. B 106, 10845 (2002)
[22] N. Hurduc, R. Enea, A.M. Rezmerita, I. Moleavin, M. Cristea, D. Scutaru, In: F. Ganachaud, S. Boileau, B. Boury (Eds.), Silicon Based Polymers (Springer, Netherlands, 2008) 65
[23] D. Anghel, F. Winnik, N. Galatanu, Coll. Surf. A: Phys. Eng. Aspects 149, 339 (1999)
[24] F.M. Winnik, S.T.A. Regismond, E.D. Goddard, Coll. Surf. A: Phys. Eng. Aspects 106, 243 (1996)
[25] A. Domínguez, A. Fernández, N. González, E. Iglesias, L. Montenegro, J. Chem. Ed. 74, 1227 (1997)
[26] K.P. Ananthapadmanabhan, E.D. Goddard, N.J. Turro, P.L. Kuo, Langmuir 1, 352 (1985)
[27] I. Moleavin, S. Grama, I. Carlescu, D. Scutaru, N. Hurduc, Polym. Bull. 65, 69 (2010)
[28] J. Kevelam, J. Engberts, J. Colloid and Interface Science, 178, 87 (1996)
[29] S. Wang, X. Wang, L. Li, R. Advincula, J. Org. Chem. 40, 179 (2004)
[30] K. Kazmierski, N. Hurduc, G. Sauvet, J. Chojnowski, J. Polym. Sci.: Part A: Polym. Chem. 42, 1682 (2004)