

BULETINUL INSTITUTULUI POLITEHNIC DIN IAȘI
Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iași
Volumul 68 (72), Numărul 2, 2022
Secția
CHIMIE și INGINERIE CHIMICĂ

AZO-POLYSILOXANES - SURFACE PROPERTIES STUDIES

BY

CRISTINA-MARIA HERGHILIGIU* and NICOLAE HURDUC

“Gheorghe Asachi” Technical University of Iași,
“Cristofor Simionescu” Faculty of Chemical Engineering and Environmental Protection,
Department of Natural and Synthetic Polymers, Iași, Romania

Received: March 9, 2022

Accepted for publication: April 24, 2022

Abstract. Due to the latest studies on the potential applications of azopolymers in the biological field as a support for cell seeding, it is necessary to study how azo-polysiloxanic chains are reorganizing depending on the film thickness and the type of support on which polymeric film is deposited. In addition to the fact that there are not many articles that try to explain the modification of azopolymers under the influence of aqueous media, this study helps to form an overview of how the chains are reorganized at the surface of the film and its depth, studying the variation of water contact angle of azo-polysiloxanic samples deposited on different supports with variable film thicknesses. Results indicate pattern behaviour of chain arrangements function of film thickness no matter the type of support.

Keywords: contact angle, surface properties, azo-polymers, polysiloxane, azo-derivates.

1. Introduction

Numerous papers have shown that cell adhesion and proliferation on polymeric surfaces (Martino and Netti, 2020) depend on the material characteristics: chemical structure, surface energy, wetting degree, roughness,

*Corresponding author; *e-mail*: cristina-maria.herghiligiu@academic.tuiasi.ro

rigidity (Rocha *et al.*, 2014; Hurduc *et al.*, 2013; Păiuș *et al.*, 2012; Stevens and George, 2005; Choi *et al.*, 2007; Voisin *et al.*, 2010) molecular weight of polymers (Choksakulnimitr *et al.*, 1995, Wang *et al.*, 2004), etc.. For a better understanding of the response of the surface in contact with the aqueous medium / cell culture medium, it should be noted that polymeric solids have a distinct ability to change their ordering in contact with different media, in order to minimize the interfacial energy and therefore the free energy of the system (Ruckenstein and Gourisankar, 1986).

As a result of the surface reorganization induced by the environment, the surface of the polymeric film tends to have a hydrophobic character in a non-polar environment, such as air, but brought into contact with a polar environment (*e.g.* water) is induced a certain degree of hydrophilicity in the material. It should also be noted that the reorganization of the polymeric film in a certain environment is dependent on the chemical structure of the surface. Thus, in the case of rigid or crosslinked polymers, the reorganization of surfaces may be too slow to be perceptible on a reasonable time scale, while in the case of flexible polymers, the process may take place immediately in the first minutes of contact with the fluid medium (azo-polysiloxane materials deposited on the glass substrate) method (Resmerita *et al.*, 2009, Resmerita *et al.*, 2010; Ruckenstein and Gourisankar, 1986).

The dynamics of polymeric surfaces reorganization play a very important role in their use in biological applications (*e.g.* as a substrate for the development of cell cultures). In this context it should be noted that most biological fluids contain aqueous medium as a continuous phase and consequently the study of the polymer-water interface will be representative for characterizing the interactions between polymers and cell culture medium (Ruckenstein and Gourisankar, 1986).

A particularly important role in these surface reorganization processes has the flexible chain of polysiloxane which can allow a very high mobility of the lateral groups and implicitly the surface reorganization processes. In addition to previous results published until now related to azo-polysiloxanes surface properties modification measured by contact angle method (Resmerita *et al.*, 2009, Resmerita *et al.*, 2010) this study tries to explain the correlation between polymeric chain arrangements on the surface film influenced by the type of support on which is deposited the sample (glass or poly(methyl methacrylate) – PMMA) and film thickness.

2. Experimental

2.1. Azo-polymer synthesis

The investigated azo-polysiloxanes (Fig. 1) were obtained by the chlorobenzyl groups nucleophilic substitution of poly[2-(4-

chloromethylphenyl)-ethyl]methylsiloxanes, using the sodium salt of 4-hydroxy-4'-substituted azobenzene. Details concerning polymer syntheses and characterizations have been previously reported (Hurdac *et al.*, 2007).

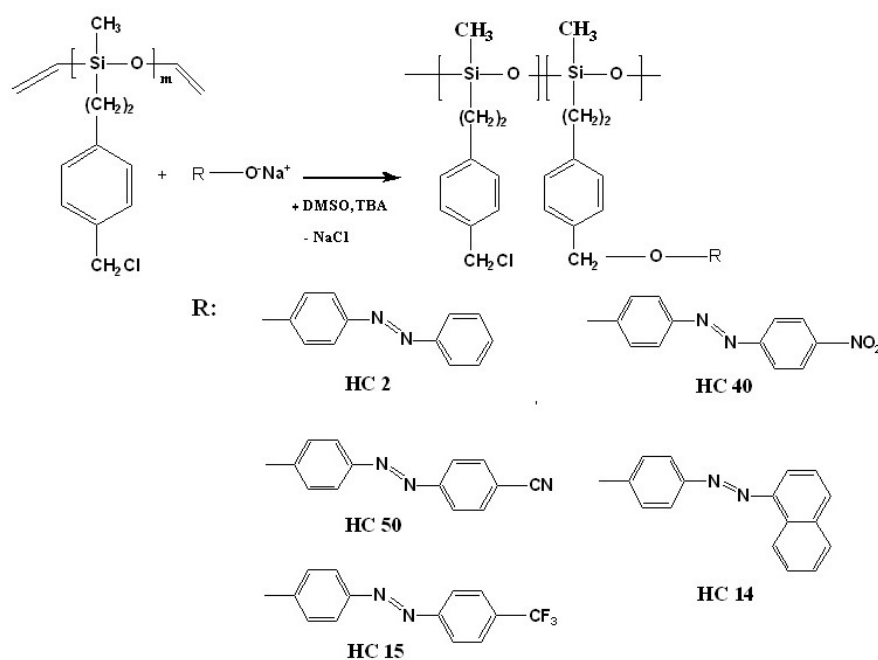


Fig. 1 – Synthesis of polysiloxanes containing azo-aromatic side groups.

The polymers chemical structure was confirmed by $^1\text{H-NMR}$ spectroscopy.

2.2. Measurements

Azo-polysiloxanic films were deposited by spin-coating technique on siliconized glass coated with amino-silane and PMMA supports, using 1,1,2-trichloroethane as solvent. Film thickness was measured using a Bruker Dextak XT profilometer with Vision 64 interpreter software. To eliminate the influence of the cis-trans relaxation processes induced by the visible light, the films were kept in complete dark for 24 h at 22 C. The experiments were performed in the absence of visible light using an EASYDROP Shape Analysis System (KRÜSS) equipped with DSA 1 evaluation software. Using a syringe, a liquid drop (15 μL) is placed onto the polymeric film spread out onto a moveable table. The drop is illuminated from one side and a video camera at the opposite side records an image of the drop. This image is transferred to a computer equipped with a video-digitizer board (frame-grabber).

3. Results and Discussions

Linear polysiloxane modified with 4-phenilazo-phenol, 4-(4'-hidroxi-phenilazo)-benzonitril, 4-(4'-nitro-phenilazo)-phenol, 4-hidroxy-diphenyl azophenole, and 4-trifluoromethylazophenol were investigated. The synthesized polymers were modified with azobenzene derivates with 69 - 81% substitution degree. The molecular weights (M_n) of the polymers are situated in the range of 17450 to 18900. The glass transition temperature (T_g) values are strongly influenced by the para-substituent of the chlorobenzyl groups, being located between 33 and 67 C. The main characteristics of synthesized polymers are listed in Table 1.

Table 1
Characteristics of the synthesized polymers

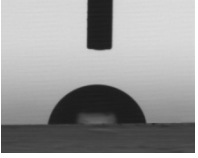

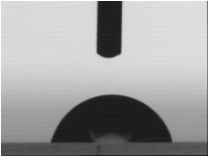
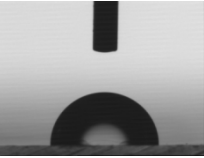
| Sample code | Substituent | Gs (%) | Tg (°C) | Dipole-moment (D) trans |
|-------------|--------------------------------------|--------|---------|-------------------------|
| HC 2 | 4-phenilazophenol | 81 | 33 | 1.1 |
| HC 50 | 4-(4'-hidroxi-phenilazo)-benzonitril | 79 | 67 | 3.8 |
| HC 40 | 4-(4'-nitro-phenilazo)-phenol | 78 | 55 | 6.5 |
| HC 14 | 4-hidroxy-diphenyl azophenol | 80 | 35 | 1.4 |
| HC 15 | 4-trifluoromethyl azophenol | 69 | 40 | 4.0 |

Gs – substitution degree; Tg - glass transition temperature;

To reveal the way that chains are arranged on the film surface, first water contact angle (CA) measurements correspond to linear polysiloxane, where chlorobenzyl groups have not been substituted, deposited on silanized glass and PMMA supports. The measurements indicate a difference of 13° according to Table 2, confirming the necessity of this study. Therefore, for the listed azopolymer (Table 1) a study of water CA variation was performed depending on the film thickness deposited on glass or PMMA support.

For studying the influence of film thickness of water CA values for polymeric films deposited on two different substrates was taken into account three different thickness intervals: (1) 0.4 μm – 0.6 μm , (2) 1.2 μm - 1.4 μm and (3) 2.5 μm – 2.8 μm .

Table 2
Contact angle values of the water drop

| Type of support | Contact angle [°] | |
|-----------------|-----------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|
| | uncoverd | with linear polysiloxane |
| Silanized glass | 69  | 83  |
| PMMA | 77  | 96  |

3.1. Water CA variation influenced by azopolymeric film thicknesses deposited on glass support

The measurement of the water CA corresponding to the linear polysiloxane with chlorobenzyl groups in the unsubstituted side chain deposited on the glass support, places it in the intermediary hydrophilic-hydrophobic range with a value of 83° (Table 2). By substituting chlorine atoms with azobenzene derivatives, the value of the CA increases by at least 7°, which can give us an approximate picture of how the side groups are placed relative to the surface. Table 3 shows the values of the CAs according to the film thickness for the samples deposited on the glass support. The placement of the studied polymeric materials in the hydrophobic field, with values of CAs between 90° - 104°, is a very important aspect in order to explain the reorganization phenomena that occur in contact with the aqueous environment when using them as support for cell culture development.

Table 3
Water contact angle values [°] of studied samples depending on film thickness deposited on silanized glass support

| | Film thickness (μm) | Sample code | | | | |
|--------------------------|---------------------|-------------|-------|-------|-------|-------|
| | | HC 2 | HC 40 | HC 50 | HC 14 | HC 15 |
| Contact angle values [°] | 1 | 96 | 94 | 93 | 90 | 103 |
| | 2 | 100 | 96 | 95 | 92 | 104 |
| | 3 | 94 | 95 | 102 | 93 | 105 |

Film thickness (μm) 1: 0.4 – 0.6; 2: 1.2 – 1.4; 3: 2.5 – 2.8

The literature specifies that one of the most hydrophobic materials is poly(dimethylsiloxane) with a CA value of 110° due to the polysiloxane type base chains present on the surface of the film (Graubner *et al.*, 2003). It was found in the case of the HC 2 sample with film thicknesses 2 and HC 50 with film thickness 3, as well as for the HC 15 sample that the values of the CA exceed 100° , meaning that the side groups of the polysiloxane chains are ordered on the film surface. For thicknesses up to $2.5 \mu\text{m}$ it is observed that two of the azopolymers with polar substituents in para position (samples HC 40, HC 14) show similar CA values compared to the polysiloxane modified with 4-phenyl-azophenol (HC 2), which may be the result of attraction interactions development between the polar substituents and the water drop, which also has a polar character (Fig. 2). It is also possible to perform physical interactions such as dipole-dipole or hydrogen bonds. A good correlation can be observed between the polarity of the groups and the CAs value (the CA decreases with increasing of the dipole moment). The exception is the HC 15 sample which has a larger CA value, no matter the film thickness. This can also be explained by a specific organization of the p-CF₃ substituent at the film surface, respectively given the degree of conversion limited to 69% (due to steric hindrances and influence of electron-withdrawing trifluoromethyl groups). For thickness 3, sample HC 50 presents a higher CA value, highlighting also a reorganization of the p-CN substituent on the surface films.

3.2. Water CA variation influenced by azopolymeric film thicknesses deposited on a PMMA support

The measurement of the water CA corresponding to the linear polysiloxane with chlorobenzyl groups in the unsubstituted side chain deposited on the PMMA support, places it in the hydrophobic range with a value of 96° (Table 2). This indicates a specific mode of organization dictated by the polarity of the support. By substituting chlorine atoms with azobenzene derivatives, the value of the CA decreases by at least 7° , in the case of sample HC 2 meaning that azo-groups are placed inside the film surface (Table 4). For this sample, film thickness doesn't influence the chain arrangements. Sample HC 40 present no typical behaviour. A film thickness of $1.2 \mu\text{m}$ induce a rearrangement of the azo-groups inside the film. Sample HC 50 present a linear increase of hydrophobicity with film thickness, meaning that majority of p-substituted azobenzene side-chains with electron-withdrawing cyano groups are ordered on the film surface with thickness 3.

Table 4
Contact angle values [°] of studied samples depending on film thickness deposited on PMMA support

| | Film thickness (μm) | Sample code | | |
|-----------------------------|-------------------------------------|-------------|-------|-------|
| | | HC 2 | HC 40 | HC 50 |
| Contact angle values [°] | 1 | 86 | 94 | 90 |
| | 2 | 87 | 88 | 95 |
| | 3 | 89 | 98 | 104 |

Film thickness (μm) 1: 0.4 – 0.6; 2: 1.2 – 1.4; 3: 2.5 – 2.8

3.3. Water CA variation influenced by azopolymeric para-substituent of samples deposited on different supports with variable film thicknesses

The type of support on which the polymeric film is deposited influences the CA value; thus, the value of the CA corresponding to the linear polysiloxane with chlorobenzyl groups in the unsubstituted side chain deposited on PMMA support increases with 13° more than on glass support (Table 1). Contrary to the previous behaviour of films deposited on glass support, the ones deposited on PMMA with substituents in the para position have higher CA values than in the case of polysiloxane modified with 4-phenyl-azophenol (Fig. 2).

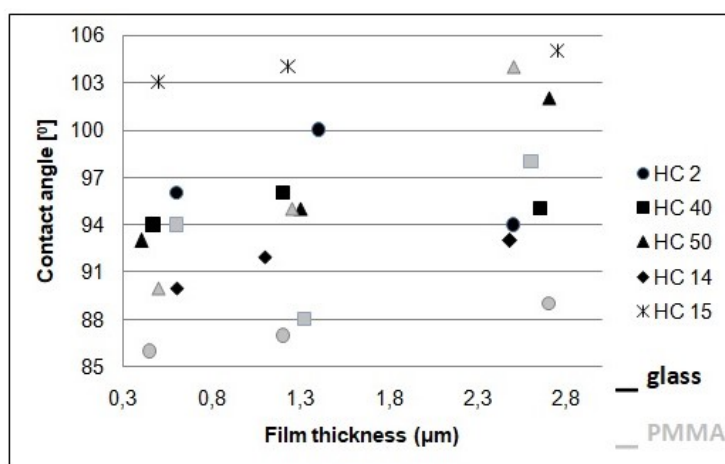


Fig. 2 – Graphical representation of water CA values for samples deposited on glass and PMMA supports, with different film thicknesses.

Sample HC 2 sample deposited on PMMA support present a decrease of CA value from 5° to 13° compared to the same sample deposited on glass

support (Table 3), indicating an orientation of the azobenzene molecules towards the inside of the polymer chain. In the case of introducing substitutes in para position, we are witness of a specific mode of organization dictated by the p-substituted azobenzene side-chains and not polarity of the support. CAs values of almost all samples present a linear increase of hydrophobicity with film thickness, an aspect found in the case of depositing the sample on both type of supports. This indicates a pattern behaviour of chain arrangements. There are and some exception on both supports, a sign of the appearance of attractive forces between the polar substance and the drop of water.

4. Conclusions

Was studied the influence of film thickness and type of support over the arrangements of azopolysiloxanic groups on the film surface by measuring CA value. CA values are different depending on p-azo-substituent. Polysiloxanes modified with the studied azobenzene derivatives are located in the hydrophobic domain with majority of a CA values located above 90° , confirming that the azo-groups are placed on the film surface.

The film thickness influences the polymer chains surface arrangements:

i) in the case of the sample HC 2 and HC 15 with film thicknesses between $1.2 - 1.4 \mu\text{m}$ the CA values exceed 100° , the macromolecules are ordered mainly with the basic chains inside therefore the chains and a certain number of azo groups on the outside;

ii) for thicknesses below $2 \mu\text{m}$, attraction interactions take place between the polar substituents and the water drop, which also has a polar character, fact materialized by the decrease of the value of the CAs compared to the characteristic of polysiloxane modified only with azobenzene;

iii) a good correlation is observed between the polarity of the groups and the values of the CAs (the value of the CAs decreases with the increase of the dipole moment), excepting sample HC 15.

The support on which the polymer film is deposited influence the arrangements of the azo-polysiloxanic chains. Thus, for samples deposited on glass, the value of the CA is slightly lower than that of the base polymer modified only with azobenzene, and in the case of deposition on PMMA support the situation is reversed.

We also found a pattern behaviour of chain arrangements function of film thickness no matter the type of support. In consequence the CA values increase with film thickness. This brings a clearer view on how azo-polymeric chains and azo-groups arrange at the film surface and can be correlated with actual and future studies of cells development on azo-polysiloxanic surfaces.

REFERENCES

- Choi C.-H., Hagvall S.H., Wu B.M., Dunn J.C.Y., Beygui R.E., Kim C.J., *Cell interaction with three-dimensional sharp-tip nanotopography*, *Biomaterials* (Elsevier) **28**: 1672-1679 (2007).
- Choksakulnimitr S., Masuda S., Tokuda H., Takakura Y., Hashida M., *In vitro cytotoxicity of macromolecules in different cell culture systems*, *Journal of Controlled Release*, **34**: 233-241 (1995).
- Graubner V.-M., Jordan R., Nuyken O., Kötz R., Lippert T., Schnyder B., Wokaun A., *Wettability and surface composition of poly(dimethylsiloxane) irradiated at 172 nm*, *Polymeric Materials; Science and Engineering*, **88**: 488 (2003).
- Hurduc N., Adès D., Belleney J., Sauvet G., Siove A., *Macromol. Chem. Phys.*, **208**, 2600 (2007).
- Hurduc N., Macovei A., Paius C., Raicu A., Moleavin I., Branza-Nichita N., *Azopolysiloxanes as new supports for cell cultures*, *Materials Science and Engineering: C*, **33** (4), 2440-244 (2013).
- Martino S., Netti P.A., *Dynamic azopolymeric interfaces for photoactive cell instruction*, *Biophysics Reviews*, **1**, 011302 (2020).
- Păiuș C.-M., Macovei A., Branza-Nichita N., Rocha L., Hurduc N., *Nanostructured azopolysiloxanic films for biological applications*, *Environmental Engineering and Management Journal*, **11**(11), 2029-2034 (2012).
- Resmerita A.-M., Epure L., Grama S., Ibănescu C., Hurduc N., *Photochromic Behaviour of nano-structurable azo-polysiloxanes with potential applications in biology*, *The Open Chemical and Biomedical Methods Journal*, **2**, 91-98 (2009).
- Resmerita A.-M., Epure L., Hurduc N., *Surface properties, thermal behavior and molecular simulations of azo-polysiloxanes under light stimuli. Insight into the relaxation*, *Macromolecular Research*, **18**, 8, 721-729 (2010).
- Rocha L., Păiuș C.M., Luca-Raicu A., Resmerita E., Rusu A., Moleavin I.A., Hamel M., Nichita N., Hurduc N., *Azobenzene based polymers as photoactive supports and micellar structures for biological applications*, *Journal of Photochemistry and Photobiology A Chemistry*, **291**:16-25 (2014).
- Ruckenstein E., Gourisankar S.V., *Surface restructuring of polymeric solids and its effect on the stability of the polymer-water interface*, *Journal of Colloid and Interface Science*, **109**(2): 557-566 (1986).
- Stevens, M. M., George, J.H., *Exploring and Engineering the Cell Surface Interface*, *Science* **310**(5751): 1135-1138 (2005).
- Voisin M., Ball M., O'Connell C., Sherlock,R., *Osteoblasts response to microstructured and nanostructured polyimide film, processed by the use of silica bead microlenses*, *Nanomedicine: Nanotechnology, Biology, and Medicine*, **6**: 35-43 (2010).
- Wang Y.-X., Spillman W.B., Robertson J.L., Spillman Jr., William B., Claus R.O., *Effects of the Chemical Structure and the Surface Properties of Polymeric Biomaterials on Their Biocompatibility*, *Pharmaceutical Research*, **21**(8): 1362-1373 (2004).

AZO-POLISILOXANI - EVALUAREA PROPRIETĂȚILOR DE SUPRAFAȚĂ

(Rezumat)

Datorită celor mai noi studii privind potențialele aplicații ale azopolimerilor în domeniul biologic ca și suport pentru însămânțarea celulelor, se impune inițial studierea modului de aranjare a lanțurilor azo-polisiloxanice funcție de grosimea filmului și tipul de suport pe care este depus filmul polimeric. Pe lângă faptul că nu sunt multe articole care încearcă să explice modificarea azopolimerilor sub influența mediilor apoase, acest studiu ajută formarea unei imagini de ansamblu a modului în care lanțurile se reorganizează la suprafața filmului și în profunzimea acestuia, studiind variația unghiului de contact al apei pe suprafața probelor azo-polisiloxanice depuse pe diferite suporturi cu grosimi variabile ale filmului. Din rezultatele obținute se poate extrage un tipar al modului de aranjare a lanțurilor azo-polisiloxanice la contactul probelor cu mediul apos, funcție de variabilele studiate.