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Preparation of Perfluorinated Surfactant Activates for Antifouling Paints

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ABSTRACT

Antifouling paints are the most reliable way to prevent biofouling of submerged surfaces. The high toxicity of organotin paints, prompted us to look for ideas to develop paints that do not present environmental risks. In this work, we prepare a painting by a modification of acrylic acid monomer containing a free carboxyl group. The biocide that is selected is the perfluorinated chain with eight carbons. Chemical modifications of the resins are made through a radical reaction. The magnitudes of changes are monitored by proton nuclear magnetic resonance NMR, gel permeation chromatography (GPC) and the light scattering (LS) at a fixed angle 90°. The glass transition temperature of the surfactant is obtained by the differential scanning calorimetry (DSC). The antifouling properties of the paint are followed by exposure of panels to the marine environment by visual observation.

Keywords: Surfactant; Antifouling; Glass Transition Temperature; Aluminum Panels; Differential Scanning Calorimetry; Critical Micelle Concentration (CMC)

1. Introduction

The paintings with fluorine atoms are used in many applications and this is due to their unique properties like low surface tension, non-adhesive nature and antifouling properties along. Fluorine is difficult to polarize. This is especially advantageous for their applications in surface coatings. Hence fluoropolymers can hinder water reaching the metallic surface in tow ways: fluorinated polymers are not wetted by water and secondly the molecular absorption of water into these polymers is relatively small [1]. During recent years, the most successful antifouling marine paints are those consisting of triorganotin-based. They are hydrolysable polymers containing triorganotin ester groups that are released by a reaction with seawater. However, the high toxicity of these compound has been shown [2-4]. These environmental concerns lead to develop new antifouling paints, environmental friendly and effective over the long term. Our work concerns the synthesis of products (perfluorinated surfactants) that can enter into the formulation of antifouling paints by an economic way.

Perfluorinated surfactants are classified as biocides [5]. In particular salts with perfluorinated chain with at least eight carbons are effective biocides [6]. The most common way to present these compound is the radical telomerization [7]. The synthesis involves a single step (**Figure 1**).

The product is a surfactant with a hydrophobic carbon chain and a hydrophilic portion represented by a function in the same loaded organic molecule [8-9]. This property provides a potentially effective antibacterial effect [9]. This article describes the synthesis, characterization and biocidal potential of this new surfactant molecule.

2. Experimentation

2.1. Materials

The perfluorinated acrylic surfactant (PAS) was synthesized in the physics laboratory materials, Faculty of Science and Technology (University of Djelfa (Algeria)), this synthesis is described in detail in Section 2.3.

The product used is compared with tributyltin (TBT) nonfluorinated synthesized in the laboratory of polymer chemistry at the University of Oran Es-Senia (Algeria) [10]. The product was vacuum distilled before use and stored at 0˚C to avoid thermal polymerization. Azoisobutyronitrile (AIBN) and perfluorinated thiol were used

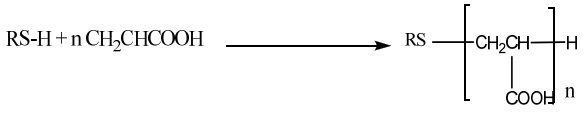


Figure 1. Telomerization of acrylic acid (R ≡ $C_8F_{17}C_2H_4$-)

as a free radical initiator and a chain transfer agent, respectively. The solvents like tetrahydofuran (THF), acetonitrile, pentane, diethyl ether (Merck) and analytical products were used directly without further purification. Water was deionized.

2.2. Measures

Proton NMR measurements were performed on a Brucker WB 360 spectrometer (ref. Internal $CDCl_3$). Chemical shifts are expressed in 10^{-6}.

The determination of critical micelle concentrations of PSA product is given by the light scattering (LS) at a fixed angle 90°. The optical constant of the device (under the experimental conditions used here) is $K = 0735.10^2$.

The relative molecular weight and molecular weight distributions were determined by the gel permeation chromatography (GPC), the device with THF as eluent, flow rate: 0.8 ml/min, volume of injection loop: 0.2 ml, with two columns as support a mixed gel porosity and particle size of 10 μ and differential refractometer (Brice-Phoenix) as concentration detector ($\lambda = 632$ nm).

Thermogram of Differential Scanning Calorimetry (DSC) was taken on an appliance model Mettler TA 4000 at a heating rate of 10˚C/min. Temperature (*Tg*) was taken at the beginning of the jump corresponding to the heat capacity

2.3. Telomerization of Acrylic Acid

A mixture of 7.2 g (0.1 mol) of acrylic acid, 36 g (0.075 mol) of perfluorinated thiol is added dropwise to 0.164 g (10^{-3} mol) of AIBN in 100 ml of THF. The mixture was left stirring under nitrogen bubbling at THF reflux for four hours at 80˚C. After concentration, the reaction mixture was precipitated in acetonitrile to remove the thiol and the remaining monomer. The product obtained was dried under vacuum. ^{1}H NMR (D_2O): δ (ppm): 2.6; 2.75 (m, 4H, CH_2SCH_2); 2.8; 2.9 (t, 2H, CH_2COO); 3.3; 3.4 (s, $C_8F_{17}CH_2$).

2.4 Determination of Critical Micelle Concentration

Fundamental solutions are obtained by dissolving the product in 50 ml of distilled THF solvant. The solutions were then diluted volumetrically generally reports 3/4, 1/2 and 1/4, different solutions were clarified by centrifugation at 18000 rev/min for 4 hours.

The concentration range studied, respectively: 0.36×10^{-4} and 2.04×10^{-4} g/ml.

2.5 Preparation of Painting and the Panels

The panels used are of rectangular shapes (7.5 cm × 6.5 cm) aluminum, 3 mm thick; test paints were applied directly using a flat brush on the surface of the panel with the previously scraped sandpaper, cleaned and washed with methanol. Each panel is painted on both sides by double layers, leaving at least 24 hours between the two applications.

After a drying time (up to one week), the panels are arranged and fixed on a metal support. The painted panels are called as a witness P1, P2 perfluorinated acrylic surfactant (PAS), and P3 (TBT).

The painting of the PSA is prepared by dissolving the resin (35 parts) in methoxy-propanol-2 (65 parts). The formulations are prepared in a laboratory dissolver.

2.6. Exposure to the Marine Environment

All panels are put to tests to evaluate its biocidal properties. For this, the panels were painted immersed to a depth of 4 m in the port of Oran, near the wharf customs dock in the sports complex (Rowing), during twenty-four months corresponding to four cold and warm seasons.

Oran is the second economic city located west of Algeria. The salinity and temperature of the location are in **Table 1**.

Panels are photographed and study of the behavior of marine fouling deposit is made (the date of immersion is March 2009).

Photos were taken by a camera Samsung Lens 3X zoom 6.2 - 18.6 mm 2.8 - 5.2. 10.2 Mega Pixels Intelligent LCD.

3. Results and Discuss

3.1. Synthesis of Perfluorinated Acrylic Surfactant (PAS)

The preparation of acrylic polymers of low molecular mass [11] is of major importance. The products obtained are soluble in water and found many applications.

The presence of fluorescent atoms along the chain determines the degree of polymerization of the surfactant.

3.2. Gel Permeation Chromatography of PAS

The curve of **Figure 2** shows the evolution of the signal intensity as a function of elution volume of surfactant (PAS).

It is observed that the maximum intensity of the peak in the chromatogram appears to 36.06 ml, the peak is narrow and symmetric product of typical well-defined

Table 1. Changes in physicochemical parameters of the natural sea water at the port of Oran in 2010.

Temperature	pH	Salinity (‰)	Conductivity (mS/cm)
10 - 23	8.4 - 8.8	34 - 36	39 - 45

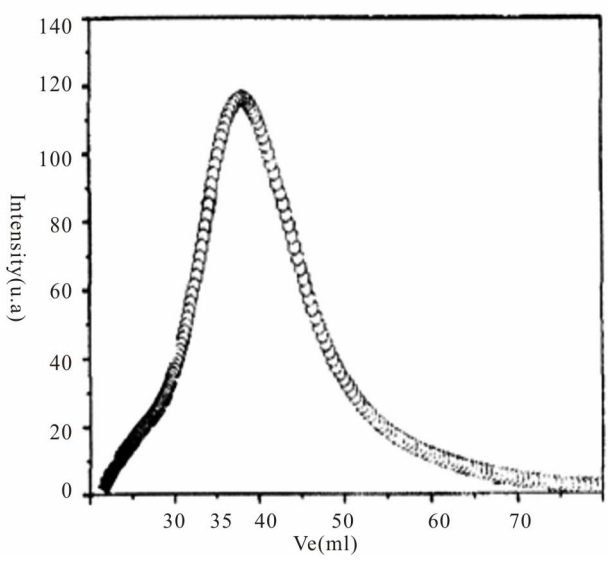


Figure 2. Gel permeation chromatography of perfluorinated acrylic surfactant (PAS).

and iso-molecular. The polydispersity M_w/M_n was 1.24, see the **Table 2**, this chromatogram confirms the homogeneity of the product (**Figure 2**).

3.3. Critical Micelle Concentrations (CMC)

The value of the critical micelle concentration (CMC) of perfluorinated acrylic surfactant (PAS) in the solutions was examined by the technique of light scattering (LS).

The light scattering is sensitive to dust, for this reason we work in harsh conditions.

The general equation for the scattering of light in the case of small molecules (or micelles of small size: less than 12 nm) can be written [12,13]:

$$\frac{K'\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)^2 \cdot c}{\Delta I} = \frac{1}{M} + 2A_2$$

Or K' is the optical constant of the device (in the experimental conditions used here, we have $K' = 0.735 \times 10^2$).

The intensity difference ΔI between the solution concentration (c) and the solvent.

The

$$\frac{\mathrm{d}n}{\mathrm{d}c}$$

of the surfactant is –0.0519. The negative value which is obtained for this product is due to the presence of fluorine atoms.

Fluorine significantly lowers the refractive index of molecules, A_2 the second virial coefficient related to thermodynamic properties (A_2 actually represents the effect of concentration on the scattered intensity) [13].

Table 2. Characterization of perfluorinated acrylic surfactant (PAS)

Surfactant	V_{el} (ml)	M_n	M_w/M_n
Surfactant PAS	36.60	3800	1.24

The results obtained (in a concentration range between 0.36×10^{-4} and 2.04×10^{-4} g/ml) are shown in **Tables 3(a)** and **(b)** and illustrated in **Figure 3** which shows the variations of the scattered intensity as a function of concentration**.**

These results allow us to located the critical micelle concentration (CMC) around to 1.545×10^{-4} g/ml. Below this concentration, the slope of curve is relatively large, is explained by the fact that there is not yet micelle formation and because of the translational mobility, the charges from molecules completely dissociated, are free to move. Above the CMC, the slope is smaller than the first and indicates the formation of micelles. Indeed, they have distributed loads (ionized heads) on the micellar surface, and are neutralized by counterions found in the solution. All these factors contribute to the stability of the micelle, which results in a decrease in the mobility of monomers charged.

3.4. Glass Transition Temperature

The glass transition temperature was determined by DSC. This method was used in the research laboratory of the Thermophysics in Dunkerque (France). And once validated, this type of analysis could be used for substrates already applied paint finishes. The results obtained by this method are presented in **Figure 4**.

As a result, one must conclude that there is a critical number of carbon atoms (carbon atoms bond to fluorescence atoms) where the growing reach does not affect the value of the temperature. This could be parsed by the fact that there is no steric effect or significant obstacle in the acrylic matrix between carbons, while that given by the well-TBT alters the thermal properties of the resin [14]. Many studies have been made by DSC to determine the phase diagrams of mixtures and polymer systems [15,16], the thermal properties were carried out in a temperature range from 0˚C to 200˚C (**Figure 4**).

In this curve, three characteristic temperatures were detected.

The emulsion of perfluorinated acrylic surfactant (PAS) showed some weight loss of 2%, which are due to the solvent. The box in **Figure 5** shows a change endothermic around 50˚C, which corresponds to the glass transition temperature *Tg*, then the product is stable up to 60˚C. Chemical decomposition will start after this temperature

Table 3. (a) Critical micelle concentration (CMC) of perfluorinated acrylic surfactant (PAS); (b) Measurements of light scattering of perfluorinated acrylic surfactant (PAS), after the CMC.

(a)

c.10^{-4} g/ml	I (u,a)	△ I (u,a)	(c/I) 10^{-4}
0	I_o = 28.85	-	-
0.495	32.69	3.0	1.20
0.863	35.58	5.5	1.20
1.182	37.50	8.0	1.18
1.41	39.42	8.0	1.22
C. M. C. = 1.545	40.38	-	-

(b)

c.10^{-4}g/ml	I(u,a)
1.772	46.16
2.04	52.88

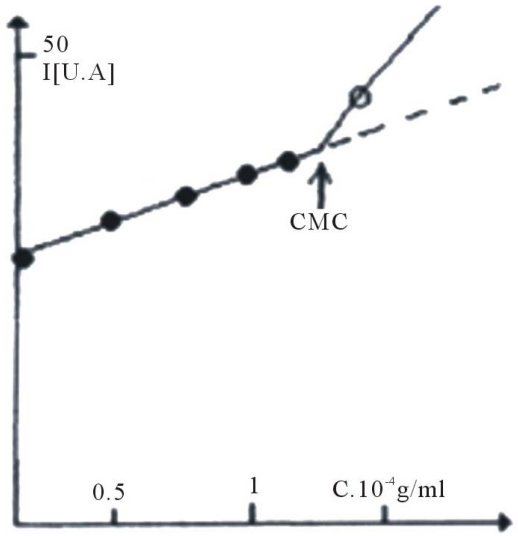


Figure 3. Light scattering of perfluorinated acrylic surfactant (PAS).

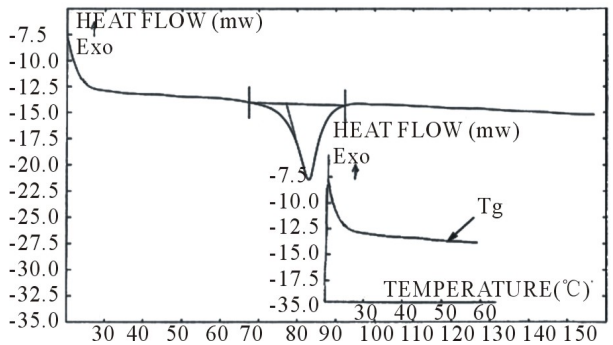
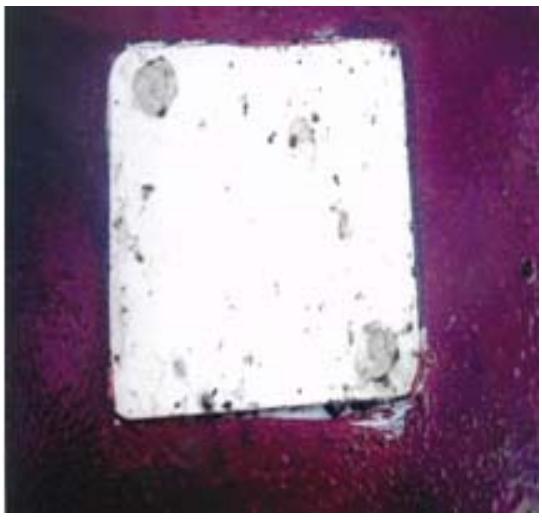


Figure 4. The DSC curve and the value of the glass transition temperature of perfluorinated acrylic surfactant (PAS).

P1

P2



P3

Figure 5. After seven months of immersion, p1 control panel, p2 PAS and p3 TBT.

and maximum decomposition is around 84˚C represented in the **Figure 4** by a strong endothermic peak (*Tm*).

From these data, it is interesting to note that the surfactant is thermoplastic and its temperature *Tm* remains unchanged even after a second heating.

Experiments are limited to a temperature of 200˚C to avoid the evaporation of the product.

3.5. Application to the Marine Environment

Perfluorinated surfactants are very effective agents, antifouling properties are monitored for exposure to the marine environment, the images corresponding to the seventh month (September 2009) of immersion are presented in **Figure 5**.

There no attack and no fixing of fouling. All panels have excellent protection against the development of organisms, except a slight difference in the panel P2, which corresponds to the acrylic resin there was spots on its surface.

On the other hand, there are several inhomogeneous spots on the panel P3 (TBT). The witness panel P1 is just slightly swollen, no real attack.

After twelve months (**Figure 6**), the panel P1 is attacked by marine organisms, a green layer appeared all along the surface; there is a higher swelling of the left side of the panel P3 (TBT). This phenomenon seems to be the first part of the erosion, which propagates the inside of the panel.

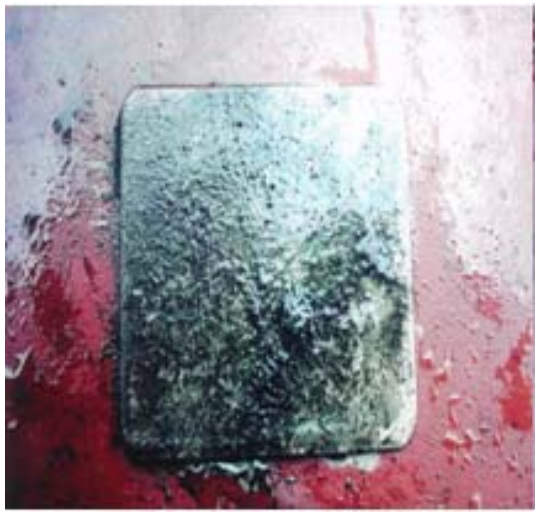
These results were confirmed after twenty months of immersion (see **Figure 7**). For the panel P2, the paint is still present. However this behavior seems to be mainly controlled by hydrophobic-hydrophilic balance of the surfactant.

In this period, first we announce that the witness panel P1, is completely covered by fouling, as green algae and barnacles. These organizations are well attached marine. On the contrary, the panels P2 and P3 have a swelling in the surrounding, which propagates progressively towards the inner panel. These paintings show an effective biocide. Note that the rate of swelling of P2 is less than P3 (TBT).

Regarding the development of green algae, and comparing the images c and b of **Figure 7**, we see that the second (P2), has a potential biocidal important. This result is in good agreement with literature [9].

The panel P2 has a biocidal effect of long-term than the P3 and more the perfluorinated surfactant has not effect as TBT toxicity [14].

In other words, the nature of the atoms that are external ($-CF_3$) is independent of the nature and the arrangement of atoms which are located inside the chain (backbone chain), this gives mechanical stability and surface properties specific to the surfactant (wettability of the surfaces) [17-19].



P1

P2

P3

Figure 6. After 12 months P1) control panel, P2) PAS and P3) TBT.

P1

P2

P3

Figure 7. After 20 months P1) control panel, P2) PAS and P3) TBT.

Therefore, the perfluorinated compound (PAS) has a strength that allows him to stay on the surface, it is perpendicular to the matrix [20,21].

4. Conclusions

The need to file biocide performance is always larger in the field of paint, this paved the way in recent years, a fruitful research both fundamental and applied. The desired properties are primarily to improve the effectiveness, duration of action, and decreased toxicity and reduced usage price. The solution adopted is to temporarily fix a biocidal agent, chosen for its extensive range of activity based on the protection needed.

Our research efforts have focused primarily on the preparation of biocide molecule (surfactant PAS) and see its behavior as antifouling paint.

The results obtained are:

1) From the study by the gel permeation chromatography (GPC), we can say that the chromatogram led to noticeable results that are qualitatively consistent. In addition, for this surfactant, the mass ratio gave 1.24. Furthermore, the results of the **Tables 3(a)** and **(b)**, allow us to see that the perfluorinated surfactant PAS present in dilute media (before the CMC), a significant degree of association (Mn = 3800), then a critical micelle concentration (CMC) of 1.545×10^{-4}g/ml, and beyond the CMC, the surfactant PAS has a large mass, we are in the presence of large micelles repellency.

2) The plot of differential scanning calorimetry (DSC) gives excellent results, which makes this method a reliable tool in the study of glass transition temperature of organic coating systems. From these data, it is interesting to note that the acrylic surfactant resulting is thermoplastic and temperatures *Tg* and *Tm* remains unchanged even after a second heating.

3) The processing of panels, gives us the most obvious difference when their protective capacity of corrosion. The perfluorinated product showed better protection than non-fluorinated (TBT). The presence on a fluorine of quantity of 2% - 10% showed significantly improved the protective properties.

4) In this study, the amount of agent used PAS (5% - 10%) was much less than that used in conventional paints, which is 20% - 30% of the total. Thus the mechanical properties of surfactant PAS can be further improved.

These fluorinated products can be used as coat, which may limit moisture from reaching the outside and inside the metal and generally give a longer life to the paintings.

In this study, we used a simple product non-hazardous with fluorine atoms as a main chain. The panels are in the water until now.

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