Continuous Flow Reactor For Miniemulsion Chain

Photopolymerization: Understanding Plugging Issue

Abraham Chemtob,^{1,2*} Agnès Rannée,¹ Laurent Chalan,¹ Diane Fischer,¹ Sophie Bistac¹

¹ Laboratory of Macromolecular Photochemistry and Engineering, University of Haute-Alsace, 3 rue Alfred Werner, 68093 Mulhouse Cedex, France

² Institut de Science des Matériaux de Mulhouse CNRS UMR 7361, University of Haute-Alsace, 15 rue Jean Starcky, 68057 Mulhouse, France

*Corresponding author: Dr. Abraham Chemtob; E-mail: abraham.chemtob@uha.fr; Tel: +33 3 8960 8804.

Abstract

Plugging is probably one of the most challenging issues facing further continuous polymerization process development. Starting with the photopolymerization of *n*-butyl acrylate miniemulsion in a continuous photoreactor composed by fluoropolymer coiled tubing, we show that three parameters have a critical role on the occurrence of plugging: solids content (≥ 30 wt%), surfactant concentration (≤ 1 wt%) and tubing diameter (≤ 1 mm). In contrast, monomer droplet stability, size and flow rate have a minimal impact. The use of nanodroplets, as individual reactors able to confine the solid products to these droplets, is in no way an efficient strategy to prevent channel clogging. Polymer adsorption occurs locally on macroscopic nucleation sites, where polymer build-up leads gradually to plugging. Based on interfacial tension measurements, we show adhesional wetting as the main trigger of plugging. In this process driven by the high cohesive energy of water, the monomer droplets not originally in contact with the reactor wall makes contact with that surface by displacing water, adhere to it, and polymerize.

Keywords : plugging, continuous process, photoreactor, photopolymerization, interfacial tension

1. Introduction

In the polymer industry, there are currently considerable societal and legislative constraints to become compliant with more stringent environmental and health regulations: formulations with low or no volatile organic compounds (VOCs), less energy-consuming processes, greater integration of renewable energy source and monomer resources, and minimal waste production. At the forefront of this emerging sustainable polymer economy are two major VOC-free technologies: *polymerization in dispersed media* [1] — mostly emulsion and suspension polymerizations — and *UV-vis photopolymerization* [2] performed respectively in water and without solvent. By merging these two eco-efficient approaches, there is the potential for a synergistic *photopolymerization in dispersed media*, paving the way for a more energy-efficient and environmentally friendly way to synthesize polymer materials [3].

Most exploratory experiments in this field routinely use batch operations with UV-transparent quartz glassware [4-6], far from the technological and ecological optimum. Continuous operations, or flow operations, may be a much better way to conduct the photopolymerization of monomer emulsions. Two considerations primarily drive the development of continuous flow reactors for heterogeneous polymerizations:

- Any wave-induced reaction, either based on photo-, sono- or microwave-chemistry, operates to best advantage when ensuring a close contact between energy source and reaction streams [7]. Distinctive by their low optical path and efficient mixing, continuous photoreactors are thus best positioned to mitigate the significant loss of photon flux when the distance from the lamp is increased [8]. In the specific case of a reactive dispersed medium, the issue of light attenuation is even exacerbated because scattering (droplet, particle) and absorption (photoinitiator, monomer) both limit the irradiated volume fraction within the reactor [9].
- Polymerization in dispersed medium relies on the reaction of unsaturated monomers by chain-growth polymerization. The chain polymerizations of typical olefin monomers employed in emulsion polymerization are highly exothermic, thereby requiring a very efficient heat dissipation. For instance, the changes in enthalpy during the polymerization of vinyl acetate (-88 kJ/mol) or methyl acrylate (-78 kJ/mol) [10] are very close to the theoretical difference between the bond energies of the π -bond in an alkene and the σ -bond in an alkane. Due to the inherent high surface-to-volume

ratio in continuous reactors, the removal of heat can be highly efficient, allowing for fine control of reaction temperatures [11].

To date, performing photochemical reactions in continuous reactors has been so far a very successful approach for purifying water via photo-oxidation of organic pollutants [12], growing algae exploited as non-fossil energy source [13], or boosting the yield of specific organic reactions including photochlorination and singlet oxygen-mediated oxidation in the pharmaceutical industry [14]. In the field of photopolymerization in dispersed media, there are much fewer examples and none of the known processes has been implemented industrially. In 2012, Tomovska et al. were the first to implement a quartz tubular reactor to synthesize a polyurethane-acrylate latex (20 % solids content) [15-17]. Their continuous miniemulsion photopolymerization process involved a mean residence times, τ , of at least 4 min; and any decrease of τ did not afford enough time for sufficient reaction completion. In a variant emulsion-type process, Seeberger showed that styrene continuous photopolymerization ($\approx$ 20 % solids content) could result in full conversion with a shorter residence time of 36 s [18]. Recently, we reported the continuous photopolymerization of *n*-butyl acrylate (BA) miniemulsion (25 % solids content) in a compact helix minireactor prepared in poly(tetrafluoroethylene) (PTFE) coiled tubing, yielding 95% conversion after 27 s residence time [19].

Common to these studies are relatively low solids contents, and the fact any increase resulted in reactor fouling and plugging issue. Previous studies have hinted that reactor clogging may originate from the lower monomer/reactor wall interfacial tension compared to water/reactor wall interfacial tension, thus driving a progressive diffusion of monomer from the droplets to the reactor surface through the aqueous phase [20]. Because the increase of solid contents is a critical issue for the commercial use of any continuous photopolymerization process, developing a better understanding of this mechanism is of prime importance. In this work, the photoinitiated miniemulsion photopolymerization of BA in a helix-type photoreactor forms the basis to identify some key parameters — surfactant concentration, solids content, reactor surface, inner tube diameter — responsible for the plugging. This set of results suggests that a three-step mechanism of plugging should take place. Under thermodynamic control, the “diffusional wetting” [21] of monomer droplets on reactor surface may be the trigger,

resulting in the displacement of water by a thin layer of monomer film. Due to the difference of osmotic pressure between this low curvature monomer wetting film and the monomer nanodroplets, Ostwald ripening may contribute subsequently to higher film thickness. Finally, a polymerization-induced solid builds up on reactor surface because irradiation is optimal in the peripheric section of the tube, leading ultimately to clogging of the channels. Herein, only the initial step of adhesional wetting has been extensively investigated.

2. Experimental Section

2.1 Materials

Technical grade monomers, *n*-butyl acrylate (BA, > 99 mol%), was supplied by Sigma-Aldrich and used as received (i.e. without distillation or any purification step). Sodium dodecyl sulfate (SDS) and hexadecane, acting respectively as surfactant and hydrophobic agent, were purchased from Sigma-Aldrich. Freshly distilled water was used for the preparation of all monomer miniemulsions. Darocur TPO, also referred to as diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide, is a α -cleavable water-insoluble radical photoinitiator, which was kindly donated by BASF. Panels of bare aluminum AR 2024 T3 (Labomat) and glass substrate (P80120 AN1 type, Brotlab) were used.

2.2 Miniemulsion continuous photopolymerization of BA

The helix minireactor was constructed by winding a PTFE tubing (Bola®, Germany) of dimensions 1.5 mm inner diameter (i.d.) $\times$ 2.1 mm outer diameter (o.d.) around a quartz cylinder (diameter: 60 mm, length: 400 mm). 27 coils of PTFE tubing were assembled, leading to an internal volume of 9 mL. All photopolymerizations were performed using a 18 W black light fluorescent tube (Osram, diameter: 26 mm; length: 590 mm). The black light lamp was placed in the axis of the quartz cylinder. The distance between the lamp surface and the coiled PTFE tubing was 17 mm. At this distance, an irradiance of 2.6 mW/cm² was measured by radiometry (Ocean Optics HR4000 spectrometer) within the 350-410 nm range (maximum emission at 370 nm). The monomer miniemulsion was circulated in the helically coiled tube at a constant flow rate, and for simplicity processes was developed to be complete after a single passage through the reactor. A membrane pump (Ismatec Reglo-Z, with pump head Z-181) ensured the circulation of fluid from the reservoir to the minireactor, and the flow rate was initially determined and regularly checked to detect any deviation. In conventional experiments, the flow rate was fixed at 20 mL/min ensuring a mean residence

time, τ , of 27 s (i.e. the average time needed for a droplet to pass through the reactor). The reactor was fed from a reservoir (250 mL Erlenmeyer flask) containing the as-emulsified miniemulsion (100 g) and stirred with a magnetic stirrer at ambient temperature. The reservoir was covered with aluminum foil to prevent adventitious polymerization caused by exposure to ambient light. Gravimetric measurements confirmed the photolateness of the monomer miniemulsion stored in the reservoir. The minireactor was initially filled with the monomer miniemulsion before exposure to UV light, and the initial time of the reaction was taken when the black light lamp (already switched on) was placed in the axis of the quartz cylinder. Samples were collected at the outlet of the tube for different analyses (size measurement, conversion) described below. A 250 mL Pyrex beaker was used to collect the resulting latex product at the outlet tube. No temperature increase between the inlet and the outlet of the reactor was found in all runs. Samples were collected at different reaction times corresponding to multiples of the theoretical residence time in order to determine the number of residence times needed to reach the steady-state operation. To prevent post-polymerization, the samples were collected in an amber glass flask covered with aluminum foil to prevent light exposure. A droplet of 1 mol% hydroquinone solution was added immediately after collection to inhibit polymerization.

Except when stated in the text, the typical monomer miniemulsion had a monomer content of 25 wt%. Miniemulsions were prepared by mixing an organic reactive phase containing BA, hexadecane (4 wt% / monomer), photoinitiator (0.75 wt% / monomer) and an aqueous phase containing SDS (4 wt% / monomer). The two phases were mixed together using a magnetic stirrer during 10 minutes at 600 rpm. The resulting coarse emulsion was then emulsified under ultrasonification (Branson Sonifier, 450 W/L) for 7 minutes at 90 % amplitude while maintaining the stirring.

2.3 Characterization techniques

Droplet and particles diameters, respectively labeled as D_d and D_p , were determined by dynamic light scattering (DLS) using a Zetasizer Nano ZS (Malvern Instrument). Typically, the monomer miniemulsion or the resultant latex was diluted 125 times in filtered and distilled water before measurement. Monomer miniemulsion stability was evaluated by monitoring the temporal evolution of the backscattering signal (reflectance) at ambient temperature (temperature set point 25 °C) through a TurbiscanLAB equipment (Formulation). A steady signal provides an indirect proof that a stable miniemulsion was formed. The number-average molecular weight ($\bar{M}_n$) and molecular weight distribution

$\bar{M}_w/\bar{M}_n$, designated as PDI, were determined using size exclusion chromatography (SEC). The analysis was performed on a Shimadzu LC-20AD liquid chromatograph equipped with two Varian PL gel 5 μm MIXED-C columns (column, injection and refractometer temperature: 30 °C; injection volume: 100 μL) and a refractive index detector (Shimadzu RID-10A). THF was used as the eluent at a flow rate of 1.0 mL/min. The $\bar{M}_n$ values were determined relative to linear polystyrene calibration standards. Fouling was assessed on a cut tube internal surface by (single-reflection) attenuated total reflection infrared spectroscopy (ATR-IR, Bruker Vertex). Each ATR-IR spectrum was based on the averaged results of 50 scans at a resolution of 4 cm^{-1} . The monomer conversions were determined by a conventional gravimetric technique. Contact angle measurements were performed with a drop shape analyzer –Krüss DSA 100 with the software Drop Shape Analysis. The deposited volume was 0.2 μL with a 0.50 mm diameter syringe. The surface energy γ was calculated from Owens and Wend equation [22] from the contact angles of two polar liquids (water and glycerol) and one non-polar liquid (hexane). Surface tension of BA and interfacial tension of BA/water systems were measured using the pendant drop technique (Krüss DSA 100). The drop volume was equal to 11 mm^3 . The evolution of the interfacial tension was followed as a function of time and the value of surface tension was taken at an equilibrium time of 34 s.

3. Results and Discussion

3.1 A review of key parameters causing plugging

The macroflow photochemical set-up consists of an energy-saving black light lamp emitting a UV-A broadband emission centred at 370 nm (irradiance = 2.6 mW/cm^2). As shown in **Figure 1**, the lamp was surrounded by a quartz cylinder (60 mm i.d.), around which a poly(tetrafluoroethylene) tube (1.5 mm i.d.) was coiled up allowing the irradiation of a total volume of 9 mL. The BA miniemulsion (25 % solids content, $D_d = 80$ nm) containing a water-insoluble phosphine oxide-type photoinitiator (PI, 0.75 wt% with respect to monomer) was circulated at a controlled flow rate (20 mL/min, $\tau = 27$ s). Our first study served to initially set up equipment and find optimal concentrations, irradiance, and flow rates [19]. For sake of simplicity, the process was developed to be almost complete (95 %) after one passage through the continuous minireactor, and to reach steady-state operation after only two residence times, limiting the portion of products being out of specification. **Figure 2** shows monomer conversion as a function of the number of residence times up to 10. The output is an acrylate latex having an average particle diameter of 120 nm and $\bar{M}_n = 103$ kDa.

Figure 1. Schematic representation of the photochemical polymerization set-up comprising a helix minireactor

Figure 2. Evolution of conversion versus the number of residence times for the BA miniemulsion polymerization ($\tau = 27$ s, flow rate = 20 mL/min, $D_d = 80$ nm).

The above mentioned conditions gave reproducible results (based on 5 replicates) as regards conversion (Figure 2) but also D_p , and $\bar{M}_n$, with no apparent sign of fouling or plugging. Nevertheless, only 10 residence times were investigated. A longer experiments involves the preparation of larger volumes of monomer miniemulsion (> 200 mL) by ultrasonication, which resulted in broader and larger droplet size distribution. As shown in **Table 1**, beginning with this model miniemulsion (run **A**), three parameters were found to have a critical role on the occurrence of plugging: solids content (run **B-C**), SDS concentration (run **D-F**) or tubing diameter (run **G-H**). Above a threshold solids content of 30 wt% (run **B-C**), the minireactor systematically plugs after only 2-3 residence times. The clogging of channels is also manifested upon decreasing the amount of SDS from 2 wt% (run **A**) to 1 wt% (run **D**) or 0.7 wt% (run **E**). Interestingly, all these monomer miniemulsions have a similar average diameter (80 nm) and are stable against coalescence and Ostwald ripening as suggested by a relatively steady backscattering signal measured with Turbiscan® (**Figure 3**). In

addition, there is no apparent destabilization resulting from the contact with the PTFE tubing as checked by a stable droplet size (DLS data) for miniemulsion staying up to 3 hours in the minireactor in the absence of UV irradiation (data not given). To rule out the hypothesis that emulsion instability may be a major cause of plugging; an instable miniemulsion has been deliberately produced by removal of hexadecane (run **F**). Although these conditions gave lower conversions (72 %) presumably due to the lower penetration depth of this larger size emulsion (size cannot be determined precisely by DLS), the system does not suffer any plugging. The last parameter triggering blockage of the stream is the use of a thinner tube diameter of 1 mm (run **G**), while larger tubes of 1.5 mm (run **A**) or 1.9 mm (run **H**) run smoothly. This result clearly points out the difficulty of implementing microreactor for photopolymerization in dispersed media.

Table 1. Effect of solids content, tubing diameter, surfactant (SDS) and co-stabilizer (hexadecane) concentrations on plugging during continuous-flow photopolymerization of BA miniemulsion. Irradiance = 2.6 mW/cm², [PI] = 0.75 wt% / monomer, τ = 27 s, flow rate = 20 mL/min, number of residence times = 10.

Run	D_d nm	Inner diameter of PTFE tubing mm	[SDS] wt% / monomer	[Hexadecane] wt% / monomer	Conv % mol	Solids content % wt	Number of τ (27 s) before plugging
A	80	1.5	2	4	95	25	No plugging
B	80	1.5	2	4	-	30	3
C	80	1.5	2	4	-	40	2
D	80	1.5	1	4	-	25	4
E	80	1.5	0.7	4	-	25	3
F	> 100	1.5	2	0	72	25	No plugging
G	80	1	2	4	-	25	3
H	80	1.9	2	4	90	25	No plugging

Figure 3. BA miniemulsion stability assessed by the reflectance measurements during ageing time in the middle of the sample vial (Turbiscan data). The miniemulsion comprises different concentrations in SDS: 2 wt% (D_d = 80 nm, run **A**, ▲), 1 wt% (D_d = 80 nm, run **D**, ●), 0.7 wt% (D_d = 80 nm, run **E**, ◆).

Several conclusions can be inferred from this series of scouting experiments.

- The use of dispersed phase nanodroplets, as individual reactors able to confine the solid products to these droplets, is not an efficient strategy to prevent channel clogging. This suggests that monomer diffusion through the aqueous phase is possible even in the presence of costabilizer.
- The use of a low-energy and low-adhesive PTFE surface is in no circumstances a way to keep polyacrylate away from the tubing walls, and avoid clogged channels.
- Against all prediction, the relatively fast flow rates (20 mL/min) remains ineffective in protecting against the adsorption of polymer chains on the reactor wall.
- Although the reactor clogging upon solid formation has been a commonly cited concern of microreactor, it can also plague macroreactors (with an internal channel diameter ≥ 1 mm).
- Clogging can occur with highly stable monomer miniemulsions. Based on droplet size analysis by DLS, there is no sign of early destabilization in the reactor before the formation of solid (without UV irradiation). Therefore, a long-term kinetic stability of the initial miniemulsion makes no guarantee regarding plugging.
- The solid content (≥ 30 wt%), surfactant content (≤ 1 wt%) and tubing diameter (≤ 1 mm) are the most sensitive parameters as regards plugging. In contrast, droplet size, irradiance, photoinitiator concentration, flow rate have much less impact (see results published in a spate study).
- There are several evidences indicating that channel clogging may be related to wetting phenomena, i.e. the displacement from a surface (reactor wall) of one fluid (water) by another (monomer). While, the change in SDS concentration has almost no effect on droplet size (runs **A**, **D** and **E**, Table 1), it can strongly affect the values of interfacial tensions. In addition, a decreased tube diameter causes a larger interfacial area for polymer adsorption, which can increase the surface free energy.

Visual inspection of the tubes after plugging (run **B**, Table 1) shows that the phenomenon is highly localized. Accordingly, ATR-FTIR analysis (not given) of the unplugged “clean” surface of the reactor wall surface did not reveal any coated polymer. To move forward, we have also studied the model miniemulsion (run **A**, Table 1) which does not show any sign of plugging. After several residence times, the entire internal tubing surface was systematically analyzed by SEM and optical

microscopy on its whole length for presence of incipient signs of precipitates. As revealed in **Figure 4**, after 10 or even 1 residence time, the internal section of the PTFE tube shows, at very specific sites, that solid build-up occurs even though channel clogging has not manifested. These deposits were attributed to polymer adsorption despite the lack of conclusive evidence from EDX surface compositional analysis. Plugging seems to originate from nucleation sites on channel surface, proceeding by subsequent accumulation of polymer.

Figure 4. Images of the inner section of the PTFE tube before reaction and after 1 or 10 residence times ($\tau = 27$ s) in the helix minireactor taken by optical microscopy (1st line) and SEM (2nd line).

3.2 Can plugging be driven by adhesional wetting of monomer droplets?

In a conventional spreading wetting, a liquid in contact with a solid substrate and another fluid (typically air) increases its surface area of contact with the substrate at the expense of this fluid. By contrast, our assumption is that an adhesional wetting may be effective in our case and account for the occurrence of plugging. In this case, a liquid (BA) not originally in contact with the substrate (PTFE), and in the form of droplet, makes contact with that surface by displacing another fluid (Water) and adhere to it [21]. **Figure 5** is a graphical depiction of this process. Adhesional wetting can be also expressed in terms of decrease of surface free energy by the equation:

$$\Delta G = a(\gamma_{PTFE-BA} - \gamma_{PTFE-W} - \gamma_{BA-W}) \quad eq\ 1$$

Where a is the contact surface area gained by BA when it comes in contact with the substrate, $\gamma_{PTFE-BA}$ is the interfacial tension of the PTFE substrate in equilibrium with BA, γ_{PTFE-W} the interfacial tension at the PTFE-water interface, and γ_{BA-W} the interfacial tension at the BA-water interface.

Figure 5. Adhesional wetting of BA droplet on a PTFE substrate in a water medium. θ is the contact angle of BA on this substrate surrounded by water

If this quantity $\Delta G/a$, or $\gamma_{PTFE-BA} - (\gamma_{PTFE-W} + \gamma_{BA-W})$ — also termed work of adhesion, or total decrease in surface free energy per unit area of the system due to adhesional wetting — is negative, the system decreases in surface free energy, and the adhesion of BA can then occurs spontaneously, leading ultimately to the formation of a thin layer of BA. It is clear from this expression that a low-energy-surface, which is the case of PTFE (i.e. $\gamma_{PTFE-Air} = 21.1 \text{ mN/m}$), does not influence adhesional wetting, the driving force of this type of wetting is rather the competition between the wetting of the two liquids (BA and water) on a given substrate reflected by the quantity $\gamma_{PTFE-BA} - \gamma_{PTFE-W}$. In this process, any decrease of the interfacial tension $\gamma_{Substrate-BA}$ increases the tendency for adhesion to occur, while any reduction of the interfacial tension $\gamma_{Substrate-W}$ decreases the extent of adhesional wetting. Our assumption is that the high cohesive energy of water should disfavor the wetting compared to a less cohesive organic liquid like BA [23], such difference should be manifested by a negative quantity $\gamma_{PTFE-BA} - \gamma_{PTFE-W}$. Consequently, $\Delta G/a$ can become a measure of the driving force behind the adhesional wetting process, but requires determination of interfacial tensions. A 3-step approach was conducted to evaluate $\Delta G/a$ for the BA/water/PTFE system without surfactant (3.2.1), with surfactant at different concentrations (3.2.2), and in the miniemulsion form (3.2.3).

3.2.1 Adhesional wetting of Water / BA / PTFE system

Table 2 gathers the values of the 3 interfacial tensions appearing in *eq 1*. They were determined by a series of conventional methods described in the experimental section: liquid/liquid interfacial tensions were measured by pendant drop method while the solid/liquid

interfacial tensions were based on Owens-Wendt model and Young equations. As expected, a much higher interfacial tension was found for γ_{PTFE-W} (40 N/m) compared to $\gamma_{PTFE-BA}$ (2 mN/m) reflecting a much lower affinity of water for the PTFE substrate. The consequence is a strongly negative value of the adhesional wetting coefficient $\Delta G/a$ estimated at -63 mN/m. Obviously, continuous photopolymerization requires specific tubing both solvent-resistant and transparent to UV or visible light (with suitable photoinitiators). Nevertheless, the determination of $\Delta G/a$ using other substrates than PTFE can shed light on the influence of reactor wall material on plugging. Changing the PTFE for aluminum (the surface energy of cleaned aluminium is close to 29 mJ/m² [24]) leads to a strong negative value of -49 mN/m, while a more hydrophilic surface such as glass yields -11 mN/m. The fluid to be displaced being water and not air, it is consistent to find that a more hydrophilic substrate can be less favorable to adhesional wetting. In summary, changing the tube composition does not appear as an efficient lever for action, as a way of limiting plugging. The values of contact angle summarized in **Table 3** are relevant for demonstrating the better wetting of BA compared to water regardless of the substrate, this is because the high intermolecular attractive forces between water molecules tend to decrease its tendency to wet. The larger the discrepancy between the contact angles of the two liquids (water and BA), the stronger is the tendency for adhesion to occur.

Table 2. Calculated interfacial tensions values involved in the Water / BA / PTFE system

Medium 1 / Medium 2	γ mN/m
Water/PTFE	40
BA/PTFE	2
Water/BA	25

Table 3. Equilibrium contact angles of BA and water deposited on PTFE, aluminum and glass

Liquid/Substrate	θ °
Water/PTFE	105
BA/PTFE	41
Water/Glass	57
BA/Glass	10
Water/Aluminum	92
BA/Aluminium	10

3.2.2 Adhesional wetting of Water / BA / PTFE system in presence of surfactant

Much of the driving force for adhesional wetting is related to high γ_{PTFE-W} and γ_{BA-W} values because of the high cohesive energy of water molecules. Liquid water has an exceptionally high cohesion, which manifests also through high melting point, boiling temperature, surface tension (72 mN/m) and a large specific heat. This unusual cohesion lies on the strength of hydrogen bonds that bind the water molecules together, yielding an exceptional cohesive energy per molecule of 18 kT. As shown in **Table 4**, the addition of a surface-active agent can shield intermolecular forces and decrease the values of these two interfacial tensions. The addition of 1 wt% SDS to water causes a reduction of almost 30 mN/m of γ_{PTFE-W} and 10 mN/m of γ_{BA-W} . The modification of the wetting power by surfactant is also noticeable from the contact angles of water on PTFE that decrease from 105° to 72°. **Figure 6** shows that an addition of surfactant, by reducing the water-BA and water-PTFE interfacial tensions, may cause the empirical factor $\Delta G/a$ to have a less negative value (maximum is -20 mN/m) and make adhesion wetting less thermodynamically favored. With a value of $\gamma_{BA-PTFE}$ close to 0 (2 mN/m), there is little possibility to get a positive wetting coefficient. This suggests that inverse emulsion methods (employing for example water-soluble acrylamide or acrylic acid monomers dispersed in an inert hydrocarbon solvent) may operate without plugging.

Table 4. Effect of the addition of SDS on γ_{PTFE-W} and γ_{BA-W}

Liquid/PTFE	θ °	γ_{PTFE-W} mN/m	Liquid/Liquid	γ_{BA-W} mN/m
Water/PTFE	105	40	Water/BuA	25
Water+SDS _{0.7%} /PTFE	79	14	Water+SDS _{0.7%} / BA	17
Water+SDS _{1%} /PTFE	75	11	Water+SDS _{1%} / BA	16
Water+SDS _{2%} /PTFE	72	10	Water+SDS _{2%} / BA	14

Figure 6. Evolution of the adhesional wetting coefficient $\Delta G/a$ of BA/water/PTFE system as function of the SDS concentration in the aqueous phase.

3.2.3 Adhesional wetting of BA miniemulsion / PTFE system in presence of surfactant

Table 5 gives estimations of γ_{PTFE-W} and $\Delta G/a$ in the case of 3 miniemulsions of variable SDS concentrations: 2 wt% (run **A**, no plugging), 1 wt% (run **D**, plugging) and 0.7 wt% (run **E**, plugging). For the calculations, the emulsions were assumed to act as water phase. The excellent wetting of BA on PTFE ($\gamma_{BA-PTFE}$) does not permit $\Delta G/a$ to be positive. However, SDS addition has a significant effect on wetting coefficient, which at 2 wt% concentration is very close to the minimal value (-21.5 mN/m) achieved in the previous non dispersed system BA/Water/PTFE (section 2.2). As shown in Table 1, an increase of SDS concentration is not really accompanied by a decreased droplet size, meaning that this supplement of surfactant is more readily available to modify the surface tensions of the system, in particular to reduce γ_{PTFE-W} . Nevertheless, the slight differences of $\Delta G/a$ between these 3 samples does not fully account for the fact that the miniemulsions prepared with a SDS concentration lower or equal to 1 wt% (runs **D** and **E**) plug, whereas the continuous process runs smoothly at higher concentration (run **A**). For now, two hypotheses can be put forward: on the one hand, plugging is likely to be simply retarded in run **A** (at [SDS] = 2 wt%), and may occur at a residence times higher than 10. On the other hand, plugging may never take place experimentally, even though it is thermodynamically favored. Whether a monomer droplet can adhere to reactor wall depends on both thermodynamic and kinetic considerations. The clogging will be impossible under any and all reaction conditions if it does not pass the test of thermodynamic feasibility. Clogging is possible only if the free energy difference ΔG for adhesional wetting is negative (Sec. 2.1). A negative ΔG does not, however, mean that plugging will be observed under a particular set of operating conditions in particular the optimization of flow rate. The ability to avoid a thermodynamically feasible plugging depends

on its kinetic non feasibility — on whether the process proceeds at a low enough rate under a proposed set of reaction conditions.

Table 5. Contact angle, solid/liquid interfacial tension and adhesional wetting coefficient for the BA miniemulsion prepared with different concentrations of SDS.

Liquid/Substrate	θ°	γ_{PTFE-W} mN/m	$\Delta G/a^a$ mN/m
MiniE _{0,7%SDS} /PTFE	79.0	13	-26.5
MiniE _{1%SDS} /PTFE	74.8	11	-23.8
MiniE _{2%SDS} /PTFE	70.7	8	- 21.5

^a $\Delta G/a$ was determined considering a constant value of $\gamma_{PTFE-W} = 15$ mN/m

4. Conclusions and perspectives

Continuous processes have become a popular approach to increase polymer productivity, yield high-quality products, and recently make optimal photopolymerization processes in dispersed media. The continuous flow photoreactor for miniemulsion photopolymerization of BA showed promising results, however, reactor plugging and its consequence as regards maintenance and operating costs may limit its widespread application. Our report provides a first insight into the parameters causing plugging, and the complex plugging mechanism. This study revealed that miniemulsion stability, size or flow rate have minimal impact, while solids content, surfactant concentration or tubing diameter are crucial elements to avoid channel clogging, and should be carefully selected. Plugging occurs on localized sites of the tubing, where polymer build-ups gradually. Although there is no consensus on the precise mechanism, adhesional wetting is presented as the main triggering event, mainly driven by the high cohesive energy of water. However, adhesional wetting accounts only for the formation of a thin BA film, and should be completed by a more complete plugging mechanism discussing the role of Ostwald ripening and light depth in the growth of this initial monomer layer.

Calculation of $\Delta G/a$ has been used as a quantitative marker to assess the plugging propensity. There was no possibility to find thermodynamically disfavored conditions ($\Delta G/a > 0$) preventing adhesional wetting. More severe plugging is expected when hydrophobic tubes are used, and efforts should be focused on increasing hydrophilicity through surface modification. However, optimization of operating conditions through tubing composition may be difficult because UV light transparency must be also

maintained. In the future, synergistic interactions with different surfactants could be a solution to improve water wetting on reactor surface compared to BA. The best approach may be to further reduce γ_{PTFE-W} and $\gamma_{Monomer-W}$ with the use of specific surfactants such as aerosol OT (sodium bis(2-ethyl-1-hexyl) sulfosuccinate) or fluorosurfactant. Aerosol OT is known in surfactant science for its exceptional ability to decrease surface and interfacial tensions, and for this reason, it is widely used in microemulsion composition. In the search for an efficient solution to prevent plugging, continuous polymerization should also take advantage of the experience of other fields such as membrane bioreactors used in waste water treatment [25] where intermittent bubbling, pulsing air or more complex reactor design have been implemented for more than 20 years to prevent risks of clogging.

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