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Flash Latex Production in a Continuous Helical Photoreactor: Releasing the Brake Pedal on Acrylate Chain Radical Polymerization^a

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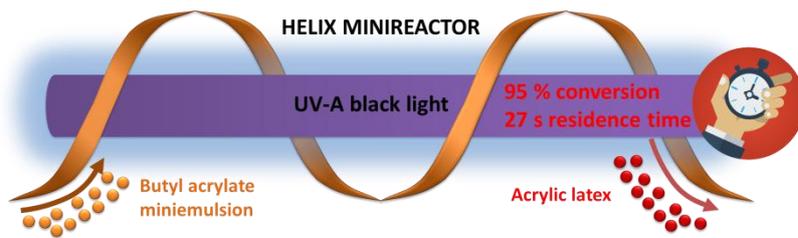
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Abstract

The continuous photopolymerization of acrylate and methacrylate monomer miniemulsions (25 % solids content) was investigated at room temperature in a compact helix minireactor. Using n-butyl acrylate, the process yields 95 % conversion after only 27 s residence time, and gel-free high-molecular-weight products. Under optimized conditions, a 25-fold increase in efficiency was obtained when compared to a batch photopolymerization. The reaction set-up offers a frugal process because of moderate irradiance (2.6 mW/cm²), photoinitiator concentration (0.75 wt%), and low-power UV–A fluorescent lamp.

^a **Supporting Information** is available online from the Wiley Online Library or from the author.



1. Introduction

Pushing chemical production processes to their limits with regard to efficiency, emission control, compactness, safety and energy consumption is a currently spreading trend. As a major route to commodity and high-performance plastic materials, the intensification of polymerization reactions is a subject of high technological significance.^[1] At the forefront is the radical chain polymerization, that represents 40 % of all processes for the production of commercial polymers, including some of the most common plastics such as polystyrene, acrylic or vinyl polymers. It is of high interest that the propagation step governing the chain-growth may be very fast, given that the propagation rate coefficient (k_p) is for most monomers in the range of 10^2 – 10^4 L mol⁻¹ s⁻¹. Nevertheless, the paradoxical observation is that polymer chemists have always strived to limit reactivity. The highly exothermic nature of radical chain polymerizations, the high activation energies involved, and the tendency toward the gel effect combine to make heat dissipation and polymer architecture control very challenging on an industrial scale. To avoid uncontrolled acceleration of the polymerization rate that may cause disastrous “runaway” reactions, the conventional approach consists in limiting the concentration of free monomer within the reactor through semi-continuous operations, with obvious adverse consequences for productivity.^[2]

With this limitation in mind, we have developed a novel eco-efficient, “flash”, radical chain linear photopolymerization,^[1] able to reduce reaction time scales from hours to seconds. Our synergetic approach integrates *macroflow photochemistry* and *emulsion-type polymerization*. The result is a practical “single pass” helix photochemical reactor for the continuous photopolymerization of n-butyl acrylate (BA) miniemulsions. We show that high conversions can be achieved within short residence

times at ambient temperature, yielding a stable high molecular-weight (MW) acrylic polymer latex.

As sketched in **Scheme 1**, our flow photochemical system comprises a black light lamp, with a broadband emission centred at approx. 370 nm and a low irradiance (2.6 mW/cm²). The lamp is positioned in the axis of a quartz cylinder (60 mm i.d.), around which a UV-transparent and solvent-resistant poly(tetrafluoroethylene) tube (1.5 mm i.d.) is coiled up (Peschl Ultraviolet, Mainz, Germany). A total volume of 9 mL was irradiated, but the tube length can be varied to accommodate higher or lower volume. The monomer dispersion is introduced at a controlled flow rate (20 mL/min), and the polymerized latex is collected at the outlet of the tube. Such macroflow photoreactor design is a variant of the Birr/Booker-Milburn model released in 2005 that has been extensively used in preparative organic chemistry.^[3, 4]

Although continuous emulsion polymerizations in micro-^[5, 6] and macro-reactors^[7, 8] (in particular tubular reactors^[9, 10]) have always attracted significant attention, some recent results have emphasized the advantage of using photochemical processes and corresponding photoreactors.^[11-14] Chemists have realized that improvements involve not only the distribution control of MW and particle size,^[15, 16] but also high MW values,^[13] polymerization rates,^[14] film properties,^[17] energy efficiency, installation costs and size. Aiming at a rational approach for a smarter way of conducting linear radical chain photopolymerization, we chose a simple and highly efficient reaction set-up. Several features are significant in this set-up with regard to the photoreactor (i.), the UV lamp (ii.) and the monomer emulsion (iii.).

i. The high surface-to-volume ratio of a helical minireactor provides optimal polymerization heat transfer capability. Furthermore, in a dispersed medium, the combined effect of scattering and absorption limiting light penetration may be mitigated by an efficient mixing within shallow channels. In an industrial context

requiring productivity and minimal plugging issues,^[11] a macrofluidic reactor with millimetric channels seems more suitable than a microreactor with i.d. < 500 μm .

ii. Though UV-curing heavily relies on medium-pressure Hg arcs, we believe that a low power UV-A black light fluorescent tube^[18] may be better suited to linear photopolymerization. It features low price, good conversion of electrical energy to UV radiation (30 %), safer UV-A emission, and last but not least negligible heat release. Therefore, radical polymerization can take place at ambient temperature without the need for a water cooled jacket, and with potentially less transfer reactions.

iii. Viscosity and solvent emission problems are avoided by the heterogeneous polymerization conditions in water. In addition, a monomer miniemulsion overcomes many of the disadvantages of a conventional macroemulsion. Smaller nanosized monomer droplets (< 100 nm) are instrumental in promoting a better through polymerization, while kinetic stability prevents major size changes between emulsification stage and polymer product.

2. Experimental Section

2.1 Materials

Technical grade monomers, n-butyl acrylate (BA, > 99 mol%), methyl methacrylate (99 mol%) and butyl methacrylate (99 mol%) were supplied by Sigma-Aldrich and used as received (i.e. without distillation or any purification step to remove the radical inhibitor). Sodium dodecyl sulfate and hexadecane, acting respectively as surfactant and hydrophobic agent (against Ostwald ripening), 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 Specialty Chemicals. (E)-[1-(2,5-Dimethyl-3-furyl)ethylidene](isopropylidene)-succinic anhydride (DFIS, formerly known as

Aberchrome 540, > 95 mol%) was supplied by Extrasynthèse, and used as chemical actinometer. Ethyl acetate (> 99.7 mol%) and tetrahydrofuran (THF, > 99 mol%) were purchased from Aldrich.

2.2 Miniemulsion polymerization in a continuous-flow helical minireactor

As sketched in **Scheme 1**, the helix minireactor was constructed by winding a poly(tetrafluoroethylene) (PTFE) tubing (Bola®, Germany) of dimensions 1.5 mm inner diameter (i.d.) × 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. Except when stated, all reactions were performed using a 18 W black light fluorescent tube (Osram, diameter: 26 mm; length: 590 mm). The black light lamp was introduced into a Pyrex protecting tube 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, the estimated irradiance was 2.6 mW/cm^2 within the 350-410 nm range. A plastic grid wrapped several times around the Pyrex sleeve enabled to vary the irradiance values. Irradiance measurement and emission spectrum of the black light lamp (**Figure S1** in supporting information) were determined with an Ocean Optics HR4000 spectrometer. The UV spectral output shows a broadband FWHM spectral bandwidth of the 370 nm peak of about 20 nm. The tiny secondary peak at 404 nm leaking through the filter gives the lamp its purple glow. As the lamp does not emit heat, no external cooling jacket was installed. The monomer miniemulsion was circulated in the helically coiled tube at different flow rates (7 – 40 mL/min). 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 an irradiation time (residence time) of 27 s. 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 exposure to ambient light. Gravimetric measurements confirmed the photolateness of the monomer miniemulsion stored in the reservoir. Note that dissolved oxygen was not removed from the miniemulsion, and that all formulations were processed continuously in a single pass. 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. Advantageously, fluorescent lamps require only a brief warm-up period (30 – 60 s after being switched on) to achieve a steady and full light output. During this short period, the lamp was placed in a UV-opaque box. Samples were collected at the outlet of the tube for different analyses 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 flow (steady conversion and constant properties, in particular constant particle size of the polymer obtained). 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.

Note that some specific experiments were performed with two other UV lamps: a second black light (5 W, Osram, $I = 5.2 \text{ mW/cm}^2$ in the 350-410 nm range) and a medium-pressure Hg arc (TQ150, Heraeus Noblelight, 150 W, effective arc length: 44 mm). In contrast to the black light, this lamp provides a polychromatic light, with the most powerful UV output within the spectral range of absorption of the photoinitiator at 367 and 313 nm. The measured irradiance within the 350-410 nm region was 310 mW/cm^2 . Miniemulsion polymerization in a

conventional immersion-type photochemical reactor (photo-batch) and in a stirred tank batch macroreactor (thermal-batch) is described in supporting information.

Except when stated in the manuscript text, the monomer miniemulsion had a monomer content of 25 wt%, and its typical composition is given in Table 1. Miniemulsions were prepared by mixing an organic reactive phase (monomer, hexadecane, photoinitiator) and an aqueous phase (sodium dodecyl sulfate, distilled water). First, 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. These conditions were optimized to achieve the steady-state droplet size distribution for a miniemulsion of 100 mL. To achieve larger droplets, the surfactant concentration was adapted (1.5 wt% / monomer) without affecting the stability.

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 (Formulaction). 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. Macroscopic gel content was determined gravimetrically by means of a Soxhlet extraction under THF reflux during 12 h. UV-Visible spectroscopy was conducted with a Varian Cary 4000 double-beam spectrophotometer. Its wavelength range is typically comprised between 200 and 800 nm. With regard to the as-formed BA miniemulsions, the transmittance (absorbance) measurements were performed using a quartz cell of 0.1 mm optical path. For the determination of the PI absorption spectrum (in acetonitrile), a 1 mm quartz cell was used.

The experimental procedure for actinometric measurements (using (E)-[1-(2,5-dimethyl-3-furyl)ethylidene]-(isopropylidene)-succinic anhydride (DFIS), formerly commercialized as Aberchrome 540) was published elsewhere. For these specific measurements, the typical monomer/PI/hexadecane organic phase was replaced by ethyl acetate/DFIS/hexadecane for the preparation of the non polymerizable miniemulsions. The organic phase content was 30 wt% and 0.08, 0.15, 0.5 and 1.5 wt% SDS (with respect to the organic phase content) was employed to produce a series of miniemulsions of variable average diameter. By applying the same emulsification methodology described above, miniemulsion droplets with an average size of 150 nm, 100 nm, 80 nm and 50 nm were prepared (DLS data). To respond to the need of actinometric experiments, the sample was diluted about 7 times to get a 4 wt% organic phase content miniemulsion. The resultant system was passed several times in the helix minireactor with a residence time of 27 s at a flow rate of 20 mL/min (similar conditions as those of photopolymerization).

3. Results and Discussion

We initially chose to investigate the photopolymerization of a BA miniemulsion (25 % solids content) containing a water-insoluble phosphine oxide-type photoinitiator (PI, 0.75 wt% with respect to monomer). Diphenyl-(bis(2,4,6-trimethylbenzoyl) phosphine oxide was chosen for its UV-A absorption spectrum being consistent with the emission spectrum of the light source (see **Figure S1** of supporting information), as well as for its photobleaching that enables depth polymerization. Furthermore, BA is an ubiquitous monomer of waterborne acrylic dispersions, mass produced for applications as coatings and adhesives. This monomer is amenable to a continuous polymerization process at room temperature because of fast propagation ($k_p = 1.3 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ at 20 °C),^{[[19]]} highly exothermic polymerization ($\Delta H = -78 \text{ kJ/mol}$)^[20] difficult to control in a macrobatch reactor, and strong tendency to chain transfer.^[21] We used SDS and hexadecane, a conventional surfactant/hydrophobe pair, to stabilize the BA miniemulsion. After emulsification provided by an ultrasonifier, an average droplet diameter (D_d) of 80 nm was determined by DLS. Minor changes of the backscattering signal during 4 h indicated that the as-produced miniemulsion was relatively stable against coalescence and Ostwald ripening (see Turbiscan data in **Figure S2** of supporting information). The DLS data nonetheless showed a small size drift from 80 nm to 110 nm during the same period. Prior to UV irradiation, we also checked that the type of container (glass vial or Teflon tube), as well as several passes in the minireactor, did not affect the stability.

Figure 1 shows the kinetic results of a continuous single pass photopolymerization carried out at a residence time of 27 s (flow rate 20 mL/min). Under these conditions, a steady-state flow at 95% conversion was reached very fast after only 2 residence times, yielding a latex product with an average particle diameter of 120 nm. The reactor construction enabled reproducible results (5 replicates), and no temperature increase at

the reactor outlet was noted. This reflects the good heat transfer properties provided by both high surface-to-volume nanodroplets and minireactor. In comparison, for a batch process in an immersion well photoreactor of 100 mL, 2 hours at room temperature were required to reach 90 % conversion, as shown in **Table 2**. Featuring a productivity of 300 g of polymer/h, the flow set-up employed thus enables an approx. 25-fold increase of reaction efficiency compared to a conventional photochemical batch process. The rate difference is less pronounced for a thermally induced batch polymerization (35 g/h) in a stirred tank reactor of 100 mL, but the reactor types are too different to make really meaningful comparisons. Another key difference between photochemical flow, photochemical batch and thermal batch processes is related to polymer architecture (Table 2). In contrast to the thermal polymerization, the UV processes yielded gel-free latexes. Our hypothesis is that chain transfer to polymer leading to gel in acrylate polymerization may be suppressed at ambient temperature because its activation energy is higher than that of propagation.^[12] As a result, higher number average MW values ($\bar{M}_n > 100$ kDa) can be obtained in the photochemical processes compared to a thermal one ($\bar{M}_n = 79$ kDa) with even a slight improvement in the MW distribution: polydispersity index (PDI) of 4.2 *versus* 4.9 for a thermal batch.

The reason for the highly increased productivity of the continuous photochemical process was addressed by examining both (i.) the extent of irradiated volume; and (ii.) the PI absorption within the helix minireactor.

i. Previous investigations demonstrated that below a threshold average diameter of ca. 150 nm, any decrease of droplet size caused a significant decrease of scattering, thus improving light penetration and reaction rates.^[22] Scattering and absorption coefficients of acrylate miniemulsions were also determined in diluted^[22] and concentrated^[23] media using an integration sphere or the Kubelka-Munk theory respectively. In this work, we employed a

simple spectroscopic set-up to assess light penetration. At 365 nm, the extinction (sum of absorption and scattering) coefficient of a BA miniemulsion (80 nm) was measured to be 150 cm^{-1} . As a result, at the beginning of the irradiation time, only 3 % of the incident photons are transmitted beyond 0.1 mm of the optical path within the reactor tube (1.5 mm i.d.). Consequently, most of the reactor volume receives little (or none) of the actinically relevant radiation. The main difference is that the "dark" volume accounts for 85 % in the minireactor, as compared to more than 98 % in the immersion macroreactor. Yet, increasing the diameter of the reactor tube (e.g. to 1.9 mm) or the droplet size (e.g. to 160 nm) did not diminish conversion ($> 90 \%$ still achieved after 2 residence times). This result suggests that mass transfer could, to some extent, compensate for a limited depth of light penetration. Accordingly, several studies reported the increased mixing properties of helical minireactors compared to straight tubular reactors, and their ability to approach plug flow.^[24]

ii. Even though PI absorption contributes to non-uniform irradiation, it remains necessary to trigger the polymerization process. In a recent publication,^[25] we proposed a method to evaluate the efficiency of light absorption in highly scattering systems such as miniemulsions, using non-polymerizable (diluted) ethyl acetate miniemulsions containing a chemical actinometer (DFIS) to replace the oil-soluble PI. A chemical actinometer undergoes a well-characterized photochemical reaction and allows the estimation of the incident and absorbed photon flux.^[26] We could reach the interesting conclusion that, despite a rather large variation in the scattering properties of the miniemulsions, the efficiency of light absorption was hardly affected. However, the actinometric experiments were performed in quartz cells of 1 cm optical path length (irradiated at 367 nm under stirring). Therefore, considering the drastic differences in photoreactor geometry and operating conditions, control experiments were carried out to verify that the conclusions reached in reference 25 still hold for a continuous helical photoreactor where the miniemulsion is pumped through a coiled tubing of 1.5 mm diameter. **Figure 2** shows the evolution of the accumulated number of absorbed photons after

several passes (residence time: 27 s) in the minireactor. Each pass caused a steady increase of the number of absorbed photons by the actinometer solubilized within the hydrophobic droplets. Similarly to experiments performed in quartz cells, varying droplet size in the nanoscale range (50-150 nm) did not give rise to any significant change despite very large differences in extinction (scattering + absorption) coefficients ($0.15 - 2.20 \text{ cm}^{-1}$ at 365 nm). This result is also consistent with the observed minimal effect of the larger size of the BA miniemulsion droplets ($D_d = 160 \text{ nm}$) on conversion ($> 95 \%$) and polymer characteristics ($\bar{M}_n=110 \text{ kDa}$, PDI = 4.5). Additionally, it is important to mention that no problem of plugging was observed during the tests carried out up to 18 residence times. In addition, the absence of fouling was assessed by scanning the internal tube wall with ATR-IR spectroscopy.

Nevertheless, two limitations should be mentioned: i. Runs carried out with higher solids contents (40 wt% and 50 wt%) led to plugging. As recently emphasized,^[27] the origin of clogging may be sought in the lower monomer/reactor wall interfacial tension compared to the aqueous phase/reactor wall interfacial tension. Under these conditions, there is displacement of the aqueous phase by monomer on the reactor wall, referred to as adhesional wetting. This issue and possible solutions will be investigated in a separate study. ii. The described positive effect on reaction kinetics and control of polydispersity was much less pronounced for monomers exhibiting a slower rate of addition of macroradicals to monomer units, and polymers with much higher glass transition temperature (glass effect) were obtained, as it is the case for methacrylic acid esters. For example methyl methacrylate ($k_p = 6.5 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1}$ at $50 \text{ }^\circ\text{C}$)^[19] and n-butyl methacrylate ($k_p = 7.6 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1}$ at $50 \text{ }^\circ\text{C}$)^[19] exhibited only a limiting conversion of 40 % for a residence time of 27 s (see **Table 3** for complete characterization data). These early findings emphasize that the added value of the

minireactor presented in this work is probably most important for highly exothermic and rapid polymerization reactions.

As summarized in **Table 4**, the BA photopolymerization was optimized by varying PI concentration, irradiance and flow rate. Keeping the residence time unchanged (27 s), a decrease of the PI concentration (from 0.75 to 0.25 wt%, runs **A-C**) resulted in a lower polydispersity (3.3) without affecting significantly conversion (90 %) (see size exclusion chromatography traces in **Figure S3** of ESI). However, the improvement in molecular weight distribution control is rather limited compared to previous results, using the same monomer^[15] but working with a microreactor and in a homogeneous reaction medium. Interestingly, an oil-soluble PI is not inconsistent with a flash polymerization, although the initiating (phosphinoyl and benzoyl) radicals are generated in pairs within the confined monomer droplets with a high probability for fast bimolecular termination. We believe that the formation of high MW polymers can only be accounted for by a large radical desorption ability from particles.^[28]

In order to investigate the effect of irradiance (runs **D-G** in Table 4), a grid wrapped several times around the quartz cylinder was used to lower gradually the irradiance. A two-fold decrease of the irradiance (1.3 mW/cm^2 , run **E**) caused the conversion to drop from 95 % to 60 %, while a very low irradiance of 0.6 mW/cm^2 (run **D**) still ensured 20 % conversion. Conversely, a stronger irradiance of 8.2 mW/cm^2 (run **F**) provided by another black light lamp did not affect the kinetic profiles. More surprisingly, a 40-fold increase in irradiance (310 mW/cm^2 , run **G**) provided by a medium-pressure Hg arc resulted in a drop of the conversion (50 %). Irradiance is known to control the rate of producing primary radicals with direct consequence on kinetic chains. This means that molecular weights can be modulated somehow (see \bar{M}_n values in Table 4) without the necessity of changing the formulation (*e.g.* initiator concentration). With regard to kinetics, limited conversions occur if primary radicals are produced at too low

concentrations (irradiance $\leq 1.3 \text{ mW/cm}^2$). Conversely, at too high concentrations (high irradiance), the termination mode may change from the normal bimolecular termination between propagating radicals to primary termination that involves propagating radicals reacting with primary radicals.^[29] It is most interesting to note that the medium-pressure Hg lamp, which is the established workhorse for carrying out UV-curing, is therefore of little relevance for linear photopolymerization using flow processes. A high radiant power is mostly justified for open-air polymerization of high surface-to-volume coatings adversely affected by the presence of oxygen. Obviously, the closed reaction medium ensured by the minireactor prevents oxygen permeation, thereby decreasing the risk of excited states quenching and radicals scavenging. Furthermore, the fast reaction rates were achieved without nitrogen purging or monomer purification. Therefore, a too high irradiance leading to a high radical count is not only unnecessary, but even detrimental to reaction progress. Interestingly, a low priced actinic black light used traditionally for fluorescence excitation in non-destructive material inspection or clinical diagnosis can become a valuable tool in designing a more efficient photopolymerization process.

Finally, Table 4 gathers also the impact of changing the residence time (13 - 73 s) through flow rate variation. Residence times longer than 27 s (runs **H-I**) did not affect the final conversion (95 %), but decreased MW values ($\bar{M}_n < 100 \text{ kDa}$) and broadened MW distribution, indicating that the PI may be not totally consumed in a single pass, thereby producing more radicals under longer UV exposure. This assumption could be validated by gas or liquid chromatography measurements. Conversely, the lower initiating radical count produced at shorter residence times (17 s in run **J** and 13 s in run **K**) did not afford the same high level of conversion. However, higher MW polymer species were formed with a narrower MW distribution.

4. Conclusions

Latex is commonly referred to as a “product by process”, meaning that even details in the processing conditions (operation, temperature, etc.) can exert a strong influence upon polymerization kinetics and polymer architecture. Using a simple reactor comprised of a helically coiled Teflon tubing (1.5 mm i.d., 9 mL volume), a UV-A black light-driven continuous photopolymerization of a BA miniemulsion led to a steady conversion of 95 % after 2 residence times of 27 s. This result represents a 25-fold increase in efficiency as compared to a corresponding batch operation. In addition, high MW gel-free polymer colloids ($\bar{M}_n > 100$ kDa) with a moderate polydispersity (PDI = 4.1) were collected. No clogging or fouling was observed when the solids content was kept below 25 %. Nevertheless, it should be noted that the described positive effect on the overall reaction kinetics has been only validated for very fast propagating monomers such as acrylates. Despite their versatility, the need remains for a new generation of highly reactive, functional, and affordable monomers that may be polymerized by a mechanism adapted to the demanding conditions of aqueous emulsions.

Inspired by the research in the field of thick UV-curable coatings,^[30] our strategy retains its key features including long-wave UV irradiation, and a photobleaching PI employed at low concentration. We believe that our mild intensification process may lay the foundation for a novel, eco-efficient, “flash” chain radical polymerization approach. Limited dependence on droplet size and channel thickness, less transfer reactions, moderate MW distribution, low power consumption and low priced equipment represent the main assets. In future developments, the issue of scalability could be addressed through the increase of tubing diameter and/or length (and therefore of photoreactor volume). These two options are easy to implement within such a macroflow photochemical reactor, in contrast to a microreactor.

Supporting Information

Supporting Information is available from the Wiley Online Library

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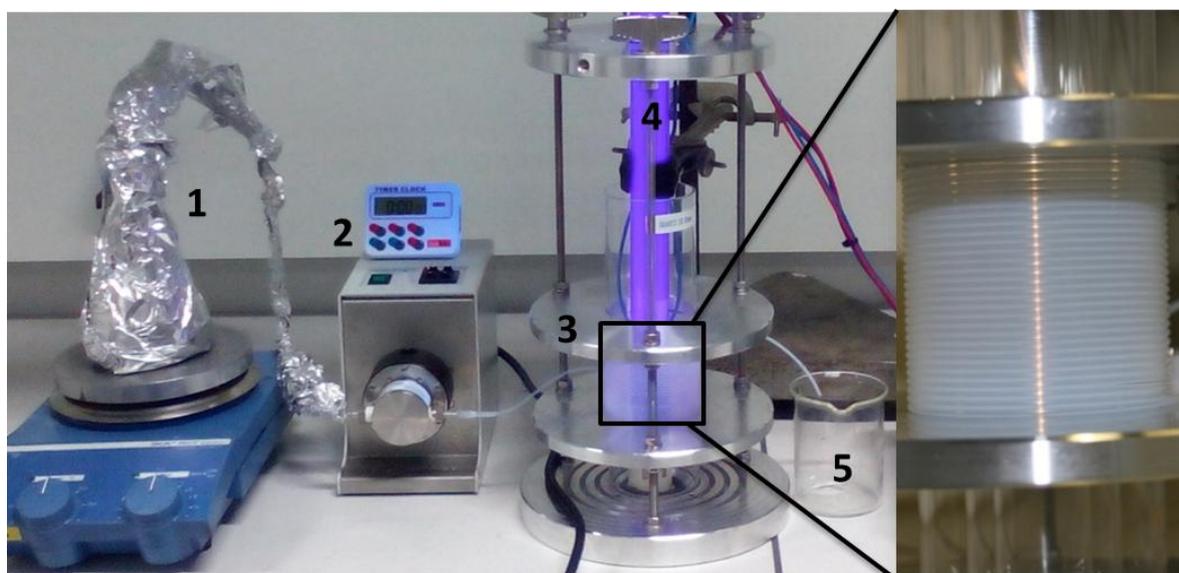
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Scheme 1. Image of the macroflow photochemical helix minireactor: monomer miniemulsion tank (1), pump (2), photoreactor (3), black light lamp (4) and collecting flask (5). The inset shows a magnification of the helically coiled Teflon tubing.

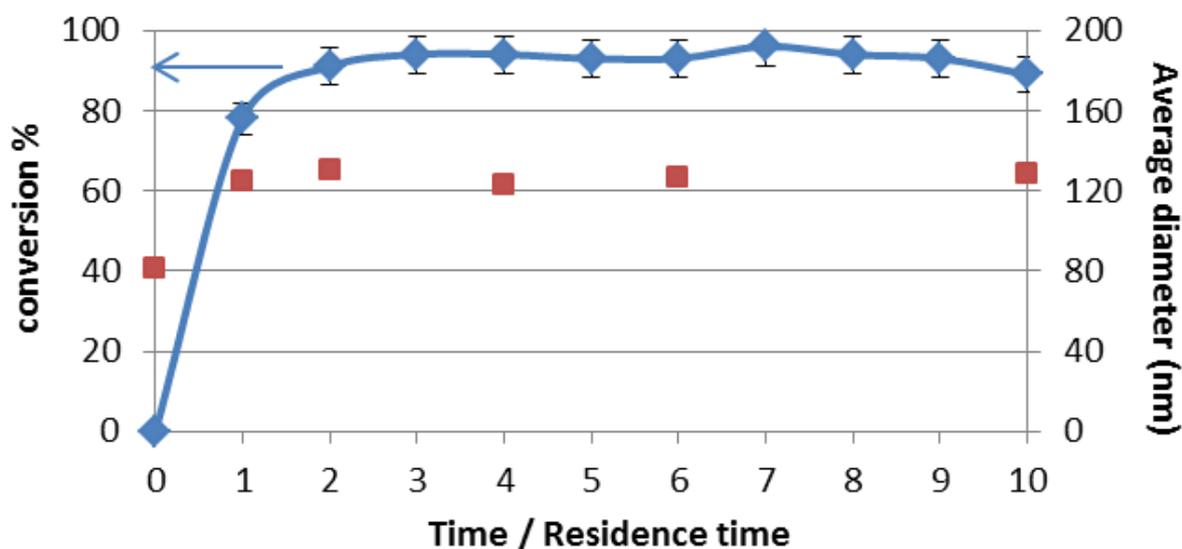


Figure 1. Evolution of conversion (left y axis) and average droplet diameter (right y axis) versus the number of residence times for the BA miniemulsion polymerization (residence time: 27 s, flow rate: 20 mL/min, $D_d = 80$ nm).

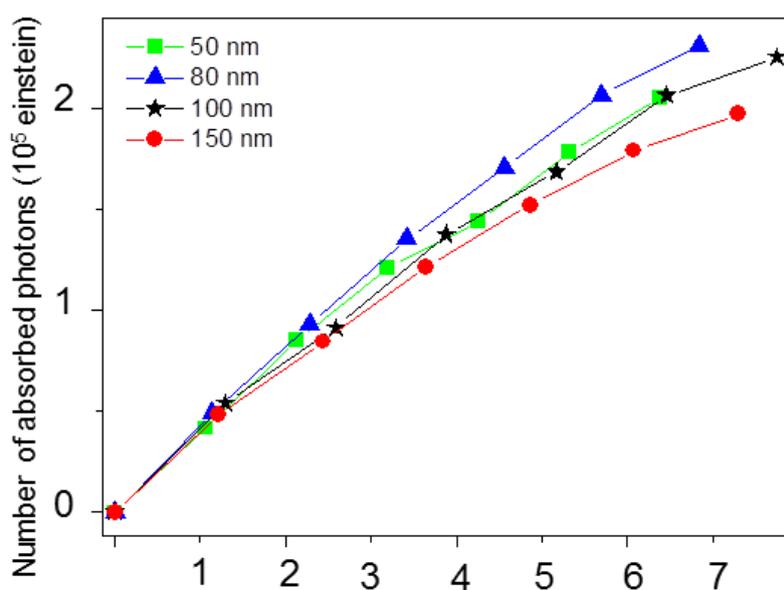


Figure 2. Number of absorbed photons versus the number of passes (each lasting 27 s) in the helix minireactor for an ethyl acetate miniemulsion containing a water-insoluble chemical actinometer (DFIS) with different droplet sizes and extinction coefficients ($0.15 - 2.20 \text{ cm}^{-1}$ at 365 nm) ($4 \text{ wt}\% \varphi_{\text{org}}$, $[\text{DFIS}] = 1.8 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$).

Table 1. Composition of BA miniemulsion (25 % solids content, $D_d = 80$ nm).

| Monomer wt% / total | Water wt% / total | Hexadecane wt% / monomer | Sodium dodecyl sulfate wt% / monomer | Photoinitiator wt% / monomer |
|------------------------|----------------------|-----------------------------|--|---------------------------------|
| 25.00 | 75.00 | 4.00 | 2.00 | 0.75 |

Table 2. Effect of operation modes on BA miniemulsion polymerization (25 wt% solids content, $D_d = 80$ nm)

| Reactor | D _p nm | Conversion % | \bar{M}_n kDa | PDI \bar{M}_w/\bar{M}_n | Productivity g/h |
|---------------|----------------------|---------------------------|--------------------|------------------------------|---------------------|
| Photo-flow | 120 | 95 (reaction time of 27s) | 103 | 4.2 | 300 |
| Photo-batch | 140 | 85 (in 2h) | 300 | 2.3 | 12 |
| Thermal-batch | 100 | 95 (in 1h) | 79 | 4.9 | 35 |

Table 3. Effect of the monomer structure on flow photopolymerization in the helix minireactor (25 wt% solids content)

| Monomer | D _d nm | D _p nm | Conversion % | \bar{M}_n kDa | PDI \bar{M}_w/\bar{M}_n |
|---------------------|----------------------|----------------------|-----------------|--------------------|------------------------------|
| Butyl acrylate (BA) | 80 | 120 | 95 | 103 | 4.2 |
| Methyl methacrylate | 70 | 75 | 40 | 32 | 4.5 |
| Butyl methacrylate | 120 | 165 | 40 | 39 | 6.1 |

Table 4. Effect of irradiance, flow rate and PI concentration on continuous-flow photopolymerization of BA miniemulsion (25 wt% solids content, D_d = 80 nm)

| Run | Irradiance ^a mW/cm ² | Residence time s | [PI] wt% | D _p nm | Conv % | \bar{M}_n kDa | PDI |
|----------|---|-----------------------|-------------|----------------------|-----------|--------------------|------------|
| A | 2.6 | 27^b | 0.75 | 120 | 95 | 103 | 4.2 |
| B | 2.6 | 27 | 0.5 | 135 | 85 | 107 | 4.3 |
| C | 2.6 | 27 | 0.25 | 170 | 85 | 161 | 3.3 |
| D | 0.3 | 27 | 0.75 | 135 | 17 | 214 | 2.8 |
| E | 1.3 | 27 | 0.75 | 120 | 65 | 146 | 3.8 |
| F | 8.2 | 27 | 0.75 | 130 | 95 | 65 | 6.0 |
| G | 310 | 27 | 0.75 | 100 | 48 | - | - |
| H | 2.6 | 73 | 0.75 | 130 | 95 | 70 | 5.1 |
| I | 2.6 | 35 | 0.75 | 135 | 95 | 80 | 5.2 |
| J | 2.6 | 17 | 0.75 | 145 | 50 | 122 | 3.8 |
| K | 2.6 | 13.5 | 0.75 | 145 | 30 | 126 | 4.1 |

^a Irradiance values are provided in the 350–410 nm region

^b The corresponding flow rate is 20 mL/min, the reactor volume of 9 mL was unchanged

Table of contents entry

A novel continuous radical photopolymerization process enables to convert acrylate monomer emulsion with surprisingly high efficiency. The combination of a photochemical minireactor, the resulting very short polymerization times, low costs of production and the simplicity of the equipment might be of interest to change the way emulsion polymerization is performed both at research and industrial levels.

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Flash Latex Production in a Continuous Helical Photoreactor: Releasing the Brake Pedal on Acrylate Chain Radical Polymerization

