RSC Advances


Volume 1 | Number 1 | Jan 2013 | Pages 1–100

RSC Advances

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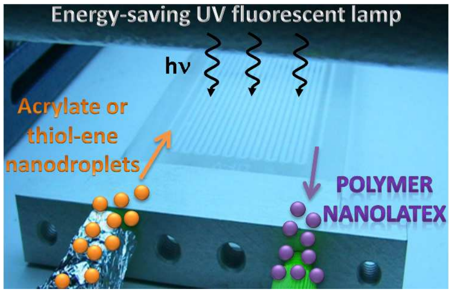

Water-based photopolymerization in microreactor using compact UV fluorescent lamps can create a breakthrough technology to produce polymer latexes in a safer, more environmental-friendly and energy-efficient way

Journal Name RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Continuous-flow synthesis of polymer nanoparticles in a microreactor via miniemulsion photopolymerization

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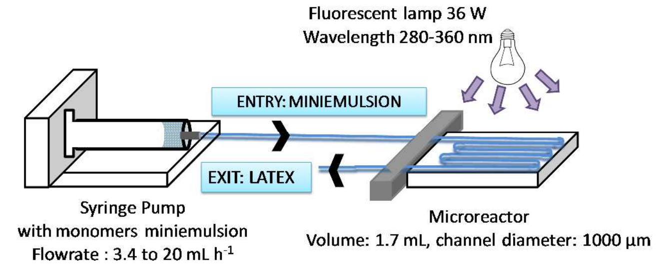
An efficient continuous synthesis of nanolatex was achieved in water using a single-lane photochemical microreactor combined with an energy-saving and safe UV fluorescent lamp. Acrylate and thiol-ene miniemulsions were polymerized in high yields at low irradiance (3 mW cm^{-2}) upon controlling droplet size, temperature and residence time.

Among the successful organic solvent-free routes to polymer synthesis, emulsion radical polymerization processes in water hold significant importance. They yield aqueous polymer dispersions used in a variety of industrial applications including coatings, adhesives, binders or foams. Although polymerization is still mostly initiated thermally, the need for process intensification emphasizes UV radiation as a promising alternative to make the process even safer, more compact, energy-efficient and environmental-friendly.[1-4] Photopolymerization has indeed distinct advantages such as ambient temperature reaction, fast reaction rates, spatial and temporal control, and the possibility to use energy-saving lamps. However, the main technological challenge remains UV light attenuation in a dispersed medium due to the combined effect of particle/droplet scattering and absorption.[5,6] Therefore, a suitable reactor design is crucial to obtain the full potential of a photoinduced heterogeneous polymerization process.

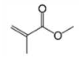
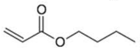
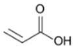
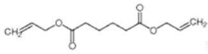
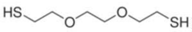
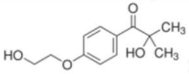
Herein, we report the results of a first attempt to combine microreaction technology and photopolymerization to generate polymer nanoparticles. Indeed, the use of a microfluidic reactor might be of great advantage mainly because of two key features: i) the small optical path length of microscale channels (100 to 1000 µm) may improve light penetration through the entire reactor volume; ii) the short diffusion path inside a microdevice enables a very efficient mixing that would likely offset problems of light attenuation. While microreactors were widely used in preparative organic photochemistry,[7] there are much fewer attempts in the domain of photopolymerization, where the main effort focused on the synthesis of cross-linked polymer beads using different microfluidic devices. In most cases, microdroplets containing multifunctional monomers were generated in situ within the channels to be subsequently cured one by one under a UV spot light.[8,9] Monodisperse microsized particles with controlled and complex morphology such as Janus[10] or core-shell particles[11,12] could be obtained by this approach. However, there is surprisingly no reference to the synthesis of nanoparticles based on linear polymers by photopolymerization methods. Yet, most latex applications require non reticulated particles having both a colloidal size range (< 1 µm) and film-forming ability.[13] Such characteristics are not easily achieved by polymerization means,[14] but rather by emulsification or nanoprecipitation of preformed polymers in a microreator.[15]



Scheme 1 Continuous production of polymer nanoparticles in a photochemical microreactor.

A completely different pathway is reported herein involving a continuous monomer miniemulsion photopolymerization carried out in a borosilicate microreactor (channel dimension: 1 mm and 1.7 mL volume, Scheme 1). Compared to conventional and unstable macroemulsions (droplets diameters ranging from 500 nm to few µm), miniemulsions

Table 1 Chemical structure of monomers (**1**-**5**) and photoinitiator (**PI**) involved in miniemulsion photopolymerization.[a]

	(Meth)acrylate	Thiol-ene
Monomer	 **1**  **2**  **3**	 **4**  **5**
Photoinitiator	 **PI** (water-soluble)	

[a] Two monomer miniemulsions have different organic phase content. The first one is a mixture of methyl methacrylate/butyl acrylate/acrylic acid (**1**/**2**/**3**: 49.5/49.5/1 wt %) and octadecylacrylate (4 wt %) used as costabilizer against Ostwald ripening. The second organic phase consists of diallyl adipate (**4**) and ethylene glycol dithiol (**5**) with stoichiometric amounts of thiol and ene functionalities costabilized by hexadecane (4 wt %). The aqueous phase was prepared separately by dissolving 0.75 wt % sodium dodecyl sulfate (SDS) in distilled water. All costabilizer and surfactant concentrations are given with respect to the monomer phase.

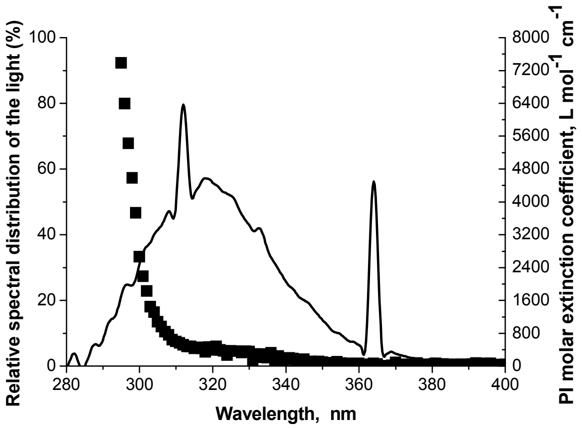


Figure 1 Spectral distribution of the UV fluorescent lamp (—) and absorption spectrum of the water-soluble α-hydroxyacetophenone **PI** (■) in acetonitrile.

exhibit smaller and metastable droplets (50 – 500 nm), which are thus less scattering and much easier to handle. As indicated in Table 1, miniemulsions were prepared by high shear homogenization of a surfactant aqueous solution (0.75 wt %) including a water-soluble α-hydroxyketone type photoinitiator (**PI**, 2 wt %) with an organic phase based on a mixture of monofunctional acrylates and methacrylate monomers (**1**/**2**/**3**) or difunctional thiol-ene monomers (**4**/**5**). Details of syntheses are available in the ESI.† The two miniemulsions (15 wt % solid content) having an average droplet diameter of 90 nm and 175 nm, respectively, were found to be stable in the absence of UV light and colloidally stable during several hours. As a result, there was no need for a complex microreactor design with multiple inlets for in situ mixing (monomers/initiator) or emulsification.

As shown in Scheme 1, a simple one-input-one-output geometry was employed to ensure both miniemulsion entry and latex recovery in a continuous-flow process. Furthermore, an energy-saving compact light source was placed at a short distance to the reactor to trigger the formation of linear polymers via radical chain-growth (acrylate) or step-growth (thiol-ene) polymerization by sequential chain transfer/propgation, which are two distinctly different mechanisms.[16] An economical and low-power consumption set-up consisting of two 36 W UV fluorescent lamps emitting between 280 and 360 nm and providing an estimated irradiance of 3 mW cm^{-2} was installed.† The spectral distribution of the light source emission and the absorption spectrum of **PI** are shown in Figure 1. Preliminary experiments demonstrated that with a residence time of 10 min, total consumption of the thiol-ene monomer in the miniemulsion was achieved at ambient temperature (Table 2, entry **A**) , while the acrylate analogue yielded a partial conversion of 35 % (entry **B**). Clearly, the use of step-growth polymerization led to higher rates of monomer conversion. The occurrence of a photoinduced thiol-ene polymerization was assessed by ^{1}H NMR spectroscopy.† In addition, a thermal analysis of the resultant poly(thioether) through differential scanning calorimetry (DSC) revealed a glass transition temperature (T_g) of -63 °C and a melting temperature of 18 °C. Linearity, structural homogeneity and interaction between ester and thioether groups may account for the high crystallinity (55%) leading to insolubility of the polymer in most organic solvents. As a result, only the lowest molecular weight fraction (< 10 %) could be characterized (M_n = 30 kDa) by size exclusion chromatography (SEC). Note that gel formation is unlikely with difunctional thiol-ene monomers because chain transfer reactions to thiol are much more probable than transfer to polymer leading to reactive sites for chain branching.[17] It should be noted that the UV fluorescent lamp did not cause any heat development, thus excluding any thermal contribution to polymerization initiation. Particle sizes of 100 nm and 155 nm were obtained, respectively, for the polyacrylate and poly(thioether) latex, indicating a good agreement with the initial droplet size (Table 2 - entry **A** and **B**). To examine the key parameters controlling this photochemical process, we focused on the less reactive acrylate miniemulsion offering a greater scope for improvement. Three different parameters turned out to be particularly significant for the evolution of polymerization: droplet size (D_d), temperature (T) and residence time (t_R). Their effect on colloidal properties, monomer conversion and molecular weight were summarized in Table 2.

Different miniemulsion droplet sizes ranging from 40 to 100 nm (Table 2, entries **B**-**F**) could be easily achieved upon varying the surfactant concentration (0.25 to 3.5 wt %). Keeping t_R unchanged (10 min), a decrease in droplet size afforded higher conversion. For example, the miniemulsion displaying an average droplet diameter of 40 nm (entry **C**, Table 2) reached a conversion of 74 %, twice as much as that of 90 nm diameter (35 %, entry **B**, Table 2). Smaller droplets promoted a better light penetration and an enhanced radical compartmentalization effect, which might account for such acceleration. Furthermore, as expected, an increase of the polymer molecular weight accompanied the decrease in the initial droplet size.

Table 2 Effect of different experimental parameters (T, t_R, and D_d) during the photopolymerization of thiol-ene (**A**) and acrylate (**B**-**L**) miniemulsions The characteristics investigated were particle average diameters (D_p), conversion (*Conv*) and number average molecular weight (M_n).

Entry[a]	T/°C	t_R/min	D_d[c]/nm	D_p[c]/nm	*Conv*[d]/%	M_n[e]/10^3 g mol^{-1}	*PDI*
A	20	10	170	155	100	30[f]	3.5
B	20	10	90	100	35	28	5.0
C	20	10	40	75	74	114	3.0
D	20	10	65	80	63	55	2.7
E	20	10	80	85	53	24	5
F	20	10	100	110	33	22	4.0
G	35	10	90	100	48	50	3.9
H	50	10	95	125	81	32	4.1
I	60	10	95	125	100	45	2.5
J	20	5	95	105	25	23	4.0
K	20	14	95	115	68	26	4.5
L[b]	20	20	90	100	69	-	-

[a]Entry **A** is for the thiol/ene miniemulsion while the other entries (**B**-**L**) are acrylate miniemulsions. [b]Two serially positioned microreactors were used. [c]Droplet and particle sizes were determined by dynamic light scattering (DLS). [d]Monomer conversion was obtained by gravimetry. [e]Molecular weights were provided by SEC. [f]Only the THF soluble fraction was analyzed by SEC, the insoluble fraction results from chain crystallinity.

A second effective means to enhance conversion rates was to operate the system at $T > T_{amb}$. Compared to the reference experiment (entry **B**) performed at 20 °C, a gradual increase in conversion was observed when increasing the reaction temperature up to 60 °C (Table 2, entries **G**-**I**), keeping t_R (10 min) and D_d (≈ 90 nm) constant. A change of only 40 °C caused the conversion to climb from 35 % (20 °C) to 100 % (60 °C). Note that the confirmation of solely photoinitiated polymerization was provided by the absence of any reaction when the miniemulsion in the microreactor was heated without irradiation. The precipitated polyacrylate particles had a T_g of 15-20 °C (assessed by DSC), suggesting that a significant increase of chain mobility and molecular diffusional mobility may occur upon heating. Indeed, several studies showed similar drastic increases of conversion when operating at temperatures above T_g.[18,19] Finally, the irradiation time was easily adjusted by varying t_R. Changing either the flowrate (Table 2, entries **J**-**K**) or channel length (entry **L**, with two reactors connected in series) allowed to vary t_R from 5 to 20 min. Longer residence times resulted in higher conversions. As expected, extending the UV exposure led to an increased absorbed energy per unit volume and, consequently, to a higher radical concentration. Despite greater conversions, the molecular weights remained unchanged. Indeed, the number of competing propagating chains was also increased, thereby yielding polymers with shorter chains. However, clogging occurred with increasing residence time (or using unstable miniemulsions). This widely reported effect[14,20] is generally related to the particle-wall interactions and to shearing-induced coagulation.

In summary, we successfully achieved the synthesis of linear polymer nanoparticles in a microreactor via a miniemulsion radical photopolymerization process using an affordable, harmless and low intensity UV fluorescent light source. High yields were obtained with a thiol-ene system, whereas the lower reactivity of the (meth)acrylate monomers was significantly improved by decreasing droplet size (< 100 nm) or proceeding at higher temperatures (35 - 60 °C) slightly above the glass transition temperature of the copolymer. To the best of our knowledge, this is the first synthesis of nanosized particles in a photochemical microreactor. However, microreactor is not intended for massive production of polymer nanoparticles, but could be used for the small-scale preparation of specialty high value-added latex. Combining small optical path and efficient mixing has proved its significance for polymerizing turbid monomer nanoemulsions, and maybe in future, for more light attenuating macroemulsions. The polymerization of monomer emulsions in photochemical microreactors could be one of the most promising environmentally improved routes to produce polymer latexes. Furthermore, the shift to visible light photoinitiator, initiatorless photopolymerization (achievable with thiol-ene click chemistry), or nanoemulsion formulation using spontaneous emulsification represent some directions to improve the green credentials of this process.

Acknowledgements

The authors gratefully acknowledge Little Things Factory (Germany) for the microreactor's loan. Emeline Lobry and Marta Penconi were supported by the French National Research Agency (ANR, Programme Chimie Durable-Industries-Innovation) under contract number ANR-2012-CDII-006-02.

Notes and references

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† Electronic supplementary information (ESI) available. [Synthesis and characterization details are provided. In addition, Fig S1 gives the technical characteristic of the photochemical microreactor, Fig S2 provides the spectral distribution of the UV fluorescent lamp, Fig S3 is the ^{1}H NMR spectrum of the poly(thioether) formed by thiol-ene photopolymerization]. See DOI: 10.1039/c000000x/

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