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The use of chemical actinometry for the evaluation of light absorption efficiency in scattering photopolymerizable miniemulsions§

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ABSTRACT

Oil-in-water miniemulsions containing a mixture of monomers as the dispersed organic phase have been shown recently to be promising media for the development of photoinitiated polymerization processes. Albeit a crucial factor for a successful application, the efficiency of light absorption by the photoinitiator in these highly scattering systems is difficult to evaluate. In this work, a well-characterized water insoluble chemical actinometer (DFIS) replaced the oil-soluble photoinitiator, and was used as a probe and a model for UV light absorption in miniemulsions of variable droplet sizes and organic phase composition (*i.e.* at different levels of scattered light). In a first step, the photon flux absorbed by the actinometer was determined in model miniemulsions based on an inert solvent (ethyl acetate), at low oil phase content (3.0 to 6.0 wt %). For these low to moderately scattering systems, the photon flux absorbed by the actinometer in the miniemulsions was comparable to that in a homogeneous solution of ethyl acetate. In a second step, the absorbed photon flux was investigated in photopolymerizable miniemulsions (mixture of acrylate monomers as oil phase). Surprisingly, in spite of much higher scattering coefficients than those found for ethyl acetate based miniemulsions of otherwise the same composition, the photon flux absorbed by the actinometer in photopolymerizable miniemulsions showed only a small decreasing trend. Such a result may be considered favorable for the further development of applications of photopolymerization in miniemulsions.

1 Introduction

In recent years, increasing attention has been devoted to heterogeneous free radical polymerization for the production of aqueous dispersions of polymer nanoparticles.[1] Such latexes are important raw materials used in a variety of industrial processes, to protect or finish metal and wood, or used as binders for pigments or fillers. They are prepared by polymerization of monomers emulsified in water. Emulsion polymerization processes are generally initiated thermally through the decomposition of a radical initiator (peroxide, azo compounds) triggered by a temperature increase.

The photoinitiated polymerization is a viable and emerging alternative to the thermal initiation and offers several advantages, such as lower reaction temperatures, higher polymerization rates due to a faster initiation and a better control on radical generation by tuning the characteristics of the light source and the irradiation time. Although photopolymerization is essentially exploited as UV-curing technology to produce cross-linked films, numerous investigations in the field of linear polymer preparation reported photopolymerizations of monomer emulsions,[2-6] microemulsions [7-12] and miniemulsions.[13-19] Recently, acrylate miniemulsions, with droplet sizes between 50 and 500 nm, have been explored as highly suitable media for the preparation of polymer latexes using UV light. To obtain a miniemulsion, a surfactant and a costabilizer are needed in order to stabilize the monomer nanodroplets in the aqueous continuous phase. In particular, the costabilizer, *i.e.* a water-insoluble low-molecular-weight compound, is needed in order to prevent Ostwald ripening and guarantee the metastability of the system.[20-22] Moreover, a high shear force, provided for instance by ultrasounds, is required to form the monomer nanodroplets. In principle, the high number of nanodroplets generated makes them the main locus of nucleation; thus polymer formation occurs in principle inside the droplets.[21,23] The size and composition of the droplets play an essential role in determining the optical properties of the miniemulsion. Despite their nanometric size range, miniemulsions are not transparent due to their polydispersity, and the light may be both absorbed and scattered by the medium. Conventional spectroscopic techniques can only provide the attenuation (or extinction) coefficient, that is the sum of absorption and scattering coefficients. Recently, the optical properties of diluted monomer acrylate miniemulsions have been investigated by Jasinski et al. [24] using different spectrophotometric methods based on an approach already applied by Sun and Bolton.[25] Results showed that when droplet size decreased, the absorption coefficient remained constant and close to that measured in a solution of monomers. In contrast, the scattering coefficient strongly decreased, leading to a faster photopolymerization reaction due to the better light penetration into the heterogeneous medium. In the case of highly concentrated miniemulsions, multiple scattering cannot be avoided and the determination of the absorption and single scattering coefficients is a more complex issue.[26] The depth of light penetration within the miniemulsion is of primary importance for the photopolymerization rate, as the generation of primary radicals occurs upon irradiation of a photoinitator system. The most common radical photoinitiators have a benzoyl-based structure and undergo homolytic α-cleavage (Norrish I cleavage) from the excited triplet state.[27-29] In order to optimize the photochemical initiation step, the photon flux absorbed by the photoinitiator should therefore be maximized.[30]

The issue to determine the efficiency of photon absorption in heterogeneous systems has been largely investigated in the field of photocatalysis in TiO_2 suspensions aiming at the calculation of the quantum efficiencies.[25,31-35] The main problem is related to the estimation of the radiation distribution field in these systems, due to the simultaneous occurrence of light scattering and absorption by the photocatalyst particles. However, the determination of the absorption and scattering coefficients is not sufficient to evaluate the absorbed photon flux, since multiple scattered photons may be subsequently absorbed giving an additional contribution. Similarly to the case of TiO_2 suspensions, both absorption and scattering are responsible for light attenuation in a monomer miniemulsion. However, in contrast to TiO_2 photocatalysis, the photochemically active species (photoinitiator) is consumed during polymerization and evaluation of the absorbed photon flux in such a system is extremely complex.

In order to improve the understanding of the photon absorption process in the core of the monomer droplets, we replaced the oil-soluble photoinitiator with a chemical actinometer that can be easily dissolved into the organic dispersed phase. A chemical actinometer undergoes a well-characterized photochemical reaction and allows the estimation of the incident and absorbed photon flux.[36] The main advantage with respect to physical actinometers (radiometers) lies in the exact reproducibility of experimental conditions using the same experimental arrangement, *i.e.* the same reaction vessel (cell, photochemical reactor), equipment (lenses, filters) and solvent or solvating system, for sample and reference chemical actinometry. To our knowledge, this study reports the first example of actinometry carried out by dissolving the chosen chemical actinometer ((E)-[1-(2,5-dimethyl-3-furyl)ethylidene](isopropylidene)-succinic anhydride, DFIS) in the organic part of a dispersed system. The absorbed photon flux has been evaluated on an optical bench under monochromatic excitation. Actinometry has been performed in miniemulsions with variable droplet sizes and organic phase contents, *i.e.* at different levels of scattered light, to better understand the effect of scattering on the efficiency of photon absorption. In a first part, actinometric experiments have been performed in a model type miniemulsion, where the organic phase consisted of the actinometer dissolved in a inert solvent (ethyl acetate). This system allowed working under low scattering conditions and represented a first and simple approach. In a second part, studies have been carried out in highly scattering photopolymerizable miniemulsions where the oil phase consisted of the actinometer dissolved in a mixture of acrylate monomers.

2 Materials and Methods

2.1 Chemicals

(E)-[1-(2,5-dimethyl-3-furyl)ethylidene](isopropylidene)-succinic anhydride (DFIS, > 95%) was supplied by Extrasynthese, France, and used without further purification. Note that DFIS is commonly known as Aberchrome 540, the commercial name of the compound produced by Aberchromics Ltd., but since 2000, Aberchrome 540 is no longer available from this company. Ethyl acetate (EtAc, > 99.7%) and technical grade monomers, methyl methacrylate (MMA, 99%), butyl acrylate (BA, > 99%) and acrylic acid (AA, 99%), were obtained from Sigma-Aldrich and used as received. Sodium dodecyl sulfate (SDS, > 99.0%, Aldrich) and octadecyl acrylate (OA, 97%, Aldrich) were used as surfactant and costabilizer, respectively. All miniemulsions were prepared with ultrapure water.

2.2 Miniemulsion preparation

Miniemulsions containing a monomer mixture (MM) as organic phase (φ_{org}) were prepared as follows. The organic phase was obtained by mixing the three acrylate monomers according to the ratio MMA/BA/AA (49.5/49.5/1 wt %). The co-stabilizer OA (4 wt/wt$_{\varphi org}$ %) was added to the mixture of monomers. The aqueous phase consisted of an aqueous SDS solution. The concentration of SDS (0.08 to 1.5 wt/wt$_{\varphi org}$ %) was varied to obtain droplet sizes ranging from 47 nm to 150 nm. The organic and aqueous phases were mixed using a magnetic stirrer at 700 rpm for at least 10 min to form a coarse emulsion. The high homogenization energy input required to form a miniemulsion was provided by sonication using a Branson Sonifier

450 (450 W/L) during 5 min under magnetic stirring. Miniemulsions, where the organic phase consisted of EtAc, were prepared according to the same procedure. All miniemulsions were prepared with an organic phase content of 30 $\text{wt}_{\varphi\text{org}}$ % (weight of MM or EtAc with respect to the total weight). When lower organic phase content is mentioned, miniemulsions were obtained by subsequent dilution of the 30 $\text{wt}_{\varphi\text{org}}$ % concentrated miniemulsion. For the actinometric experiments in miniemulsions, the organic phase was prepared by dissolving the actinometer DFIS in MM or EtAc.

2.3 Miniemulsion characterization

Droplet size (z-average diameter) was determined by dynamic light scattering (DLS) using a Zetasizer Nano ZS, Malvern Instruments. In the prepared miniemulsions, the high concentration of droplets gives rise to a multiple scattering effect of the incident light that affects the reliability of the DLS measurement. To avoid this problem, samples were prepared by diluting miniemulsions 125 times with ultrapure water. Further dilution did not affect the size of the droplet, indicating that the observed values of the diameters are practically independent on droplet concentration. Measurements were conducted within 10 minutes of sample preparation, although no significant variation of droplet size was observed over 2 hours. UV/Visible spectrophotometric measurements were carried out using a HP 8453 diode array single beam spectrophotometer equipped with a HP 89090A Peltier temperature control. The spectra were collected at 22°C in quartz cells of 1 cm, 0.5 cm or 0.01 cm optical path lengths, using water, EtAc or the monomer mixture MM as a reference.

2.4 Optical properties of heterogeneous systems

In an homogeneous isotropic medium containing an absorbing species (Ac), incident photons can be either transmitted or absorbed, and the sum of the photon fluxes absorbed ($P_{a,\lambda}$) and transmitted ($P_{\text{t},\lambda}$) is equal to the incident photon flux ($P_{0,\lambda}$) at wavelength λ. Photon fluxes are usually expressed in einstein·s^{-1} or in einstein·$\text{L}^{-1}\cdot\text{s}^{-1}$.

$$P_{0,\lambda} = P_{a,\lambda} + P_{t,\lambda} \tag{1}$$

Spectrophotometric analysis carried out by determining the transmitted photon flux ($P_{\text{t},\lambda}$) provides an estimation of the value of the transmittance ($T_\lambda = P_{\text{t},\lambda}/P_{0,\lambda}$), and the absorbance ($A_\lambda$) may be calculated according to the Beer-Lambert law,[37]

$$A_\lambda = log\frac{1}{T_\lambda} = K_\lambda \ell = [Ac]\varepsilon_\lambda \ell \tag{2}$$

with ℓ: optical path length [cm], K_λ: absorption coefficient [cm^{-1}], [Ac]: concentration [mol L^{-1}] of the absorbing species Ac and ε_λ: molar absorption coefficient of Ac [L mol^{-1} cm^{-1}]. Note that if spectroscopic cells of 1 cm optical path length are used, $A_\lambda = K_\lambda$.

The absorbed photon flux is thus related to the incident photon flux by Equation 3.

$$P_{a,\lambda} = P_{0,\lambda}(1-10^{-A_\lambda}) = P_{0,\lambda}(1-10^{-K_\lambda \ell}) \tag{3}$$

In heterogeneous systems, such as miniemulsions, light attenuation (extinction) arises not only from absorption of photons but also from scattering effects. In this case,

$$P_{0,\lambda} = P_{a,\lambda} + P_{s,\lambda} + P_{t,\lambda} \tag{4}$$

where $P_{s,\lambda}$ is the scattered photon flux.

Under these conditions, the Beer-Lambert law is expressed as

$$D_\lambda = log\frac{1}{T_\lambda} = E_\lambda \ell = N_d \sigma_\lambda \ell = K_\lambda \ell + S_\lambda \ell \tag{5}$$

where D_λ is the extinction (or attenuance),[37] E_λ and S_λ are the extinction and scattering coefficients [cm^{-1}], respectively; N_d [m^{-3}] is the number density of the droplets and σ_λ [m^2] is the overall cross section.

The sum of $P_{a,\lambda}$ and $P_{s,\lambda}$ may be expressed as a function of $P_{0,\lambda}$ using Equation 6, similar to equation 3, where the absorbance A_λ has been substituted by the extinction (attenuance) D_λ.

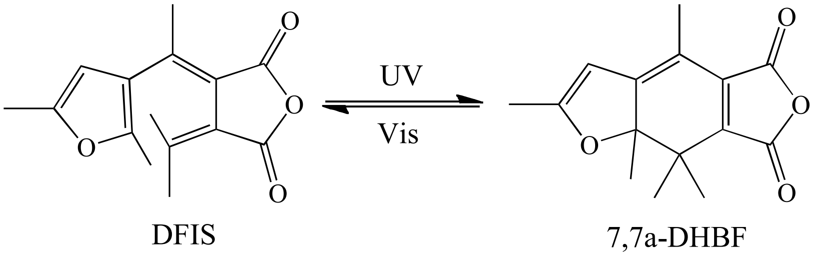
$$P_{a,\lambda} + P_{s,\lambda} = P_{0,\lambda}(1-10^{-D_\lambda}) \tag{6}$$

Under these conditions, UV/Vis transmission spectrophotometry yields the value of E_λ (= S_λ + K_λ, Equation 5) and separate determination of K_λ and S_λ is not possible with this technique. Spectroscopic methods using an integrating sphere to collect reflected and/or transmitted light have been proposed for studying the optical properties of heterogeneous systems and for determining absorption and scattering coefficients in these media.[24-26,38]

In this work, we have chosen a different approach for the evaluation of the absorption efficiency and the absorbed photon flux has been determined by chemical actinometry.[36] The spectra herein presented were recorded by collecting light transmitted both in homogeneous and heterogeneous media.

2.5 Chemical actinometry

2.5.1 Choice of the chemical actinometer. (E)-1-(2,5-dimethyl-3-furyl)ethylidene (isopropylidene)-succinic anhydride (DFIS) is a photochromic fulgide compound. It exhibits a P-type photochromism, i.e. the light-induced reaction between the two isomers having different absorption spectra is photochemically but not thermally reversible. Irradiation of DFIS in the UV spectral region (310 - 370 nm) induces an electrocyclic reaction leading to ring-closure and formation of the 5,6-dicarboxylic acid anhydride of 7,7a-dihydro-2,4,7,7a-pentamethylbenzo[b]furan (7,7a-DHBF), a compound that absorbs in the visible spectral region. The back reaction to the open-form species (DFIS) is promoted by visible radiation.



Scheme 1 Structure and reversible photochromic reaction of (E)-1-(2,5-dimethyl-3-furyl)ethylidene(isopropylidene)-succinic anhydride (DFIS) to 5,6-dicarboxylic acid anhydride of 7,7a-dihydro-2,4,7,7a-pentamethylbenzo[b]furan (7,7a-DHBF).

DFIS has been widely used as an actinometer in the UV (310-370 nm) and in the visible (436-546 nm) ranges since the 1980s.[36,39-43] It has to be pointed out that photoisomerization of DFIS (E-isomer) to the Z-form competes with photocyclization to 7,7a-DHBF. Therefore, the reuse of the actinometer in the UV region after reconversion of 7,7a-DHBF to DFIS is not recommended due to the possible underestimation of the incident photons.[44,45]

DFIS has been chosen as an actinometer (Ac) in this study as it meets some important requirements. It absorbs in the UV-A region, matching the spectra of some of the most common photoinitiators used for polymerization; its high solubility in organic solvents allows solubilisation exclusively in the monomer droplets. Moreover, the photochemical reaction can be easily followed by spectrophotometry in the visible spectral region where absorption is only due to the photoproduct (7,7a-DHBF). Finally, since DFIS is a well-known actinometer, the photochemical reaction and the actinometric procedure have been extensively discussed in the literature.

DFIS (Ac) has been used in this study to estimate the absorbed photon flux ($P_{\mathrm{Ac},\lambda}$) in miniemulsions under different experimental conditions. By definition, $P_{\mathrm{Ac},\lambda}$ is the number of moles of photons ($N_{\mathrm{p,Ac},\lambda}$, [einstein]) absorbed per unit of time by Ac at the wavelength of irradiation λ.

$$P_{Ac,\lambda} = \frac{dN_{p,Ac,\lambda}}{dt} \tag{7}$$

The value of $P_{\mathrm{Ac},\lambda}$ can be calculated from the rate of the photochemical reaction of Ac ($\mathrm{d}n_{\mathrm{Ac}}/\mathrm{dt}$, number of moles of Ac transformed or of product formed per unit of time) according to the definition of the quantum yield of a photochemical reaction:

$$\Phi_{Ac,\lambda} = \frac{dn_{Ac}/dt}{dN_{p,Ac,\lambda}/dt} \tag{8}$$

In homogeneous systems, the experimental determination of $\mathrm{d}n_{\mathrm{Ac}}/\mathrm{dt}$ was carried out by spectrophotometry following the variation of the absorbance (or of the absorption coefficient) of 7,7a-DHBF at the wavelength of its absorption maximum in the visible λ' ($A_{\lambda'}$ or $K_{\lambda'}$) during irradiation. Combining Equations (2), (7) and (8), $P_{\mathrm{Ac},\lambda}$ can be written as

$$P_{Ac,\lambda} = \frac{dA_{\lambda'}}{dt} \cdot \frac{V}{\Phi_{Ac,\lambda} \cdot \varepsilon_{\lambda'} \cdot \ell} = \frac{dK_{\lambda'}}{dt} \cdot \frac{V}{\Phi_{Ac,\lambda} \cdot \varepsilon_{\lambda'}} \tag{9}$$

with V: irradiated volume ([L]); note that λ is the wavelength of irradiation (UV spectral region) and λ' is the wavelength of analysis (visible spectral region).

In actinometric experiments in miniemulsions, even without 7,7a-DHBF, the initial value of the extinction coefficient at λ' ($E_{0,\lambda'}$) may be greater than zero due to non negligible scattering by the miniemulsion ($E_{0,\lambda'} = S_{\mathrm{ME},\lambda'}$). In this case, the values of the absorption coefficient $K_{\lambda'}$ *versus* irradiation time were calculated by substracting $E_{0,\lambda'}$ from the values of the extinction coefficient $E_{\lambda'}$ obtained by transmittance measurements (Equation 5). Therefore, in the case of scattering miniemulsions, the photon flux absorbed by the actinometer $P_{\mathrm{Ac,ME},\lambda}$ at the irradiation wavelength was calculated as:

$$P_{Ac,ME,\lambda} = \frac{dK_{\lambda'}}{dt} \cdot \frac{V}{\Phi_{Ac,\lambda} \cdot \varepsilon_{\lambda'}} = \frac{d(E_{\lambda'} - E_{0,\lambda'})}{dt} \cdot \frac{V}{\Phi_{Ac,\lambda} \cdot \varepsilon_{\lambda'}} \tag{10}$$

It should be noted that in homogeneous solution where no scattering occurs, the absorbed photon flux calculated by actinometry, *i.e.* from the number of 7,7a-DHBF molecules formed (Equation 9), is equal to the absorbed photon flux as defined by Equation 3, *i.e.* $P_{\mathrm{Ac},\lambda} = P_{\mathrm{a},\lambda}$, since $P_{\mathrm{a},\lambda}$ is directly related to the value of the absorbance at λ. This is not the case in scattering systems. In fact, in miniemulsions, scattering at λ (UV spectral region) is much larger than at λ' (visible spectral region). Even if K_λ could be precisely calculated from the measured value of E_λ after subtraction of the scattering by the miniemulsion ($S_{\mathrm{ME},\lambda}$), the value of $P_{\mathrm{a,ME},\lambda}$, calculated using Equation 3, would not account reliably for multiple scattering by the miniemulsion droplets and potential reabsorption by DFIS, especially in relatively concentrated miniemulsions. Therefore, $P_{\mathrm{Ac,ME},\lambda}$ calculated from the number of 7,7a-DHBF molecules formed should be a much better approximation of the effective photon flux absorbed by DFIS at λ.

2.5.2 Experimental procedure for actinometric measurements. The experimental apparatus used to perform actinometry consisted of a Xenon-Hg lamp HBO1000 (Müller Elektronik Optik, Germany) equipped with a water filter to cut off the IR radiation and a monochromator (JobinYvon SPEX ISA Instruments, 6 nm band width) to select the irradiation wavelength. 367 nm was chosen for the actinometric experiments, since DFIS has a relatively high molar absorption coefficient at this wavelength and self-initiated polymerization by the acrylate monomers, known to occur below 300 nm,[19] could be avoided. A gray filter having 25 % transmittance was used to reduce the radiant power of the lamp. A thermopile (Laser Instrumentation, model 154) placed after the spectroscopic cell was used for monitoring the incident radiant power. A value of approximately 0.90 mW was measured at 367 nm. All the measurements were performed in the dark and at controlled temperature. In a typical actinometric experiment, a known volume of the sample (DFIS dissolved in a homogeneous system or in the miniemulsion droplets) was placed in a quartz cell of 1 cm optical path length and irradiated at 367 nm under stirring for a given period of time. UV/Visible absorption or extinction spectra were collected after different irradiation periods and the absorbance ($A_{\lambda'}$), or the extinction ($D_{\lambda'}$) in the case of scattering media, of the coloured solution was followed at the wavelength of the maximum λ' of the 7,7a-DHBF absorption band in the visible.

For actinometric measurements in heterogeneous systems, miniemulsions were prepared with MM or EtAc as organic phase, at different SDS and organic phase contents (§ 2.2). Although high organic phase contents are desirable for photopolymerization processes, in this first approach to the issue, a diluted miniemulsion represents a simpler case study where the lower concentration of droplets leads to a more transparent medium and allows the use of spectrophotometry to follow the photoreaction. Therefore, each miniemulsion was diluted with water by factors of 5, 7 and 10, thus the resulting organic phase contents were 6.0%, 4.3% and 3.0%, respectively. Upon dilution, the amounts of surfactant and costabilizer with respect to the organic phase were kept constant. Since miniemulsions were diluted after sonication, it can be assumed that the size of the droplets remained unchanged and the only effect of the dilution was to lower the concentration of droplets in the miniemulsion.[24]

For each type of miniemulsion, the photon flux absorbed by the actinometer ($P_{\mathrm{Ac,ME},\lambda}$) was determined and compared to the value obtained in the analogous homogeneous system (MM or EtAc, $P_{\mathrm{Ac},\lambda}$) having the same DFIS concentration. After repeated measurements (at least three) on the same system, the experimental error on the absorbed photon flux was evaluated to be approx. 10% and 15% in the case of the EtAc and MM based miniemulsions, respectively.

3 Results and Discussion

3.1 Physical characteristics and optical properties of EtAc based miniemulsions

In a first approach, the efficiency of light absorption was studied for a model-type miniemulsion, where the organic phase consisted of ethyl acetate (EtAc). This latter inert solvent was chosen for actinometric measurements because: i) the photophysical properties and the photochemical reaction of the chosen chemical actinometer DFIS (Scheme 1, § 2.5.1) were investigated in detail in this solvent ;[45] ii) miniemulsions based on EtAc could be easily prepared and turned out to be stable over several hours; iii) those model miniemulsions have physical characteristics close to those of the miniemulsions based on the mixture of acrylate monomers (MM) under the same conditions of preparation. Although the optical properties of the two systems are different (§ 3.3), the strongly reduced light scattering of the model miniemulsions made them particularly well-suited for our study.

EtAc based miniemulsions were first characterized in the absence of DFIS. Four different miniemulsions were prepared, having 30 $\mathrm{wt}_{\varphi\mathrm{org}}$ % and 0.08, 0.15, 0.5 and 1.5 $\mathrm{wt/wt}_{\varphi\mathrm{org}}$ % SDS content leading to droplet average diameters of 150 nm, 100 nm, 73 nm and 47 nm, respectively. As expected, droplet sizes could be tuned by varying the ratio SDS/φ_{org}.[22] The as-prepared miniemulsions (30 $\mathrm{wt}_{\varphi\mathrm{org}}$ %) were highly scattering. For all samples the values of the extinction coefficient at the maximum of the band of the closed form of the actinometer (7,7a-DHBF, Scheme 1) in the visible region were higher than 2. Spectrophotometric analysis of the actinometric reaction under these conditions would require an optical path length several orders of magnitude shorter than 1 cm and therefore an extremely high concentration of DFIS. To overcome this drawback, miniemulsions were diluted as mentioned in § 2.5.2. The composition, droplet size and extinction coefficient at 367 nm of the EtAc based miniemulsions investigated in this work are reported in Table 1. Each sample has been named with the use of a letter indicating the increasing size: **A** for the smallest droplet size (47 nm),

B and **C** for droplet sizes of 73 nm and 100 nm, respectively, and **D** for the largest droplet size (150 nm), and a number (**6**, **4** or **3**) indicating the percent amount of organic phase (6.0, 4.3 or 3.0 $wt_{\varphi org}$ %). In absence of DFIS, there was no species absorbing at 367 nm and the value of the extinction coefficient (in the range between 0.10 and 3.06) represents the scattering coefficient.

Table 1 Characteristics of EtAc based miniemulsions: composition in weight percent (SDS and organic phase contents), droplet average diameter (*d*) and extinction coefficient at 367 nm (E_{367}, measured in spectroscopic cells of ℓ = 1 cm or 0.5 cm).

% SDS/φ_{org}	*d*, nm	Miniemulsion	% φ_{org} (EtAc)	E_{367}, cm^{-1}
1.5	47	A3	3.0	0.10
		A4	4.3	0.15
		A6	6.0	0.22
0.5	73	B3	3.0	0.35
		B4	4.3	0.48
		B6	6.0	0.70
0.15	100	C3	3.0	0.98
		C4	4.3	1.40
		C6	6.0	1.92
0.08	150	D3	3.0	1.50
		D4	4.3	2.18
		D6	6.0	3.06

Experimental errors ≈ 15% calculated from repeated measurements.

Light transmission over the entire UV and visible range was strongly dependent on the size of the droplets and also on the organic phase amount. In Fig. 1A, the effect of droplet size on the extinction spectra is highlighted for miniemulsions having 6.0 $wt_{\varphi org}$ %. By increasing the size of the droplet, miniemulsions became less and less transparent. Since aqueous solutions of SDS do not absorb in the range between 200 and 800 nm and EtAc absorbs only below 260 nm, the increasing extinction above 260 nm can only be attributed to the higher amount of photons scattered by bigger droplets with respect to the smaller ones.

In Fig. 1B, the effect of the amount of organic phase on the extinction spectra is shown for miniemulsions of 100 nm droplet size (**C3**, **C4**, and **C6**). According to Equation 5 and excluding the contribution due to absorption, the extinction coefficient was proportional to the number density of droplets N_d, thus upon dilution of the miniemulsion, a decrease of E_λ was observed in the spectra.

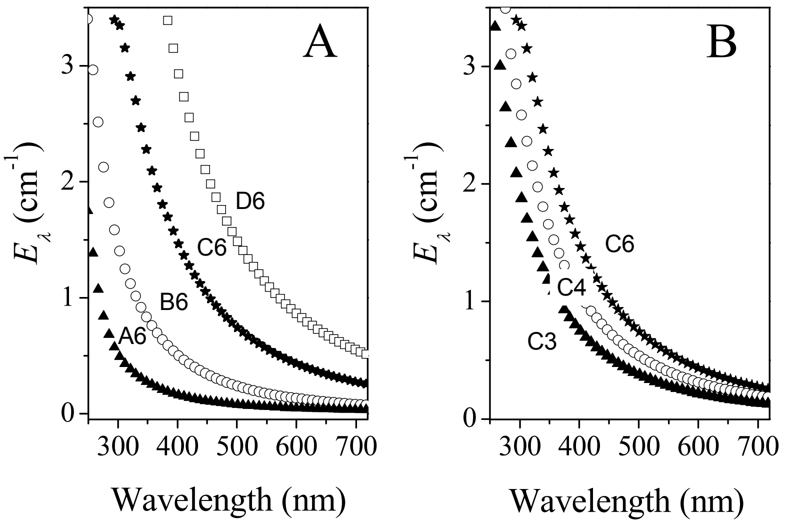


Fig. 1 Extinction spectra of EtAc based miniemulsions: (**A**) Comparison of miniemulsions containing 6.0 $\text{wt}_{\varphi\text{org}}$ % but different droplet diameters (□ 150 nm, ☆ 100 nm, ○ 73 nm and ▲ 47 nm); (**B**) Comparison of miniemulsions having 100 nm droplet diameter but different organic phase contents (☆ 6.0 $\text{wt}_{\varphi\text{org}}$ %, ○ 4.3 $\text{wt}_{\varphi\text{org}}$ %, and ▲ 3.0 $\text{wt}_{\varphi\text{org}}$ %) ($\ell = 1$ cm).

3.2 Determination of the photon flux absorbed by a chemical actinometer in EtAc based miniemulsions

3.2.1 Reference actinometric experiments in EtAc: homogeneous system. Reference experiments were performed using the chosen chemical actinometer (DFIS, § 2.5.1) in homogeneous solution of EtAc. The wavelength of maximum absorption of DFIS in EtAc is 340 nm (ε_{340} = 6270 L mol^{-1} cm^{-1}), while the closed form (7,7a-DHBF) has an absorption maximum in the visible at 492 nm (ε_{492} = 8850 L mol^{-1} cm^{-1}).[45] The quantum yield of DFIS photocyclization ($\Phi_{\text{Ac},\lambda}$) in EtAc is 0.18 in the interval 310 - 375 nm.[36]

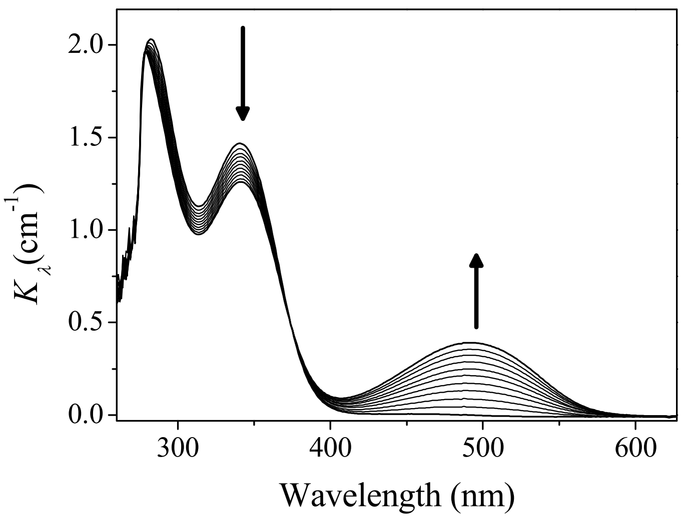


Fig. 2 Spectral evolution of a solution of DFIS in EtAc under irradiation at 367 nm ($\ell = 1$ cm); vertical arrows indicate the direction of the evolution (increase of the absorption of the closed form 7,7a-DHBF centred at 492 nm); $[\mathrm{DFIS}]_0 = 2.4\mathrm{x}10^{-4}$ mol L^{-1}.

Fig. 2 shows the spectral evolution of a DFIS solution in EtAc upon irradiation at 367 nm. The absorption band of 7,7a-DHBF in the visible (maximum at 492 nm) grew and the colour of the solution changed from yellow to red. Under conditions of total absorption of light by DFIS ($A_{367} > 2$ for $\ell = 1$ cm, *i.e.* $P_{\mathrm{Ac},367} > 99\%$, Equation 3), a straight line was obtained by plotting K_{492} as a function of the irradiation time, as shown in Fig. 3A, and its slope represents the rate of the photochemical reaction ($\mathrm{d}n_{\mathrm{Ac}}/\mathrm{dt} = (\mathrm{d}K_{492}/\mathrm{dt})(V/\varepsilon_{492})$, Equations 8 and 9, § 2.5.1). When A_{367} was significantly lower than 2, the lower concentration of DFIS led to a higher fraction of the actinometer being converted to 7,7a-DHBF (and to the Z-isomer) and a deviation from the linear trend was observed due to partial absorption of photons by the latter compounds (Fig. 3B). Under these conditions, the variation of K_{492} *versus* irradiation time was interpolated with a polynomial function (third degree) and the slope of the tangent to this function at time zero was considered as the initial rate of the photochemical reaction.

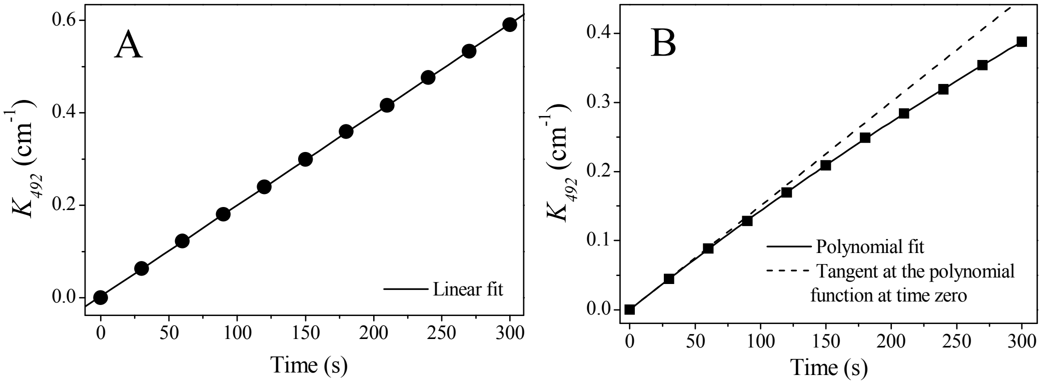


Fig. 3 Evolution of the absorption coefficient at 492 nm (K_{492}) of a solution of DFIS in EtAc as a function of irradiation time at 367 nm: (**A**) $[\text{DFIS}]_0 = 2.2\text{x}10^{-3}$ mol L^{-1} (conditions of total absorption of light: $K_{0,367} > 2$, $\ell = 1$ cm), data fitted with a linear function (solid line); **(B)** $[\text{DFIS}]_0 = 2.4\text{x}10^{-4}$ mol L^{-1} ($K_{0,367} = 0.77$, $\ell = 1$ cm), data interpolated using a polynomial function (solid line) and tangent at time zero to this function (dotted line).

3.2.2 Actinometric experiments in EtAc based miniemulsions. Fig. 4A shows the comparison of the extinction spectra of a miniemulsion in the absence and in the presence of DFIS dissolved in the EtAc droplets. As expected, the spectral region above 400 nm was not influenced by the presence of DFIS, since there was no absorption in the visible by the open-form of the photochromic compound. It can be observed that in the same spectral region the extinction due to the scattering remained unchanged after introduction of DFIS. Moreover and within experimental error, the average size of the droplets was not affected by the presence of DFIS in the miniemulsion. Within the range of concentrations used in this study, the addition of DFIS did not cause any change in the spectral and colloidal properties of miniemulsions. The absorption spectra of DFIS in homogeneous solution and in miniemulsions taken with the same DFIS concentration are shown in Fig. 4B. The spectrum of DFIS in the miniemulsion was obtained by subtracting the scattering contribution due to the medium. The spectra matched extremely well and neither spectral shift nor change in absorbance was observed, confirming that DFIS was localized within the EtAc droplets.

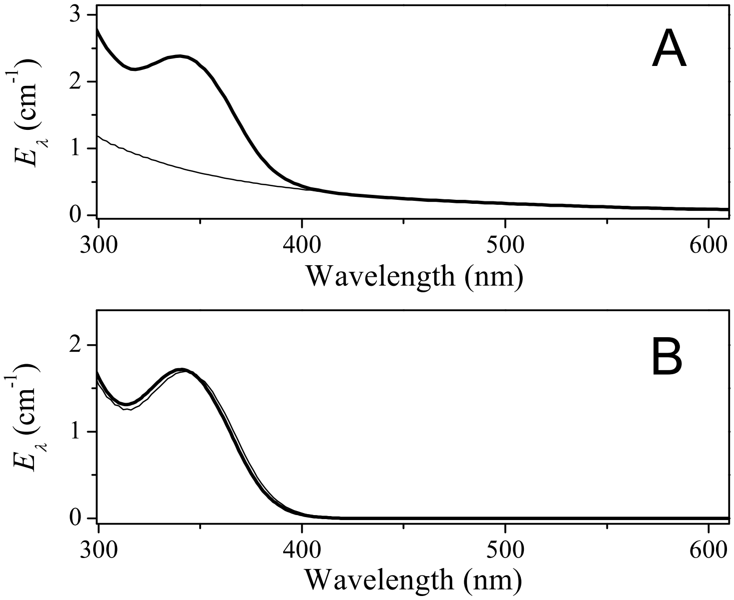


Fig. 4 (**A**) Extinction spectra of an EtAc miniemulsion containing DFIS (bold line) and DFIS-free (solid line); (**B**) Extinction spectra of DFIS in an EtAc miniemulsion after subtracting the spectrum of the EtAc miniemulsion (solid line), compared to the spectrum of DFIS in EtAc (bold line); [DFIS] = $2.6\text{x}10^{-4}$ mol L^{-1}; $\ell = 1$ cm; miniemulsion composition: **B6** (Table 1).

Fig. 5 displays the comparison of the extinction spectra of a solution of DFIS irradiated at 367 nm for 240 seconds in homogeneous solution and in a miniemulsion, after subtracting the spectrum of the DFIS-free miniemulsion from the latter. As observed for the non-irradiated systems (Fig. 4B), the spectra are also well matched in the case of the DFIS photoproduct (7,7a-DHBF). Irradiation of the actinometer in homogeneous solution and in the miniemulsion under the same conditions led to an equivalent photochemical conversion of DFIS and the quantum yield of the photochemical reaction in the miniemulsion can be assumed to be equal to that in homogeneous solution (0.18). Therefore, the literature value of the product $\Phi_{Ac,367}\cdot\varepsilon_{492}$ was used for the calculation of the absorbed photon flux in EtAc as well as in EtAc based miniemulsions (Equations 9 and 10).

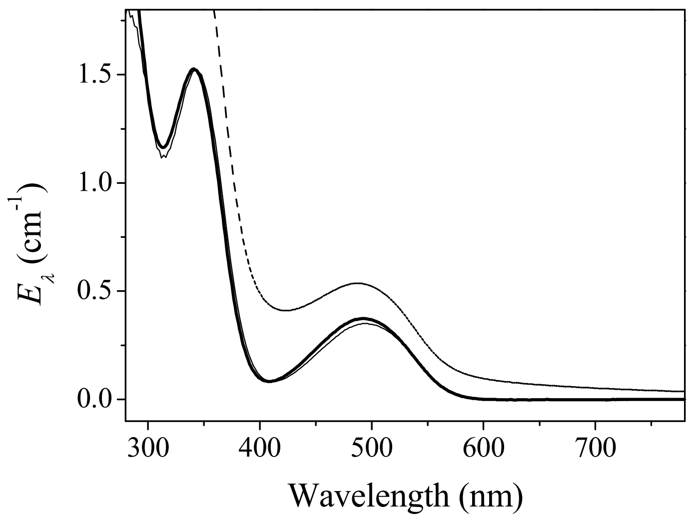


Fig. 5 Extinction spectra after irradiation of DFIS at 367 nm in EtAc (bold line), in an EtAc miniemulsion before (dashed line) and after (solid line) subtracting the EtAc miniemulsion spectrum (7,7a-DHBF absorption band centred at 492 nm); $[\text{DFIS}]_0 = 2.6\text{x}10^{-4}$ mol L^{-1}; $\ell = 1$ cm; miniemulsion composition: **B6** (Table 1); irradiation time: 240 seconds.

The data obtained from the actinometry in EtAc miniemulsions are listed in Table 2. As discussed in § 3.1, the as-prepared miniemulsions of different droplet sizes were diluted to obtain 6.0, 4.3 and 3.0 wt$_{\varphi\text{org}}$ %. Under these conditions, although the local concentration of the actinometer in the oil droplets remained constant, the nominal concentration of DFIS in the miniemulsions varied with the organic phase content. Therefore, for comparison purposes, actinometric measurements were carried out in parallel in homogeneous solutions of EtAc having the same DFIS concentration. The ratio of the photon flux absorbed in the miniemulsion to that absorbed in homogeneous solution ($R = \frac{P_{Ac,ME,367}}{P_{Ac,367}}$) was calculated in each case. Results show that, within experimental error (10%), no effect of the variable miniemulsion composition could be observed on the value of R (Table 2): for all the samples it was nearly 1.0 and the absorbed photon flux in the miniemulsion was comparable to that in homogeneous solution. This finding was unexpected if we consider that, as a result of increasing droplet size (from miniemulsions **A** to **D**) and organic phase content (from 3.0% to 6.0%), the scattering coefficient increased and miniemulsions became less and less transparent (Table 1). Surprisingly, these differences in the optical properties did not seem to affect the efficiency of light absorption by DFIS in the core of the organic (EtAc) droplets, with respect to homogeneous solution. Nevertheless, this result is in line with recent findings by Jasinski *et al.* concerning the optical properties of a series of diluted MM based miniemulsions with droplet size ranging from 40 nm to 300 nm in average diameter.[24] Using a combination of spectrophotometric methods, these authors demonstrated that a droplet size increase caused a significant and progressive increase of the scattering coefficient (S_λ), but without affecting the absorption coefficient (K_λ). The latter remained constant and comparable to that of a solution of MM at the same concentration in an organic solvent.

Table 2 Photon flux absorbed by DFIS at 367 nm ($P_{\mathrm{Ac},367}$) calculated from actinometric experiments performed in EtAc homogeneous solutions and in EtAc based miniemulsions ($P_{\mathrm{Ac,ME},367}$) (see Table 1 for the composition of miniemulsions and droplet average diameters).

[DFIS] (10^{-4} mol L^{-1})	K(DFIS)$_{367}$ in EtAc	$P_{\mathrm{Ac},367}$ in EtAc (10^{-9} einstein s^{-1})	Miniemulsion	$P_{\mathrm{Ac,ME},367}$ in EtAc miniemulsion (10^{-9} einstein s^{-1})	$R = \frac{P_{Ac,ME,367}}{P_{Ac,367}}$
1.28	0.39	2.3	A3	2.2	1.0
			B3	2.5	1.1
			C3	2.5	1.1
			D3	2.5	1.1
1.83	0.59	2.7	A4	2.7	1.0
			B4	3.1	1.1
			C4	2.5	0.9
			D4	2.5	0.9
2.56	0.84	3.2	A6	3.1	1.0
			B6	3.1	1.0
			C6	3.0	0.9
			D6	2.9	0.9

Experimental errors ≈ 10% calculated from repeated measurements (average values are listed).

Hence, it may be concluded that, similarly, the absorption properties of DFIS dissolved in miniemulsions based on EtAc were not significantly affected by scattering under the experimental conditions used, the absorbed photon flux being close to that of DFIS in pure EtAC. It should be noted that, for the 12 miniemulsions investigated, the ratio of the absorption coefficient of DFIS at 367 nm in EtAc at a given concentration to the miniemulsion extinction coefficient at the same wavelength (K(DFIS)$_{\mathrm{EtAc},367}$/E(ME)$_{367}$, Tables 2 and 1, respectively) varied in the range from 3.9 for the miniemulsions **A** (smallest droplet size) to a minimum of 0.26 for miniemulsions **D** (largest droplet size), respectively, under the experimental conditions used. Therefore, in spite of an important contribution of scattering in miniemulsions **D**, the DFIS absorption efficiency was not significantly affected.

3.3 Physical characteristics and optical properties of miniemulsions based on a mixture of monomers

EtAc based miniemulsions represent a simple model system to investigate the effect of the scattering on the efficiency of light absorption in the core of the miniemulsion droplets. In order to evaluate the absorbed photon flux in photopolymerizable systems, a step forward in the study was taken by replacing EtAc by the MM mixture. In Table 3, composition, droplet size and extinction coefficient at 367 nm of the MM based miniemulsions are reported. Miniemulsions contained 0.15 and 1.5 wt/wt$_{\varphi org}$ % SDS and they were diluted in order to obtain 3.0 and 6.0 wt$_{\varphi org}$ %. The average diameters of the MM droplets were 54 nm for the smallest one (**S**) at 1.5 wt/wt$_{\varphi org}$ % SDS and 140 nm for the largest one (**L**) at 0.15 wt/wt$_{\varphi org}$ % SDS.

Table 3 Characteristics of miniemulsions based on a mixture of monomers (MM): composition in weight percent (SDS and organic phase contents), droplet average diameter (*d*) and extinction coefficient at 367 nm (E_{367}, measured in spectroscopic cells of $\ell = 0.01$ cm).

% SDS/φ_{org}	*d*, nm	Miniemulsion	%φ_{org} (MM)	E_{367}, cm^{-1}
0.15	140	L3	3.0	57
		L6	6.0	115
1.5	54	S3	3.0	21
		S6	6.0	41

Experimental errors ≈ 15% calculated from repeated measurements.

Miniemulsions based on EtAc and MM having otherwise the same composition showed similar colloidal properties; only slightly higher droplet average diameters were observed for the latter from DLS measurements (Tables 1 and 3). Nevertheless, the optical properties of the two types of miniemulsions were definitely different, in particular light scattering in the

MM based miniemulsions was quite strong even at high dilution (*i.e.* at low organic phase content). An example is presented in Fig. 6 for miniemulsions containing 0.5 wt/wt$_{\varphi org}$ % SDS and 0.6 wt$_{\varphi org}$ %.

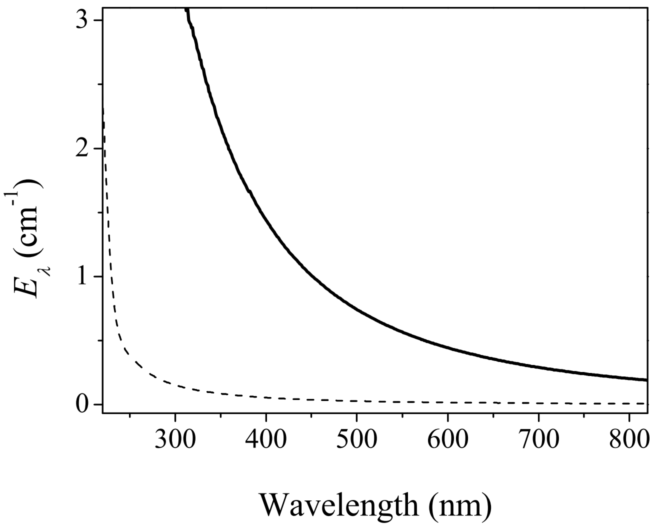


Fig. 6 Comparison of extinction spectra of miniemulsions based on MM (solid line) and on EtAc (dotted line) as organic phase (0.5 wt/wt$_{\varphi org}$ % SDS and 0.6 wt$_{\varphi org}$ %); $\ell = 1$ cm; $d = 85$ nm and 73 nm, respectively.

3.4 Determination of the photon flux absorbed by a chemical actinometer in miniemulsions based on a mixture of monomers

3.4.1 Reference actinometric experiments in the mixture of monomers: homogeneous system. The optical properties of DFIS in the homogeneous solution of MM were first investigated. Fig. 7 compares the absorption spectra of a DFIS solution in EtAc and in MM, before (A) and after (B) irradiation at 367 nm. A slight shift of the spectrum was observed and the maxima of the absorption bands for the open and closed forms of the actinometer in MM were found at 342 nm and 494 nm, respectively. In order to estimate the photon flux absorbed by DFIS dissolved in MM, knowledge of the product $(\Phi_{Ac,367}\cdot\varepsilon_{494})_{MM}$ value was required (Equation 9). This value was estimated from actinometric experiments carried out in EtAc and MM homogeneous solutions under the same experimental conditions. The actinometric experiment in EtAc allowed the determination of the incident photon flux

($P_{0,367}$) by using Equations 3 and 9. Then, actinometry was performed in MM, and the product $(\Phi_{Ac,367}\cdot\varepsilon_{494})_{MM}$ was calculated using the same equations rearranged to Equation 11.

$$(\Phi_{Ac,367}\cdot\varepsilon_{494})_{MM}=\frac{1}{\left(1-10^{-A_{367}}\right)}\cdot\frac{dA_{494}}{dt}\cdot\frac{V}{\ell}\cdot\frac{1}{P_{0,367}} \qquad (11)$$

The experiments were repeated four times, giving mean values of $P_{0,367} = (3.6 \pm 0.2)\text{x}10^{-9}$ einstein s^{-1} and $(\Phi_{Ac,367}\cdot\varepsilon_{494})_{MM} = (1520 \pm 11)$ L mol^{-1} cm^{-1} in MM compared to 1590 L mol^{-1} cm^{-1} in EtAc.[45] A separate determination of the quantum yield and of the molar absorption coefficient was not necessary within the scope of this study. The photon flux absorbed in homogeneous solution of MM was evaluated using Equation 12 (modified Equation 9):

$$P_{Ac,367}=\frac{dK_{494}}{dt}\cdot\frac{V}{(\Phi_{Ac,367}\cdot\varepsilon_{494})_{MM}} \qquad (12)$$

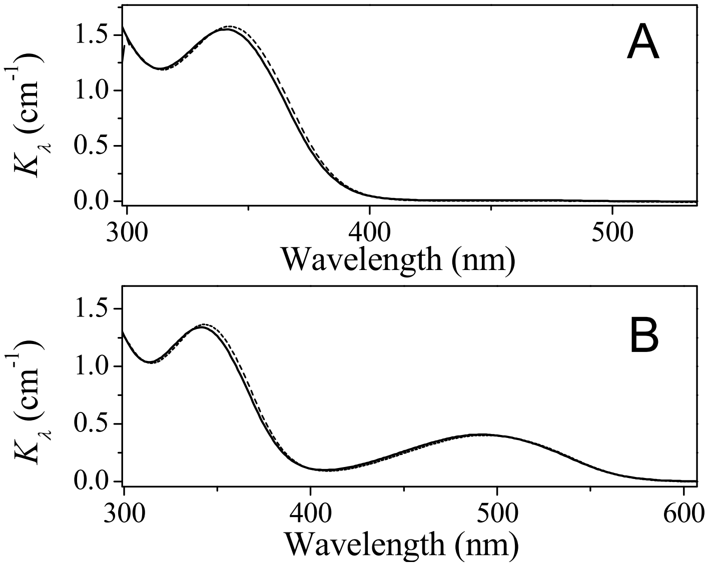


Fig. 7 (**A**) Absorption spectra of DIFS in EtAc (solid line) and in the mixture of monomers (MM) (dotted line); **(B)** Absorption spectra of the same solutions after irradiation at 367 nm for 300 seconds (7,7a-DHBF absorption band in the visible); $[DFIS]_0 = 2.5\text{x}10^{-4}$ mol L^{-1}; ℓ = 1 cm.

3.4.2 Actinometric experiments in miniemulsions based on a mixture of monomers.

Monomer miniemulsions are highly scattering media due to a broader droplet size distribution, in the UV as well as in the visible spectral ranges, and light penetration is strongly hampered even at low organic phase content. Thus, in order to estimate the photochemical conversion of DFIS to 7,7a-DHBF by spectrophotometry, a subsequent dilution was required. The irradiated miniemulsion was diluted by a factor of 3 by using an aqueous solution of SDS (200 g L^{-1}). This led to the formation of a transparent pseudo-microemulsion (PM) (Figure S1). The composition of the PMs obtained from the different miniemulsions are listed in Table S1.

As an example, the absorption spectra of DFIS (2.1×10^{-4} mol L^{-1}) in homogeneous solution of MM and in a PM obtained from the MM miniemulsion **L6**, before and after irradiation at 367 nm, are shown in Fig. 8. A bathochromic shift was observed for DFIS dissolved in PM and the new maxima of the absorption bands for the open (DFIS) and closed forms (7,7a-DHBF) were 348 nm and 512 nm, respectively. Moreover, a decrease of the absorption coefficient could be noticed. In the PM, the high amount of SDS added led to a reorganization of the interfacial region that represents a new microenvironment for the DFIS molecules. The changed solvation shell resulted in a change of the optical properties of DFIS. The value of the molar absorption coefficient at 512 nm in PM was required for the spectrophotometric determination of the number of reacted molecules and, thus, of the absorbed photon flux. Assuming that, upon irradiation, the quantum yield of the DFIS photochemical reaction in the MM organic droplets was the same as in the homogeneous solution of MM, the change in the molar absorption coefficient of DFIS at 512 nm in PM could be taken into account simply by calculating the product $(\Phi_{Ac,367}\cdot\varepsilon_{512})_{PM}$ using the following equation:

$$(\Phi_{Ac,367}\cdot\varepsilon_{512})_{PM} = \frac{K_{512,PM}}{K_{494,MM}} \times (\Phi_{Ac,367}\cdot\varepsilon_{494})_{MM} \qquad (13)$$

where $K_{512,\mathrm{PM}}$ and $K_{494,\mathrm{MM}}$ are the absorption coefficients at the maximum absorption of 7,7a-DHBF in PM and in homogeneous solution of MM, respectively.

Experimentally, a solution of DFIS (9.77×10^{-4} mol L^{-1}) in MM was prepared and irradiated at 367 nm in a 1 cm quartz cell for a long enough time period, so that a sufficiently high photochemical conversion of DFIS to 7,7a-DHBF was obtained. The PM was prepared by adding known amounts of costabilizer OA and of an aqueous solution of SDS to the irradiated MM miniemulsion, and the absorption spectrum was registered. It was compared to that of the irradiated MM solution after dilution with MM to obtain the same actinometer concentration as in PM. This method allowed the determination of the absorption coefficients in the two media at the same concentration of 7,7a-DHBF, since the two samples were obtained from the same irradiated solution. The value obtained for the product $(\Phi_{Ac,367}\cdot\varepsilon_{512})_{PM}$ was (1368 ± 25) L $mol^{-1}cm^{-1}$ and was used to calculate the absorbed photon flux in MM based miniemulsions by applying Equation 14 (modified Equation 10), where the moles of reacted DFIS were determined from the absorption spectrum of PM taking into account the dilution factor.

$$P_{Ac,ME,367} = \frac{dK_{512,PM}}{dt} \cdot \frac{V}{(\Phi_{Ac,367} \cdot \varepsilon_{512})_{PM}} \tag{14}$$

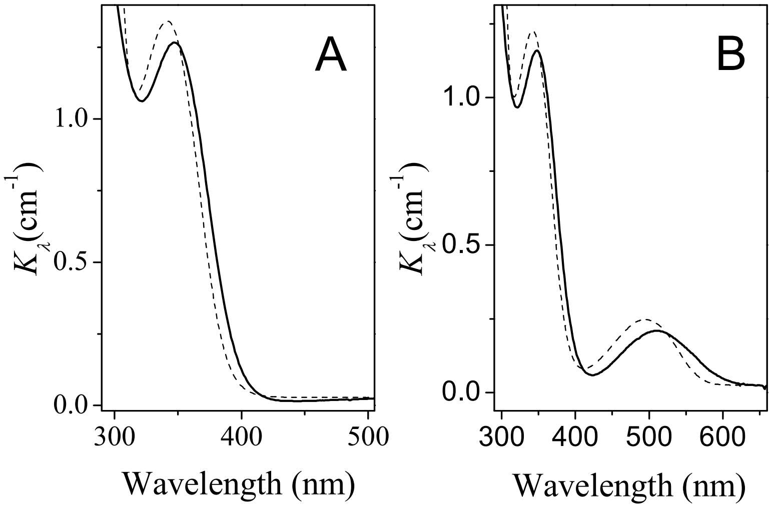


Fig. 8 (A) Absorption spectra of DFIS dissolved in MM (dotted line) and in the corresponding pseudo-microemulsion (PM, bold line); **(B)** Absorption spectra of the same solutions after irradiation of DFIS at 367 nm (note the difference in the 7,7a-DHBF absorption band in the visible spectral range); $[DFIS]_0 = 2.1\times10^{-4}$ mol L^{-1}; ℓ = 1 cm; PM composition (wt%): 11.81% SDS, 1.77% (φ_{org} + OA), 86.42% water.

The results from actinometry in miniemulsions based on a mixture of monomers are listed in Table 4. They show a decrease of the ratio $\frac{P_{Ac,ME,367}}{P_{Ac,367}}$ (0.7-0.9, Table 4) when compared to EtAc based miniemulsions (0.9-1.1, Table 2). However, the larger experimental errors in the case of MM based miniemulsions, due to the necessity of forming pseudo-microemulsions for the spectrophotometric analysis, have to be taken into account. Therefore, the decreasing trend observed may be considered significant only for the highest scattering systems, *i.e.* when the average diameter of the droplets is the largest (140 nm, **L3** and **L6**, Table 4), the effect being more pronounced for **L6** (6 $\mathrm{wt}_{\varphi\mathrm{org}}$ %) than for **L3** (3 $\mathrm{wt}_{\varphi\mathrm{org}}$ %). In any case, considering that the ratio $K(\mathrm{DFIS})_{\mathrm{MM},367}/E(\mathrm{ME})_{367}$ is only 0.02 to 0.05 in MM based miniemulsions due to considerable scattering (compared to 0.26 to 3.9 in EtAc based systems, § 3.2.2), the effect of the highly increased scattering on the photon flux absorbed by DFIS in the former systems is again surprisingly small. This result confirms that an increase of the scattering coefficient of the system has only a negligible to small effect on the absorption properties of the actinometer dissolved in model (EtAc based), as well as in photopolymerizable (MM based) miniemulsions. Within experimental error, the photon flux absorbed by the oil soluble actinometer in miniemulsions (either moderately or highly scattering) remains comparable to that of the actinometer dissolved in the homogeneous organic medium that constitutes the dispersed phase of the miniemulsion.

Table 4 Photon flux absorbed by DFIS at 367 nm ($P_{\mathrm{Ac},367}$) calculated from actinometric experiments performed in homogeneous solution of the monomer mixture (MM) and in MM based miniemulsions (see Table 3 for the composition of miniemulsions).

[DFIS] (10^{-4} mol L^{-1})	$K(\mathrm{DFIS})_{367}$ in MM	$P_{\mathrm{Ac},367}$ in MM (10^{-9} einstein·s^{-1})	Miniemulsion	$P_{\mathrm{Ac,ME},367}$ (MM based miniemulsion) (10^{-9} einstein·s^{-1})	$\frac{P_{Ac,ME,367}}{P_{Ac,367}}$
3.1	1.06	3.4	S3	3.1	0.9
			L3	2.7	0.8
6.1	1.93	3.5	S6	3.3	0.9
			L6	2.6	0.7

Experimental errors ≈ 15% calculated from repeated measurements (average values are listed).

4 Conclusion

In recent years, free radical photoinitiated polymerization in oil-in-water miniemulsions containing mixtures of monomers has been proposed as an advantageous method for the preparation of aqueous dispersions of polymer nanoparticles (latexes). In this context, the objective of our study was to evaluate to what extent the efficiency of light absorption inside the dispersed organic phase (oil droplets) was affected by the optical properties of the miniemulsions that are known to be strongly dependent on droplet size and on the chemical nature of the oil phase. To this aim, a well-characterized chemical actinometer (DFIS) insoluble in water, and thus dissolved in the oil droplets, was used as a probe and a model for light absorption in the UV spectral range. The absorbed photon flux could be determined by following the photochemical conversion of DFIS to its photoproduct 7,7a-DHBF by spectrophotometry in the visible spectral range, where scattering is much lower than in the UV.

In a first approach, actinometry was performed in model miniemulsions based on an inert solvent (EtAc), at low oil phase content (ranging from 3.0 to 6.0 wt %). For these low to moderately scattering systems, the value of the miniemulsion scattering coefficient at the irradiation wavelength (367 nm) did not exceed 4 times the value of the absorption coefficient of the actinometer in EtAc at the same concentration. In these cases, within experimental error, the photon flux absorbed by the actinometer in the miniemulsion was comparable to that in homogeneous solution of EtAc. Although surprising at first sight, this result is in line with a recent finding that, in the case of diluted miniemulsions, a droplet size increase caused a progressive increase of the scattering coefficient, but without affecting the absorption coefficient of the miniemulsion itself.

In the second part of this work, light absorption efficiency was investigated in photopolymerizable miniemulsions where the oil phase consisted of the actinometer dissolved in a mixture of acrylate monomers (MM). These systems showed much higher scattering coefficients, in the UV as well as in the visible spectral ranges, than EtAc miniemulsions of otherwise the same composition. In these cases, the value of the miniemulsion scattering coefficient at the irradiation wavelength (367 nm) was 20 to 50 times higher than that of the absorption coefficient of the actinometer in MM at the same concentration. Nevertheless, a rather small decreasing trend for the photon flux absorbed by the actinometer in the MM based miniemulsions compared to MM homogeneous solutions was observed (10% to 30%). The effect was more pronounced for the highest scattering systems, *i.e.* miniemulsions with the largest average diameter of droplets (140 nm).

Therefore, an increase of the scattering coefficient of the system, even considerable such as in photopolymerizable (MM based) miniemulsions, did not affect to a large extent the efficiency of light absorption by the actinometer. This result may be related to the fact that, although the increasing scattering contribution increases extinction and reduces the light penetration depth, photons can be scattered several times by the oil droplets and be subsequently absorbed by the actinometer, becoming efficient for the actinometer photoreaction. This effect may compensate, at least partially, the consequences of the considerably shorter optical path length. As the same would apply to any absorbing species such as a polymerization photoinitiator, this result may be considered favourable for the further development of applications of photopolymerization in miniemulsions. Nevertheless, polymerization processes require the use of concentrated miniemulsions (30 wt % of organic phase relative to the total weight). In these systems, the occurrence of multiple scattering due to a density of droplets much higher than in diluted miniemulsions, may give rise to a more significant loss of photons. The effective extent of this loss and its potential impact on the rate of photopolymerization in concentrated miniemulsions remain to be investigated. Although the present study was limited to diluted miniemulsions, this new approach, based on the use of an actinometric method, was useful for a better understanding of the correlation between the optical properties of photopolymerizable dispersed systems and the efficiency of the photoinitiation step in the presence of an oil-soluble photoinitiator.

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Captions for Scheme and Figures

Scheme 1 Structure and reversible photochromic reaction of (E)-1-(2,5-dimethyl-3-furyl)ethylidene(isopropylidene)-succinic anhydride (DFIS) to 5,6-dicarboxylic acid anhydride of 7,7a-dihydro-2,4,7,7a-pentamethylbenzo[b]furan (7,7a-DHBF).

Fig. 1 Extinction spectra of EtAc based miniemulsions: (**A**) Comparison of miniemulsions containing 6.0 $\mathrm{wt}_{\varphi\mathrm{org}}$ % but different droplet diameters (□ 150 nm, ✯ 100 nm, ○ 73 nm and ▲ 47 nm); (**B**) Comparison of miniemulsions having 100 nm droplet diameter but different organic phase contents (✯ 6.0 $\mathrm{wt}_{\varphi\mathrm{org}}$ %, ○ 4.3 $\mathrm{wt}_{\varphi\mathrm{org}}$ %, and ▲ 3.0 $\mathrm{wt}_{\varphi\mathrm{org}}$ %) (ℓ = 1 cm).

Fig. 2 Spectral evolution of a solution of DFIS in EtAc under irradiation at 367 nm (ℓ = 1 cm); vertical arrows indicate the direction of the evolution (increase of the absorption of the closed form 7,7a-DHBF centred at 492 nm); $[\mathrm{DFIS}]_0 = 2.4\mathrm{x}10^{-4}$ mol L^{-1}.

Fig. 3 Evolution of the absorption coefficient at 492 nm (K_{492}) of a solution of DFIS in EtAc as a function of irradiation time at 367 nm: (**A**) $[\mathrm{DFIS}]_0 = 2.2\mathrm{x}10^{-3}$ mol L^{-1} (conditions of total absorption of light: $K_{0,367} > 2$, ℓ = 1 cm), data fitted with a linear function (solid line); **(B)** $[\mathrm{DFIS}]_0 = 2.4\mathrm{x}10^{-4}$ mol L^{-1} ($K_{0,367} = 0.77$, ℓ = 1 cm), data interpolated using a polynomial function (solid line) and tangent at time zero to this function (dotted line).

Fig. 4 (**A**) Extinction spectra of an EtAc miniemulsion containing DFIS (bold line) and DFIS-free (solid line); (**B**) Extinction spectra of DFIS in an EtAc miniemulsion after subtracting the spectrum of the EtAc miniemulsion (solid line), compared to the spectrum of DFIS in EtAc (bold line); [DFIS] = $2.6\mathrm{x}10^{-4}$ mol L^{-1}; ℓ = 1 cm; miniemulsion composition: **B6** (Table 1).

Fig. 5 Extinction spectra after irradiation of DFIS at 367 nm in EtAc (bold line), in an EtAc miniemulsion before (dashed line) and after (solid line) subtracting the EtAc miniemulsion spectrum (7,7a-DHBF absorption band centred at 492 nm); $[\mathrm{DFIS}]_0 = 2.6\mathrm{x}10^{-4}$ mol L^{-1}; ℓ = 1 cm; miniemulsion composition: **B6** (Table 1); irradiation time: 240 seconds.

Fig. 6 Comparison of extinction spectra of miniemulsions based on MM (solid line) and on EtAc (dotted line) as organic phase (0.5 wt/wt$_{\varphi org}$ % SDS and 0.6 wt$_{\varphi org}$ %); ℓ = 1 cm; *d* = 85 nm and 73 nm, respectively.

Fig. 7 (**A**) Absorption spectra of DIFS in EtAc (solid line) and in the mixture of monomers (MM) (dotted line); **(B)** Absorption spectra of the same solutions after irradiation at 367 nm for 300 seconds (7,7a-DHBF absorption band in the visible); $[\mathrm{DFIS}]_0 = 2.5\mathrm{x}10^{-4}$ mol L^{-1}; ℓ = 1 cm.

Fig. 8 (A) Absorption spectra of DFIS dissolved in MM (dotted line) and in the corresponding pseudo-microemulsion (PM, solid line); **(B)** Absorption spectra of the same solutions after irradiation of DFIS at 367 nm (note the difference in the 7,7a-DHBF absorption band in the visible spectral range); $[\mathrm{DFIS}]_0 = 2.1\mathrm{x}10^{-4}$ mol L^{-1}; ℓ = 1 cm; PM composition (wt%): 11.81% SDS, 1.77% (φ_{org} + OA), 86.42% water.

The use of chemical actinometry for the evaluation of light absorption efficiency in scattering photopolymerizable miniemulsions§

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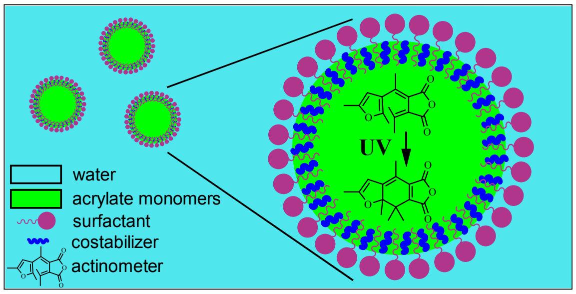

Efficiency of UV light absorption by a chemical actinometer in acrylate based miniemulsions shows only a small decreasing trend in spite of a large increase in the level of scattered light.