



PHOTOCHEMICALLY INITIATED MICROEMULSION SYNTHESIS OF ACTIVE NANOMETRIC HYDROGELS

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Abstract

Microemulsion polymerization of the reactive ester phenyl acrylate by photochemical initiation is first reported. Transparent oil in water microemulsions were produced by solubilisation of phenyl acrylate in water with dodecyltrimethyl ammonium bromide. Monomer microemulsions were photochemically polymerized using benzoin as photo initiator. Resulted crosslinked polymer nanogels presented an average diameter of 50nm which was influenced by different synthetic parameters (reaction time, crosslinker content and salt presence in dispersed media). The obtained phenyl acrylate active nanogels have resulted be an integral element for the linkage to spacer arm in the functional nanogels design. The nucleophilic substitution reaction with 2,2'-(ethylenedioxy)bis(ethylamine) was carried out and successfully corroborated by ^1H NMR.

1. Introduction

Microemulsions are thermodynamically stable and optically clear dispersions of organic and aqueous phase which are spontaneously formed with an appropriate

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formulation [1]. Microemulsions formulations include surfactant and cosurfactant mixtures which low the interfacial tension between the two immiscible medium and allow very small droplets (diameters of 10-100 nm) of the dispersed domain to form [2]. These systems may form different phase structures, most notably, oil-in-water (o/w); bicontinuous; and water-in-oil (o/w) [1-7] and allow the synthesis of ultrafine latex particles within the size range of 10-100 nm and with narrow size distribution (4-9). In contrast conventionally studied and commercialized emulsions are opaque, unstable (require mechanical agitation to prevent agglomeration) and present larger droplets diameters (0.2-10 mm) [8].

The polymerization in microemulsion is a relatively recent method that appeared only in the early eighties [9-11]. Specifically styrene and methyl methacrylate are typical monomers that have been most extensively studied in microemulsion and polymerized in oil-in-water [12, 13]. Since Atik and Thomas [14] reported the systematic study of styrene microemulsion polymerization, in the last years many authors have studied thermally-initiated microemulsion polymerizations.

Photo polymerization is the initiation by light, rather than heat, of a chain polymerization process [15]. Light-induced initiation is usually provided by the addition of a photo initiator that produces active centres upon absorption of a photon of the adequate wavelength. When compared with thermal polymerization, ultraviolet photo polymerization has many advantages, such as spatial and temporal control of initiation [16, 17], polymerization at room temperature, simple technology including very short exposure time and successful production, and less pollution [18]. Beside, as initiation is independent of temperature and phase behaviour of microemulsions can greatly depend on temperature, photoinitiation is presented like an interesting option for microemulsion polymerization.

As mentioned above, the great majority of reports on microemulsion polymerizations focus primarily on thermally-initiated polymerizations, however there are few studies about photochemically initiated microemulsion polymerizations. Capek et al. [19-21] reported several papers about photopolymerizations of butyl acrylate in o/w microemulsions and studied the effect of reaction conditions and additives on the rate of polymerization, conversion and particle size. Kuo et al. [22] characterized polystyrene synthesized by microemulsion photopolymerization and studied polymerization kinetic. David et al. have reported investigation of polymerization of methyl and butyl methacrylates in

o/w microemulsions initiated by UV-irradiation including a macromonomer as cosurfactant and comonomer [23]. More recently, Jain et al. [24] have investigated o/w microemulsion photopolymerizations of butyl acrylate using a two component initiator system.

Microgels and nanogels are colloidal particles intermediates between branched and macroscopically cross-linked polymers which typically have an average diameter between 50 nm - 5 μ m and 10-50 nm, respectively [25]. They form colloidal dispersions instead of solutions because of their porous structure [26] and can swell in good solvents. These nanometric hydrogels have a wide range of applications in different areas as coating [27], cosmetic industrial [28], lubricants [29], food [30], oil recovery [31], industrial processing [32], and biopharmaceutics [33]. Microgels may be prepared by free radical polymerization either in dilute solution or more commonly by emulsion. More recently microemulsion technique has allowed to obtain nanogel particles and many authors have employed thermally induced microemulsion system to synthesized nano scaled gels. [34, 35]

Chemical modification of preformed active polymers is conventionally employed for obtaining functional polymers. A chemical reaction on polymers makes possible new classes of systems or to modify the properties over a wide range. Reduced accessibility of functional groups in crosslinked polymer chains is generally solved by introducing a spacer arm between polymer backbone and the functional groups. The position of functional group at the end of the linker involves a multistep synthesis for which active esters provide a valuable method in polymer functional polymers design [36].

Phenyl acrylates are active esters that act as reactive monomers due to the presence of aromatic ring that allowed the introduction of functional groups by nucleophilic substitution. This methodology of active ester modification is generally applicable and covers a wide range of nucleophilic, including primary, secondary and aromatic amines [36] and assures a versatile functionalization. Functionalization of polymers is feasible in phenyl acrylate by post-polymerization techniques and by pre-polymerization strategy because phenyl acrylate is a monomer which easily reacts by radical polymerization. Despite of the great versatility and reactivity of phenyl acrylate derivatives, phenyl acrylate precursor polymers there are not extensively exploited and the great majority of investigations were presented in the

past decade. Arsahdy et al. [36] reported several studies about polymer synthesis via reactivated esters and enhanced the creativity options of these systems in macromolecular chemistry. Baskaran et al. [37] in 1991 reported the nucleophilic substitution of poly(phenyl acrylate) and different substituted poly(phenyl acrylate)s with ethanolamine and expressed the versatility of the modification reaction. Reddy [38] presented an extensive characterization of several phenyl acrylate monomers as well as their corresponding polymers and copolymers; later Thamizharasi et al. [39, 40] reported the extensive characterization of poly(nitrophenyl acrylate) and both of authors remarked the potential of activated ester macromolecules as functional polymers. Nitrophenyl acrylate has been employed by different authors as reactive monomer in the synthesis of polymer precursors for post polymerizations modifications in order to get final products with different properties, specifically in colloidal polymers [41-43]. Taking into account all above mentioned, this paper is presented the first reported of photo polymerization of reactive crosslinked particles with nanometric dimensions by microemulsion. Phenyl acrylate was polymerized in a simple way by o/w microemulsion using dodecyltrimethyl ammonium bromide as surfactant, benzoine as UV-initiator and was crosslinked with diethylene glycol tetramethacrylate. Obtained activated nanogels were characterized and modification with different aminoderivatives was performed to prove the precursor capability of the system.

2. Experimental Section

2.1. Materials

Phenyl acrylate (PhA) was synthesized from the precursor phenol (Panreac, crystallized crystals for analysis, 99.5%) as reported previously by Reddy [38] in 2-butanone (Aldrich, 99%) by addition of acryloyl chloride (Sigma-Aldrich, 96%). The crosslinking agent diethylene glycol tetramethacrylate (DEGTMA, Aldrich, > 98%) and photo initiator benzoine (Merck-Schuchardt, for synthesis > 99%) were used without further purification. Dodecyltrimethyl ammonium bromide, DTAB, (Merck, for synthesis) was employed as surfactant in microemulsion formulation. 2,2'-(ethylenedioxy)bis(ethylamine) (Aldrich), di-tert-butyl-dicarbonate (BOC-anhydride, reagent grade, Aldrich, 97%), solid sodium hydroxide (Panreac), sodium chloride (Panreac) were used as received. The following solvents were used without

further purification: triethylamine (synthesis grade, Merck, > 99%), chloroform (for analysis, > 99%), diethyl ether (for analysis, > 99.7%), N, N'-dimethyl formamide (UV, IR, HPLC grade, Panreac \geq 99.9%), methylene chloride (for analysis, Panreac), ethyl acetate (UV-IR-HPLC grade, Panreac, 99.8%) and Methanol (Panreac, synthesis grade). Water was deionised using a Milli Q water purification system (Millipore).

2.2. Construction of pseudo ternary phase diagram

In order to find the concentration range of the three components (DTAB/water/PhA) in which they form microemulsions, a pseudo ternary phase diagram was constructed. A weighed sample of phenyl acrylate was placed in a 25 ml vial and thermostated at 25°C. Surfactant solution mixtures were separately mixed at different weight ratios of, 0.5:9.5; 1:9; 1.5:8.5; 2:8; 2.5:7.7; 3:7; 3.5:6.5; and 4:6. Then the aqueous solution of surfactant was slowly added, drop by drop, under moderate stirring. The samples were classified as microemulsions when they appeared as optically transparent liquids. The final composition of the microemulsion was determined by weighing. The systems were stable for a period of at least several days.

2.3. Microgel synthesis

The polymerizations were carried out in a 50 mL glass reactor at room temperature with continuous stirring and nitrogen bubbling. The microemulsions were prepared by the pouring of the surfactant aqueous solution (15% w/w) into the glass reactor, followed by addition of the monomer in which previously benzoine (1 wt %) and crosslinking agent DMATEG (2.5 wt.%) were dissolved. Subsequently the microemulsion was exposed under high pressure mercury 100 W UV light for a certain interval of time. Figure 1 shows the wavelength distribution of radiation for a medium pressure mercury arc lamp. After the polymerization, the mixture was precipitated over methanol in which surfactant and residual monomer, benzoine and crosslinker are solubles. Purification was effected by successive washings in methanol. The microgels were dried in an oven at 50°C and fine powder samples were obtained.

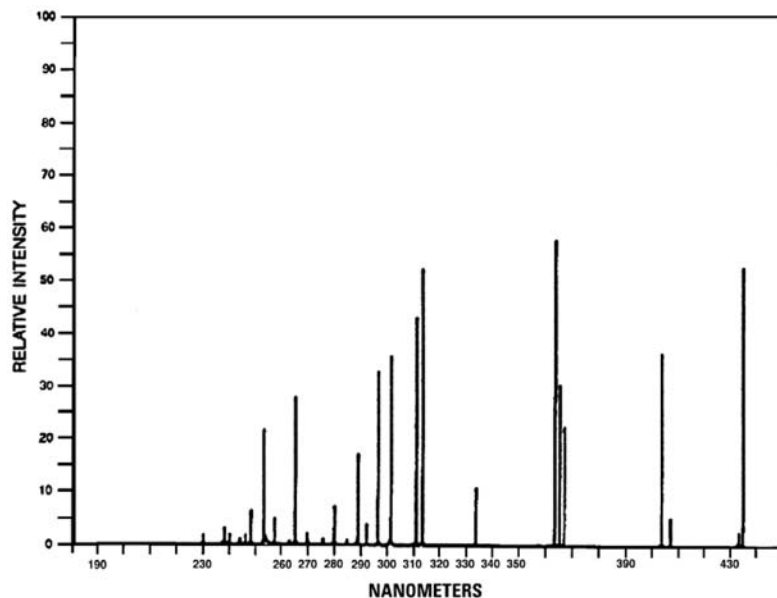


Figure 1. Typical emission spectrum of a medium pressure mercury arc lamp.

2.4. Modification reaction

Obtained reactive microgels were chemically modified in an easy way by aminolysis reaction with monoprotected 2,2'-(ethylenedioxy)bis(ethylamine), N-t-butoxycarbonyl 2,2'-(ethylenedioxy)bis(ethylamine), (eoxiA-BOC). Diamine was previously to use monoprotected to avoid undesired hydrolysis and secondary crosslinking reactions. EoxiA-BOC was synthesized following the procedure previously described [44].

Phenyl acrylate nanogels were dispersed in DMF (1 g/15 mL) and EoxiA-BOC was added (1.5/1.0). After 24 hours, DMF was vacuum-distilled and finally the microgels were purified by washing in diethyl ether. In order to remove the protecting group from terminal amino groups modified microgels were dispersed in ethyl acetate for 2 hours at pH = 1. Finally the ethyl acetate was eliminated and the final microgels were washed with diethyl ether and dried until constant weight.

2.5. UV-visible spectroscopy

UV spectra of microemulsion components were obtained in order to verify minimal absorption of them into initiator excitation operating wavelength range. UV measurements were performed using a CINTRA 303 spectrophotometer.

2.6. Nuclear magnetic resonance spectroscopy

NMR samples were prepared by dispersing dried active nanogels in D₂O and modified particles in DMSO-d₆. The spectra were recorded in a Bruker Advance (500 MHz) instrument at 20°C. Chemical Shifts (δ) are reported in ppm relative to water (δ = 4.80) or dimethylsulfoxide-d₆ (δ = 2.49).

2.7. FTIR spectroscopy

Fourier transform infrared (FTIR) spectrophotometer (Nicolet 6700) was employed to obtain spectra of synthesized species. The nanohydrogels spectrums were collected using Attenuated Total Reflectance (ATR) Smart Orbit accessory. All the spectra were de average of 100 scans whit a resolution of 4 cm⁻¹.

2.8. Scanning electron microscopy

Micrographs were obtained using a JEOL JSM 6400 electron microscope (150 s, 20 mA, 2 kV). Dispersions of gels were settled onto a metallic support, air-dried overnight and sputter-coated with a thin overlay of gold prior to inspection.

2.9. Quasielastic light scattering measurements (QELS)

Dynamic laser light scattering was employed in order to determinate the size of the microgels. The measurements were performed in a Brookhaven BI-9000AT with a goniometer and water-cooled argon –ion laser operating at 514.5 nm as the light source. The time dependence of the intensity autocorrelation function of the scattered intensity was obtained by using a 522-channel digital correlator. The size distributions were obtained by CONTIN analysis. The dried powder samples of reactive gels were dispersed in acetone and in water for modified ones (1 mg/mL in all the cases) during 24 hours. The measurements were carried out at room temperature.

3. Results and Discussion

3.1. Investigation of microemulsion formulation

For a successful photo initiation the absorption bands of the photo initiator must overlap with the emission spectrum of the source and there must be minimal competing absorption by the components of the formulation at the wavelengths corresponding to photo initiator excitation. For the initial selection of photo

polymerization system, it was confirmed that photo initiator excitation wavelengths lies in the emission spectrum of UV source, as well as in the absorption window of microemulsion formulation, as it is showed by comparing of Figures 1 and 2.

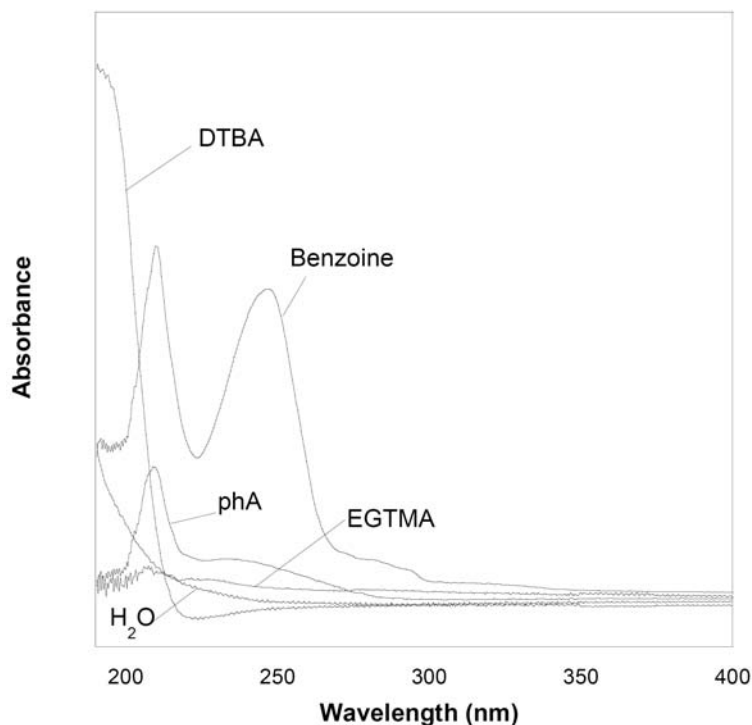


Figure 2. Absorption spectra of microemulsion components.

Once the photo chemically valid components of microemulsion were chosen, a series of studies were performed to determine surfactant/monomer/water formulations that were effective for producing microemulsions. Conductimetric titration and visual assessment were employed to obtain the pseudo ternary phase diagram of microemulsion system. Conductimetric titration method clarifies the nature of system (w/o, o/w or bicontinuous) and the micellar structure on the microemulsion. When the conductivity on the microemulsion is due to the continuous phase the formed micelles are spherical, and have laminar structure, if the conductivity measure corresponds with the dispersed phase. The phase diagram was determined according to the method described in the Experimental Section. Figure 3 shows the obtained pseudo ternary phase diagram where the curve describes the transition between a turbid emulsion and optical transparent

microemulsion. Figure 4 presents the relationship between water concentrations and conductivity values of microemulsions. The conductivity of the microemulsion was close to that of water continuous phase, and this showed that the microemulsion had a globular structure, which was formed by micelles swollen with the PhA phase.

3.2. Photo polymerization of reactive nanogels

The polymerization procedure was conducted using oil in water microemulsion system. The monomer microemulsion mixture was prepared as above described and after being purged, the polymerization was initiated by UV excitation at room temperature. A monomer soluble salt, dibutyl phosphate, was added to the system in order to decrease the micellar diameter. Different nanohydrogel samples were obtained varying the amounts of crosslinking agent, dibutyl phosphate, and reaction time and similar high conversions were obtained in all the cases as it is shown in Table 1. The polymer crosslinked nanogels were purified by selective precipitation in methanol.

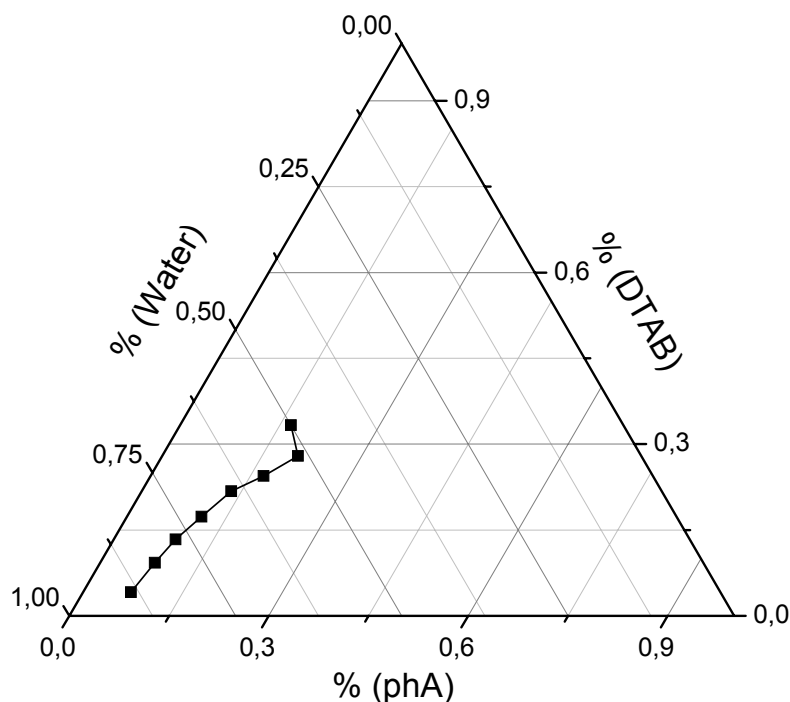


Figure 3. Pseudo ternary phase diagrams for the system at room temperature. The line is the boundary between the emulsion (right) and microemulsion (left) domains.

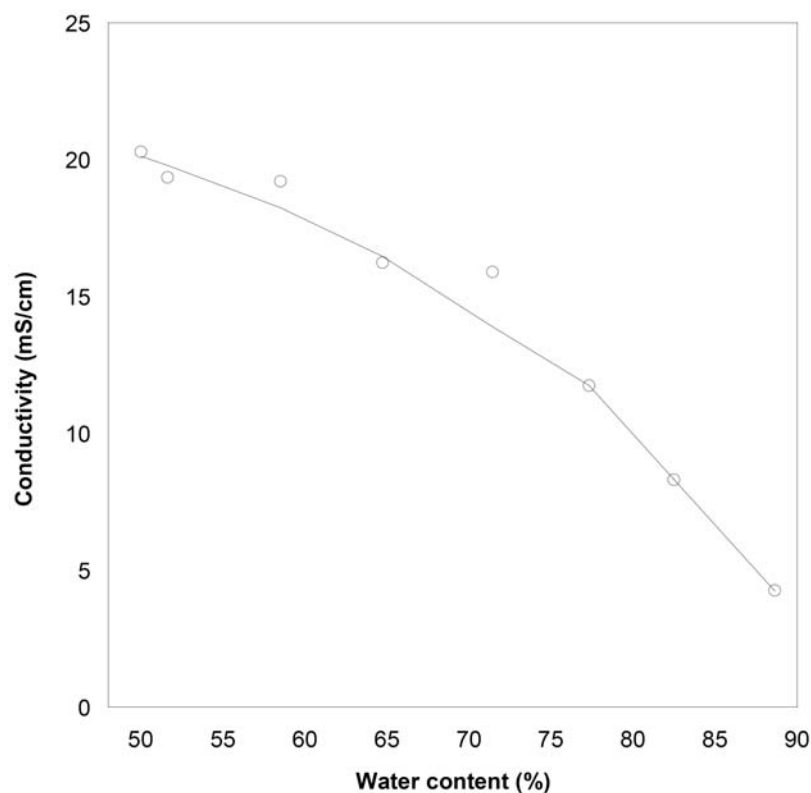


Figure 4. Conductivity of microemulsions as function of the water content.

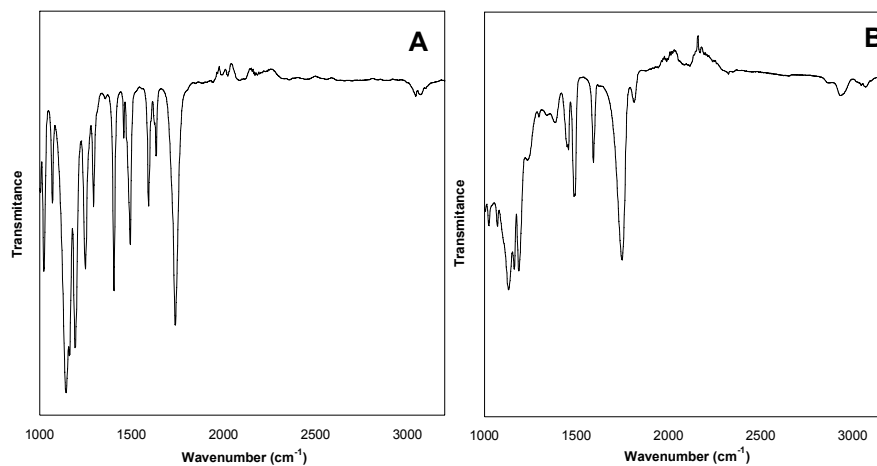
3.3. Characterization of obtained polyPhA nanogels

Obtained polyPhA nanohydrogels particles were characterized by FTIR. Figure 5 shows the FTIR spectra of synthesized monomer PhA and the resulting polyPhA nanogels.

The FTIR spectrum of the PhA monomer (A) shows almost all the characteristic bands of this compound: ester stretching absorptions ($C=O$ 1739 cm^{-1} , $C-O-C$ $1140\text{--}1290\text{ cm}^{-1}$), $C=C$ stretching 1630 cm^{-1} , $C=C$ aromatic stretching 1593 cm^{-1} , $-CH=CH_2$ stretching 1290 cm^{-1} , $C-H$ stretching $3100\text{--}3000\text{ cm}^{-1}$. The IR spectra of the nanohydrogels (B) shows the disappearance of $C=C$ stretching and $-CH=CH_2$ vinyl stretching bands at 1630 cm^{-1} and 1290 cm^{-1} , respectively, that confirm the polymerization.

Table 1. Reaction mixture composition and parameters of synthesized crosslinked polyPhA nanoparticles

DMATEG (mol. % respect to phA)	DP (wt. %)	Time (min)	Conversion (%)
2.5	0	30	95
2.5	0	90	92
2.5	0	180	90
1.0	0	30	93
2.5	0	30	96
5.0	0	30	95
2.5	1	30	86
2.5	3	30	90
2.5	5	30	88

**Figure 5.** FTIR spectra of synthesized (A) PhA and (B) polyPhA nanogels.

The comparison of ^1H -NMR spectra of the synthesized monomer and polyPhA nanoparticles is presented in Figures 5(A) and 5(B). The appearance of broad

aromatic protons signals at 7.0 and 7.3 ppm and the disappearance of vinylic protons (5.8-6.8 ppm) indicate the successful advance of photo polymerization reaction.

Obtained polyPhA crosslinked particles were analyzed by SEM microscopy and visual assessment of spherical shape, diameter and size distribution of the nanogels could be made and it is showed in Figure 7.

The size of the nanoparticles was determined by QELS. The particle size distribution and the average particle diameter were obtained from the correlation function by CONTIN analysis using standard software. Nanogels were dispersed in acetone and their hydrodynamic diameters (D_p) were measured as above described. The particle size of gel nanoparticles may be influenced by certain synthesis parameters. Despite microemulsion is a polymerization synthesis technique that restricts the final size of polymers, certain parameters could be vary to control the particle size. The crosslinker concentration in the initial reaction mixture, the presence of salts and the reaction time could be some of these tools to modify slightly the final particle dimension and they have been studied in this investigation.

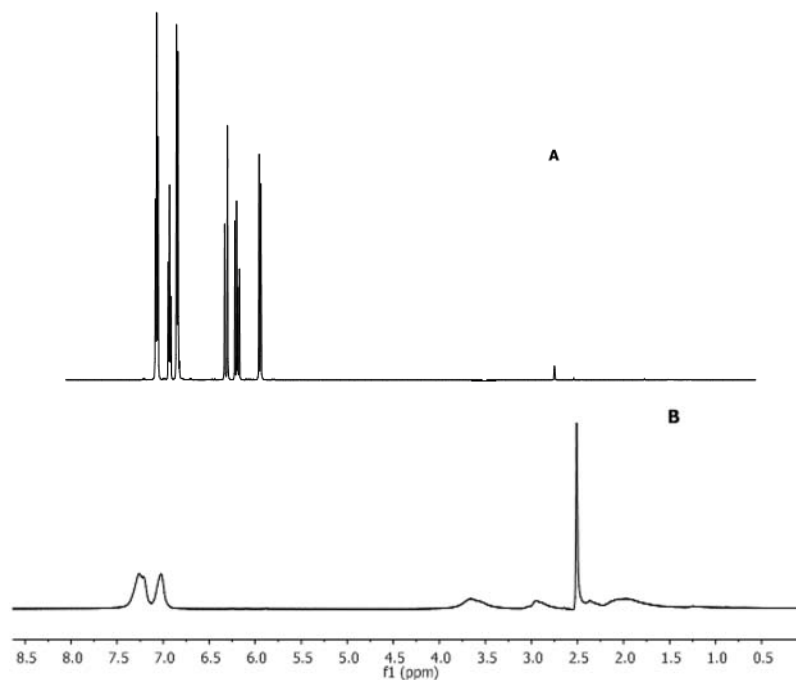


Figure 6. ^1H NMR spectrum of (A) PhA and (B) synthesized polyPhA crosslinked nanoparticles.

Figure 8 shows the influence of photo polymerization time in particle size of obtained nanogels. At short reaction time (minor to 60 min) similar dimension were obtained. However when reaction time is higher than 67 min, particle size drastically increases. This exponential behaviour could be due to the agglomeration effect and interconnection of polymer growing micelles.

Respect to the influence of crosslinking agent, it is usually observed a decrease of gel network swelling as crosslinker agent content increases [45, 46]. The higher crosslinking results in a more rigid and denser network structure which subsequently limits the swelling. Table 2 presents the hydrodynamic diameters of nanogels synthesized with different crosslinker and salt content. When DEGTMA mol. % is low, the Dp decreases slightly as its concentration increases, as it is usually observed. However, this trend does not rule for higher DEGTMA concentration values. Similar behaviour has been observed by several authors and it has been attributed to the competition of steric increase and the decrease of swelling capacity of the network and the agglomeration of polymer by bridging in the continuous phase at high crosslinker content [47-49].

In order to limit the micelle dimensions, a PhA soluble salt, DP, was incorporated into the microemulsion formulation. As Table 2 shows the presence of salt in the dispersed medium could slightly provide a particle size decrease of nanogels synthesized by microemulsion polymerization [50].

Table 2. Influence of crosslinking agent concentration and salt presence in final hydrodynamic diameter of synthesized reactive nanogels

DMATEG (mol. % respect to PhA)	DP (wt. %)	DP (nm)
1.0	0	62
2.5	0	50
5.0	0	49
2.5	1	50
2.5	3	44
2.5	5	42

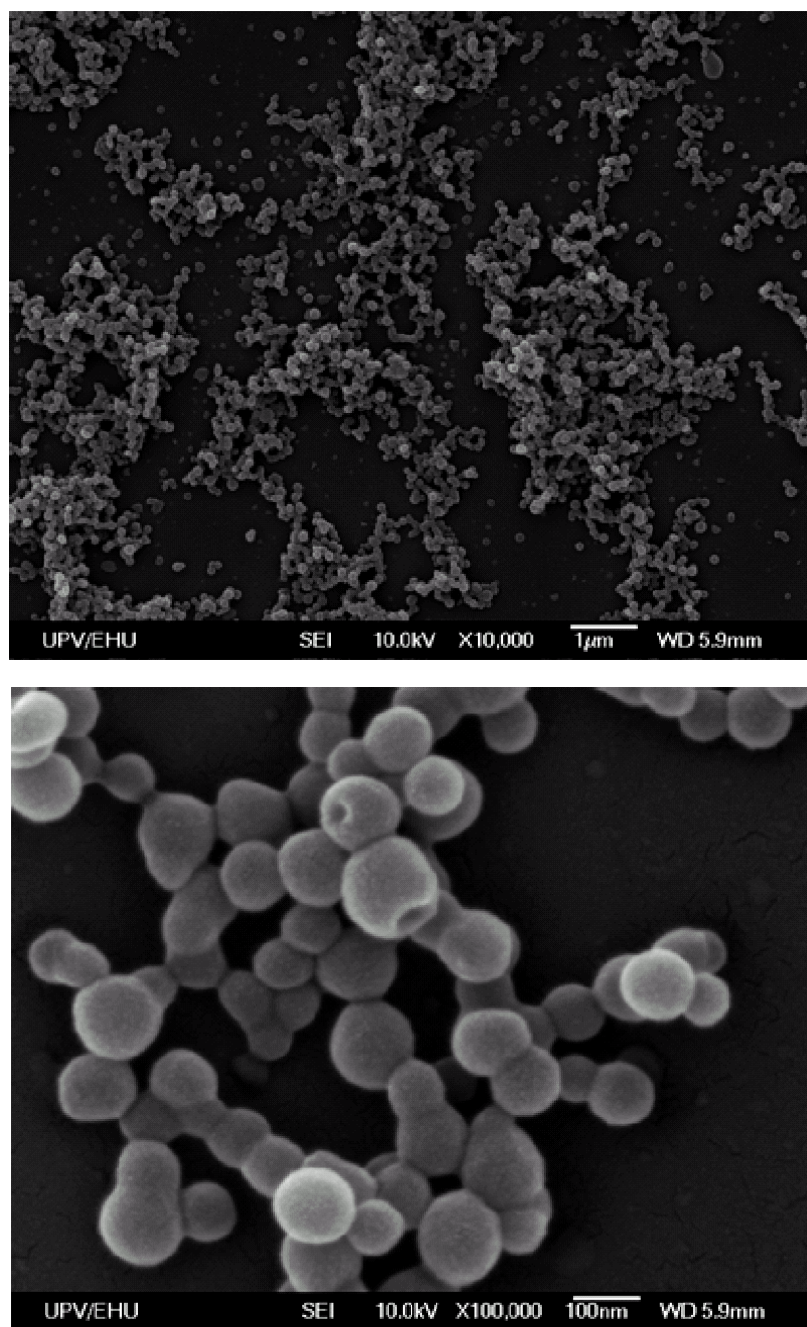


Figure 7. SEM microphotographs of obtained poly(phenyl acrylate) nanogels.

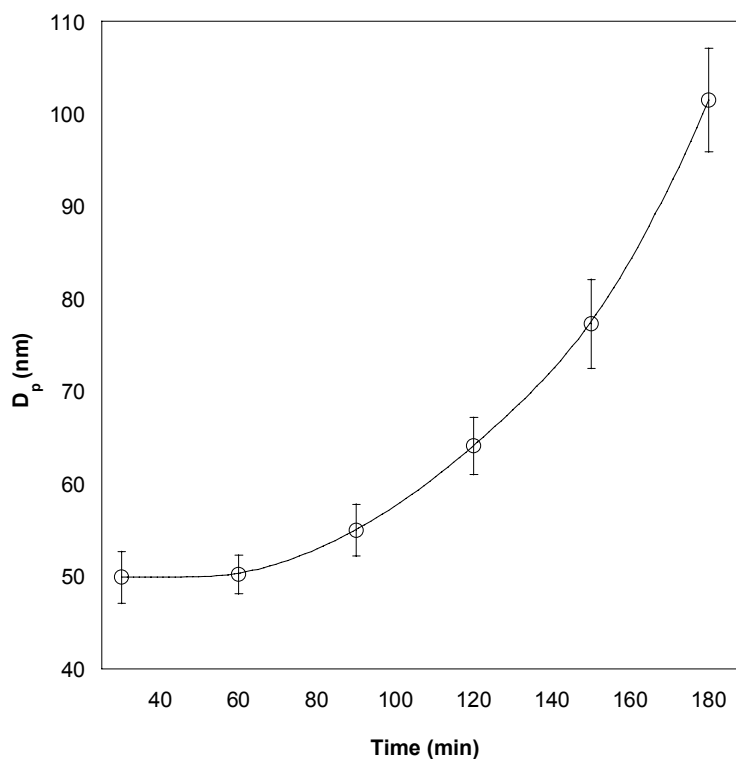


Figure 8. Hydrodynamic diameter of polyPhA nanogels in acetone at 25°C as function of photo-polymerization time.

3.4. Functionalization of active nanogels

Synthesized active polymer particles present phenyl acrylate units along the crosslinked backbone. This group assures the easy chemical modification by the nucleophilic attack of, for example, free amines. The aminolysis reaction with ethanolamine of various poly(phenyl acrylates) general polymers was successfully carried out by Baskaran et al. [37] previously Arshady also reported the reaction of various amino alcohols and amines with crosslinked phenyl acrylates polymers and copolymers [51].

Once the reactive nanogels were synthesized, the post polymerization chemical modification reaction was carried out. In order to confirm the active character of obtained precursor nanogels they were functionalized with 2, 2'-(ethylenedioxy)bis (ethylamine). The aminolysis reaction proceeds easily under mild conditions due to the good leaving group present in the macromolecular backbone as has been

Diamines on the one hand, can basify the medium enhancing the hydrolysis of the ester bond instead of the reaction to origin amide bonds, and on the other, they can also act as crosslinking agent between polymer chains. Thus, diamine was previously monoprotected as it has been described in experimental section with the protecting group tert-butoxycarbonyl. The monoprotection step requires the subsequent deprotection reaction after the insertion of the diamine into the nanogels to unmark free amine functionality. Figure 9 show the synthetic strategy for the nanogels functionalization.

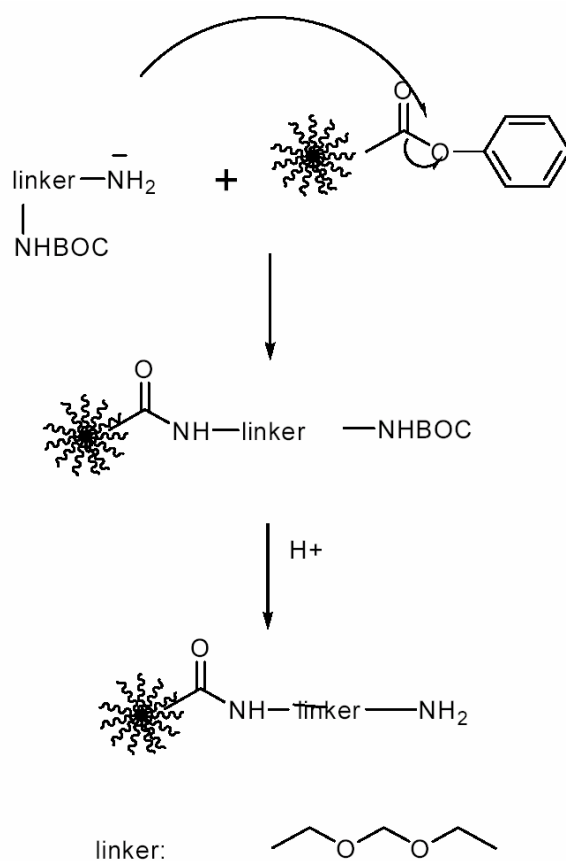


Figure 9. Scheme of functionalization reaction of polyPhA active nanogels.

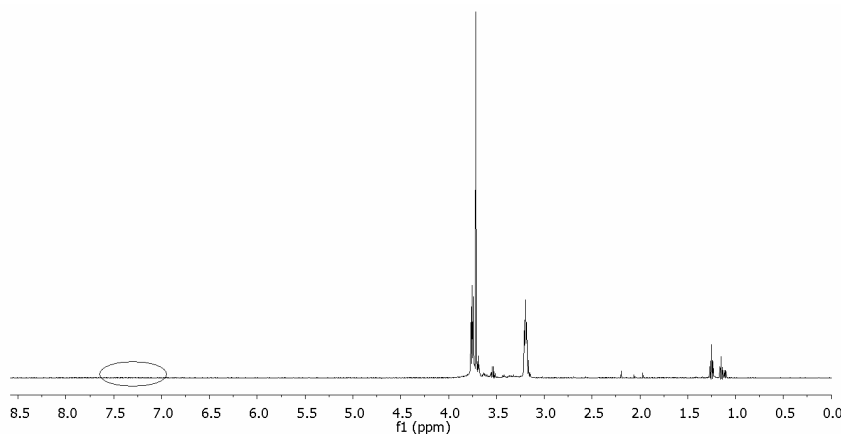


Figure 10. ^1H NMR spectra of functionalized nanogels.

^1H NMR was employed to observe the successful replacement of PhA by the diamine. The comparative spectra of the initial active polyPhA and the final resulting system of the modification (Figure 10) show the clear incorporation of the linker due to the disappearance of the peaks 7.0 and 7.3 ppm corresponding to the aromatic protons of PhA and to the appearance of the resonances of the protons of the ethylenic protons at 3.2–3.8 ppm.

4. Conclusions

Poly(phenyl acrylate) nanogels were successfully synthesized by o/w microemulsion polymerization and photochemical initiation. IR and NMR spectral data confirm the polymerization and obtained active nanogels were also characterized by SEM and QELS. The influence of synthetic parameters as reaction time, crosslinking and salt presence in dispersed medium were investigated. Obtained nanogels were functionalized with a free amine type linker (2,2'-(ethylenedioxy)bis(ethylamine)) and the good course of substitution reaction could be confirmed by ^1H NMR.

Acknowledgements

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