

## Water-Soluble Ionic Liquids as Novel Stabilizers in Suspension Polymerization Reactions: Engineering Polymer Beads

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**Abstract:** Aqueous solutions of ionic liquids have been used as novel and environmentally friendly reaction media to synthesize and “control” the size of different cross-linked polymer beads by suspension polymerization reactions. It was found that the investigated ionic liquids can act as novel stabilizing agents of the suspensions as a result of their surface-active properties. The results have demonstrated that the aver-

age size of polymer beads can be varied from the macro- to the nano-scale and their surface area can also be “adjusted” by this synthetic approach.

**Keywords:** combinatorial chemistry • cross-linked polymer beads • green chemistry • ionic liquids • ionic surfactants • suspension polymerization

Furthermore, the use of a combination of ionic liquids and water for the synthesis of polymers, the simple isolation of the products formed in this polymerization procedure, as well as the recycling of the continuous medium for further reactions open up possibilities for the development of “new and green” polymerization processes.

### Introduction

The heterogenization of polymerization processes is desirable in some cases for an easy separation of the product. Heterogeneous polymerization processes, such as water-based emulsions and suspensions, have been widely adopted for the production of commodity materials<sup>[1]</sup> as well as specialized polymers for advanced applications.<sup>[2]</sup> Materials synthesized by heterogeneous polymerization processes are regular beads with sizes between 50 nm and 3000 μm, depending on the characteristics of the procedure used (e.g., emulsion, miniemulsion, precipitation, dispersion, soap-free emulsion, seeded, or suspension polymerization). Heterogeneous polymerization can be defined as a reactive liquid–liquid disper-

sion in which the nature of the suspended drops changes as the polymerization reaction proceeds. Common suspension polymerization reactions are carried out in stirred tank reactors with a stabilizing agent (protective colloid) being added to the aqueous phase to keep the suspended organic drops from coalescing as they change from the liquid to the solid state via a sticky phase. The size of the drops is determined by the balance between the rates of drop break-up and coalescence, which are influenced by several parameters such as the density and viscosity of the continuous and dispersed phases, interfacial tension, type and concentration of the suspending agent, type of impeller, stirring speed, and temperature. The continuous change in the properties of the dispersed phase, as a result of the ongoing polymerization reaction, in addition to the aforementioned parameters, contribute to the size of the drops and to their distribution.<sup>[3]</sup> Of major importance for the stability of suspensions are the type and amount of suspending agent utilized owing to the fact that it induces electrostatic charges on the surfaces of suspended monomer–polymer particles which retard their coalescence. Examples of stabilizing agents used in suspension polymerization are poly(vinyl alcohol), poly(vinylpyrrolidone), hydrophobically modified celluloses, phosphates,<sup>[1]</sup> steric stabilizers such as hydrophilic and hydrophobic copolymers, soap solutions, water–agarose gels,<sup>[2a]</sup> and perfluoropolyethers for suspension polymerization reactions carried out in supercritical carbon dioxide.<sup>[4]</sup> The selection

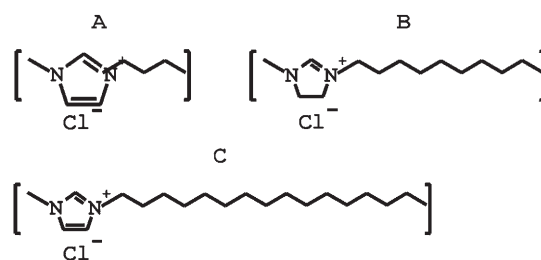
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of the suspending agent will mainly depend on the desired particle size of the polymer beads, which is determined by market requirements and/or applications (e.g., bone cement, packing for chromatographic columns, expandable polystyrene).<sup>[1,2]</sup> However, the prediction of particle size under specific polymerization conditions is still not fully understood.

Recently, the use of ionic liquids (ILs) as reaction media for the synthesis of diverse polymers and composites has led to a “new environmentally friendly” and novel synthetic approach with some kinetic advantages over the use of conventional solvents.<sup>[5]</sup> Despite the developments in polymerization reactions in ILs, a clear understanding of how to optimize the use of these novel reaction media in specific polymer systems is still lacking, since many factors must be optimized, including polymer isolation, IL recycling, and toxicity. A better knowledge of all these factors is necessary before industrial developments may be applied. Regarding polymer isolation and IL recycling, an environmentally friendly approach has recently been discussed in the literature.<sup>[6]</sup> This approach takes advantage of the poor solubility of many polymers in most water-soluble ionic liquids (WSILs), which facilitates polymer isolation and IL recycling, avoiding the use of volatile organic compounds (VOCs). The polymers obtained by this “new” sort of heterogeneous polymerization process in WSILs resulted in chalky solids, comparable to those reported in the literature using a similar synthetic approach in different ILs.<sup>[7]</sup>

ILs are defined as organic molten salts below 100 °C, therefore their use in suspension polymerization reactions may be equivalent to the use of common stabilizing agents. In other words, ILs may induce electrostatic charges on the surfaces of monomer-polymer particles to keep them from coalescence, as depicted in Figure 1. Based on this assumption, this contribution describes in detail the use of WSILs



Scheme 1. Molecular structures of A) 1-butyl-3-methylimidazolium chloride ( $[C_4MIM][Cl]$ ), B) 1-decyl-3-methylimidazolium chloride ( $[C_{10}MIM][Cl]$ ), and C) 1-hexadecyl-3-methylimidazolium chloride ( $[C_{16}MIM][Cl]$ ).

as stabilizing agents in suspension polymerization reactions, as well as their influence on the size and surface area of the synthesized polymer particles. For this purpose, three WSILs (1-alkyl-3-methylimidazolium chlorides, Scheme 1) were investigated. Furthermore, it is thought that the non-polar part of the ILs studied may act as a surfactant helping to stabilize the suspended organic phase (Figure 1). For this reason, the effect of variation of the length of the aliphatic side-chain in the ILs on the stability of the suspensions is also discussed. For the purposes of this work, the synthesis of poly(ethylene glycol dimethacrylate-*N*-vinylimidazole) cross-linked beads was chosen as the main suspension polymerization system to be studied (Scheme 2).<sup>[8]</sup>

## Results and Discussion

This work is a first attempt to elucidate the influence of ILs used as reaction media and/or stabilizing agents in “suspension” polymerization reactions.<sup>[6,7]</sup> The use of WSILs is more convenient since they facilitate the preparation of an aque-

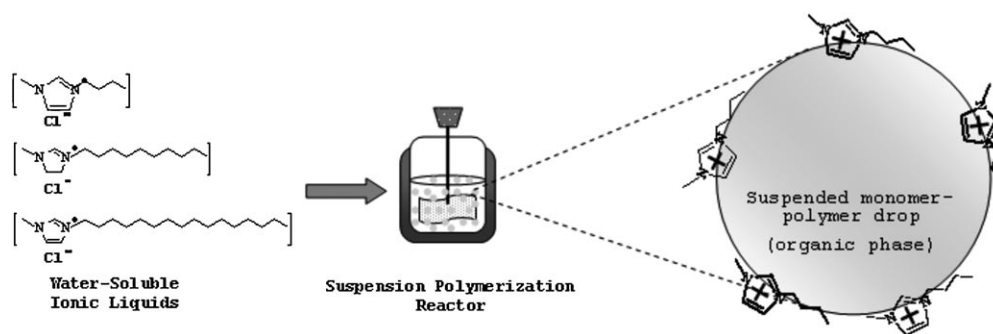
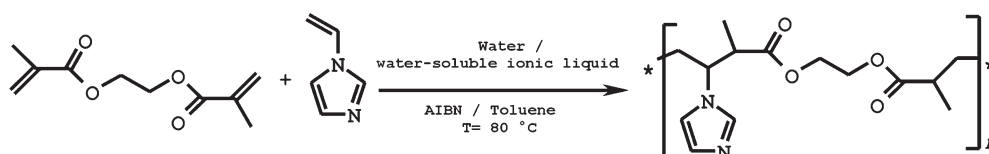


Figure 1. Schematic representation of a water-soluble ionic liquid acting as a stabilizing agent and reaction medium in suspension polymerization reactions.



Scheme 2. Reaction scheme for the synthesis of poly(ethylene glycol dimethacrylate-*N*-vinylimidazole) cross-linked polymer beads by free radical suspension polymerization using water-soluble ionic liquids as stabilizing agents. AIBN = 2,2'-azobisisobutyronitrile.

ous continuous reaction medium, the recovery of the IL for further polymerization reactions, and the isolation of certain polymers avoiding the use of VOCs.<sup>[6]</sup>

On the assumption that ILs may provide electrical charges on the surfaces of suspended monomer–polymer particles in order to keep them from coalescing during suspension polymerization, in the first experiments carried out in this research the concentration and the kind of IL (different aliphatic side-chain lengths, Scheme 1) in the aqueous phase of the polymerization reactions were varied to evaluate their effect on the stability of the suspensions and on the average particle size of the resulting polymer beads. These experiments were performed in the experimental set-up shown in Figure 2A and the results are summarized in Table 1.

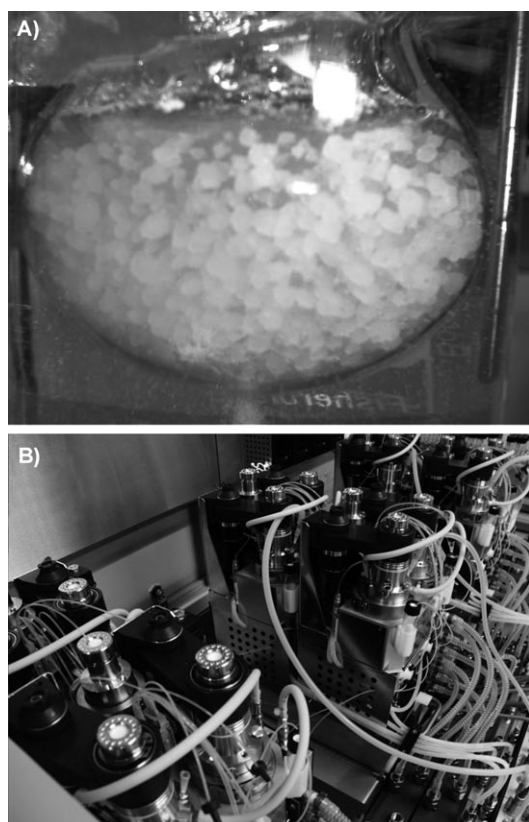


Figure 2. Overview of the set-ups used to perform the suspension polymerization experiments. A) A laboratory-scale suspension polymerization reactor (experiments summarized in Table 1). B) An automated parallel synthesizer A-100 minipilot plant (experiments summarized in Table 2).

The results shown in Table 1 reveal that the concentration of WSILs has a large effect on the as-obtained average particle size of the synthesized polymer beads. In short, for the three WSILs investigated, it was found that a low content of IL in the aqueous continuous medium of the suspension allows the synthesis of large polymer beads (with average sizes in the millimeter range), whereas for a high IL content the particle sizes decrease remarkably, down to the nanometer range in some cases. Simultaneously, it can also be seen in Table 1 that the average bead size is not only affected by

Table 1. Experiments performed in the laboratory-scale reactor (Figure 2A) to evaluate the potential of three different water-soluble ionic liquids (Scheme 1) as stabilizing agents in the investigated suspension polymerization reactions.

Expt	Ionic liquid	Concentration of ionic liquid in the aqueous phase [wt %]	Average particle size
1	[C <sub>4</sub> MIM][Cl]	10	2.7 mm
2	[C <sub>4</sub> MIM][Cl]	70	1.6 mm
3	[C <sub>4</sub> MIM][Cl]	100	0.5 mm
4	[C <sub>10</sub> MIM][Cl]	20	1.7 mm
5	[C <sub>10</sub> MIM][Cl]	40	600 nm
6	[C <sub>16</sub> MIM][Cl]	1	1.9 mm
7	[C <sub>16</sub> MIM][Cl]	5	500 nm

the IL/water ratio, but the length of the aliphatic side-chain of the WSILs (Scheme 1) also has an influence. By combining these effects (concentration and aliphatic side-chain length) one can conclude that in order to obtain a specific average particle size the concentration of the ILs in the aqueous phase of the suspension has to decrease as the aliphatic side-chain length becomes longer. For example, the average particle size remained between 1.6 and 1.9 mm when the concentration of the WSIL was 70, 20, and even 1 wt % for 1-butyl-3-methylimidazolium chloride ([C<sub>4</sub>MIM][Cl]), 1-decyl-3-methylimidazolium chloride ([C<sub>10</sub>MIM][Cl]), and 1-hexadecyl-3-methylimidazolium chloride ([C<sub>16</sub>MIM][Cl]), respectively (Expts 2, 4, and 6). When using the same WSIL to “tune” the average size of the particle, its concentration has to be increased in order to reduce the bead size (i.e., Expts 1–3). Nevertheless, the most remarkable reduction in particle size (up to the nanometer scale) is mainly influenced by the aliphatic side-chain length of the WSIL. For instance, and as shown in Table 1, nanometer-scale particles could not be synthesized when [C<sub>4</sub>MIM][Cl] was used, even at the highest possible concentration (pure IL) in the aqueous continuous medium of the suspension (Expt 3). On the other hand, when [C<sub>10</sub>MIM][Cl] and [C<sub>16</sub>MIM][Cl] (Expts 5 and 7) were used as stabilizing agents, at a specific concentration, beads with sizes in the nanometer range were obtained, as revealed by dynamic light scattering (DLS).

To end up with gel-like reaction mixtures, suspended waxy solids, and/or chalky solids similar those reported in the literature<sup>[6,7]</sup> and as shown in Figure 3, a critical concentration of a specific IL in the aqueous phase of the suspension has to be reached. For instance, for the investigated WSILs these concentration were estimated to be around 100 wt % for [C<sub>4</sub>MIM][Cl], 40 wt % for [C<sub>10</sub>MIM][Cl], and 5 % for [C<sub>16</sub>MIM][Cl] under the reaction conditions of the experiments reported in Table 1. According to this finding, it is thought that this critical concentration may establish the limit of the smallest average particle size that it is possible to obtain using a specific WSIL as stabilizing agent under certain experimental conditions (in this case under the experimental conditions used in the laboratory-scale suspension polymerization reactor shown in Figure 2A). When the beads are small enough, they can be analyzed by DLS or by atomic force microscopy (AFM). DLS provides infor-



Figure 3. Impression of the gel-like reaction mixtures obtained after suspension polymerization in a high ionic liquid content aqueous phase (Expts 3, 5, and 7).

mation on the average diameter of the cross-linked polymer beads in aqueous solution, when they are supposed to be in a swollen state due to the presence of the solvent (water), as reported in the literature for this kind of material.<sup>[8]</sup> AFM measures the diameter of the beads in dry conditions (non-swollen state).<sup>[9]</sup> For instance, Figure 4 shows an AFM image utilized to determine the average size of the polymer beads of Experiment 11 in dry conditions; a value of 100 nm was obtained, whereas in the swollen state (DLS measurements) the average size was 250 nm.

To investigate if the phenomena of “tuning” the size of the beads by utilizing WSILs as stabilizing agents in suspen-

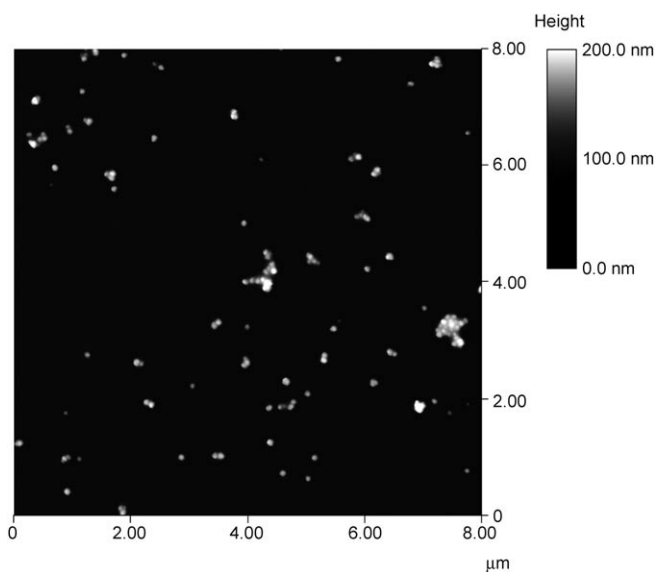


Figure 4. AFM image of polymer beads formed in Experiment 11 in dry conditions used to determine the average size of the beads.

sion polymerization reactions is just feasible with specific monomers (i.e. *N*-vinylimidazole, which has a similar chemical structure to the WSILs utilized and, therefore, may be more compatible with the phase containing ILs in the suspension), additional experiments were performed. These experiments were carried out under the same reaction conditions as those utilized in Experiments 1–3, but by using styrene instead of *N*-vinylimidazole and divinylbenzene instead of ethylene glycol dimethacrylate as co-monomers. In these experiments, findings similar to those discussed above for *N*-vinylimidazole-containing polymer beads were observed. More specifically, a gel-like suspension was obtained when pure [C<sub>4</sub>MIM][Cl] was used as the continuous medium of the suspension, an average particle size of 1.5 mm when a 70 wt % aqueous solution of [C<sub>4</sub>MIM][Cl] was utilized in the system, and polymer beads with an average size of 2.5 mm in the case of a 10 wt % aqueous solution of [C<sub>4</sub>MIM][Cl].

Note that even though the polymer beads synthesized in a high-content IL aqueous continuous medium were of a small size, the reaction systems studied in this research differ from precipitation polymerization reactions. In precipitation polymerization reactions, monomers form a continuous phase with the reaction medium (solvent) but the polymers do not and precipitate as small nanoparticles. In the polymerization reactions investigated in this work, the organic phase (co-monomers and pore former mixture), in all cases, is separated from the IL aqueous phase and therefore they can be classified as suspension polymerization reactions.<sup>[2c]</sup>

In addition to the fact that the investigated WSILs may create electrical charges on the surfaces of the suspended monomer–polymer particles in order to stabilize them, the surface active properties of ILs, which have already been discussed in the literature,<sup>[10]</sup> may also contribute to the stabilization of the system. These studies mainly report on the surface tension properties of some ILs and their aqueous solutions, as well as their dependence on temperature.<sup>[10a–f]</sup> Moreover, as an application of the surface active properties of ILs, WSILs have been utilized as novel templates in the preparation of highly ordered monolithic super-microporous lamellar silica materials by the nanocasting technique.<sup>[10g]</sup> From those studies, one can conclude that some ILs exhibit surface active properties and aggregation behavior in aqueous solutions. For this reason, surface tension measurements of the aqueous solutions of the ILs given in Scheme 1 were performed and the results are shown in Figure 5. It was found that the critical concentration of aggregation was 0.17 and 0.03 wt % for [C<sub>10</sub>MIM][Cl] and [C<sub>16</sub>MIM][Cl], respectively. In the case of [C<sub>4</sub>MIM][Cl] it was difficult to establish a value for the critical concentration of aggregation since the surface tension of the aqueous solutions decreases continuously as the concentration of the ionic liquid increases; this means a well-defined plateau was not reached. The value of the critical concentration of aggregation for [C<sub>16</sub>MIM][Cl] was the lowest of the three WSILs; this was expected since it has the longest aliphatic side-chain. However, the lowest surface tension value ob-

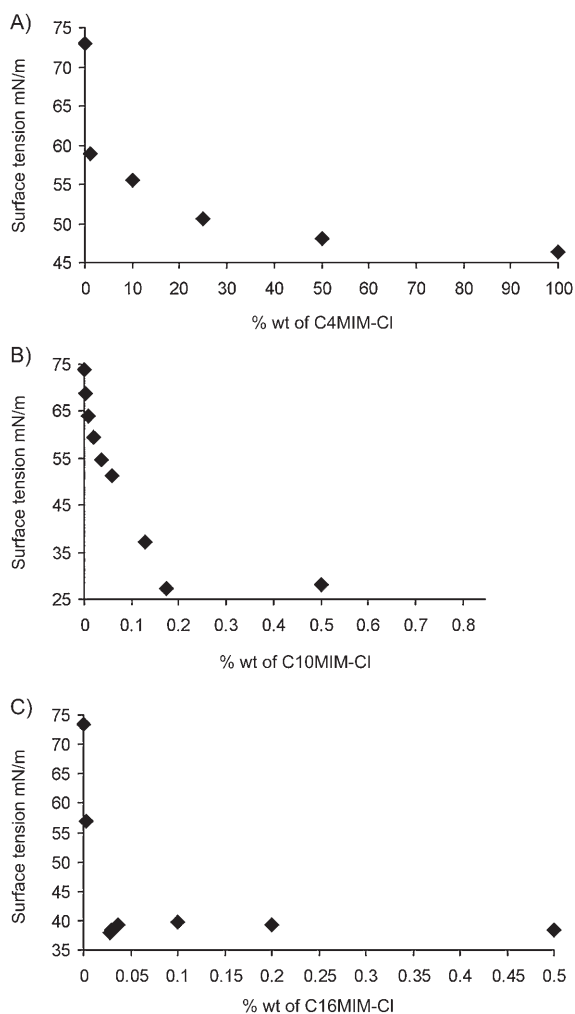


Figure 5. Surface tension measurements of the aqueous solutions of the ionic liquids of Scheme 1. A) [C<sub>4</sub>MIM][Cl], B) [C<sub>10</sub>MIM][Cl], and C) [C<sub>16</sub>MIM][Cl].

tained, once the critical concentration of aggregation was reached, was 27 mN m<sup>-1</sup> for [C<sub>10</sub>MIM][Cl] in comparison to 38 mN m<sup>-1</sup> for [C<sub>16</sub>MIM][Cl]. In the case of [C<sub>4</sub>MIM][Cl] the lowest possible surface tension was 46 mN m<sup>-1</sup> (pure IL).

An important aspect that may help us to understand the role of the WSILs in “tuning” the size of the synthesized polymer beads is the interfacial tension between the organic (co-monomers) and the IL aqueous phases. In polymerization reactions in which spontaneous emulsification occurs (e.g., microemulsion),<sup>[5c]</sup> the interfacial tension between the monomer and the aqueous continuous medium phase approaches zero due to the presence of surfactants that allow the synthesis of polymer beads in the nanometer range. In this context, interfacial tensions in some of the experiments reported in Table 1 were qualitatively estimated using the Du Nouy ring method (by considering the value of the interfacial tension recorded by the tensiometer at the maximum value of the force exerted on the ring as it passes through the interface of the organic mixture and the IL aqueous sol-

ution). For instance, the interfacial tension between the organic phase used for the polymerization reaction and pure water had a value of 4.5 mN m<sup>-1</sup>, whereas the interface of the organic mixture and pure [C<sub>4</sub>MIM][Cl] (Expt 3) had a value of 1.8 mN m<sup>-1</sup> and for the interface of Experiment 1 the value was 3.9 mN m<sup>-1</sup>. These results show that the interfacial tension indeed decreases as the content of IL in the aqueous phase increases, suggesting the possibility of a spontaneous emulsification process in the system allowing the synthesis of small-sized polymer beads.

After considering the measurements obtained for both surface tension (Figure 5) and particle size (Table 1), it is clear that the aliphatic side-chain length and not only the concentration of the WSILs plays an influential role in the stabilization of the monomer–polymer particles in suspension polymerization reactions. According to Figure 5, the experiments reported in Table 1 were performed above the critical concentration of aggregation of ILs (at least in the cases of [C<sub>10</sub>MIM][Cl] and [C<sub>16</sub>MIM][Cl]) and therefore in a low surface tension aqueous phase. Similar to the case of emulsion polymerization, the availability of hydrophobic aliphatic chains in the system promotes the creation of a greater interfacial area between the organic phase (monomer–polymer particles) and the aqueous IL solutions. Therefore, the synthesis of polymer beads with smaller average particle size is possible.

This effect may be similar in common suspension polymerization reactions in which poly(vinyl alcohol) (PVA) and other water-soluble polymers are used as protective colloids. In these cases PVA supplies covalently linked carbon chains to the interface of the immiscible phases, avoiding coalescence of the monomer–polymer particles formed. However, one of the disadvantages of using water-soluble polymers as stabilizing agents in suspension polymerizations is the fact that these materials are difficult to dissolve in water at room temperature. Added to this is the limited understanding of how the average size of the polymer beads is affected by the use of conventional active surface modifiers. To investigate whether the use of conventional ionic surfactants in suspension polymerization reactions has the same effects as those obtained with the investigated WSILs, experiments were performed under similar reaction conditions to those reported in Table 1. The main difference in these experiments is the use of sodium dodecyl sulfate (SDS) (a well-known ionic surfactant) as the stabilizing agent instead of WSILs. Four different concentrations of SDS (0.1, 0.33, 1, and 5 wt %), one below and three above the critical micelle concentration value (0.23 wt %),<sup>[11]</sup> were used for these experiments. The average sizes of the polymer beads obtained from these experiments were around 0.8 μm in all cases. Therefore, the use of SDS does not allow the average size of the beads to be “tuned” as the WSILs of Scheme 1 do (at least for the reaction systems investigated).

Furthermore, in the cases in which beads with sizes in the millimeter scale were synthesized, the polymer can be easily isolated from the reaction medium by simple decanting and/or filtration and therefore the IL aqueous solutions can be

reused to carry out new polymerization reactions. This approach was investigated by reusing the IL aqueous solution of Experiment 6 to perform more polymerization cycles under the same reaction conditions. In this case, after three polymerization cycles the average size of the beads (2 mm) was comparable to that of the first reaction cycle (1.9 mm). These results suggest that the IL aqueous solutions can be recovered and reused several times to synthesize new materials with comparable properties.

The simultaneous effects of other reaction parameters on the stability of the suspensions and on the average size of polymer beads were briefly investigated by performing additional polymerization reactions in an automated parallel synthesizer<sup>[12]</sup> (Figure 2B). The reaction conditions and the results of these experiments are summarized in Table 2. According to these results, qualitatively, it was found that the content of IL in the aqueous phase of the suspension ( $x_1$ ), acting as a stabilizing agent, is inversely proportional to the average particle size, as already discussed above. The reaction temperature ( $x_2$ ) has an effect similar to  $x_1$ ; higher reaction temperatures lead to particles with a smaller average size. The presence of *N*-vinylimidazole in the polymer beads ( $x_3$ ) also showed effects similar to  $x_1$  and  $x_2$ ; the higher the content of *N*-vinylimidazole, the smaller the average particle size. Finally, the content of toluene ( $x_4$ ) in the formulations is thought to have almost no influence on the stability of the suspensions and/or on the size of the particles, but mainly on the formation of pores in the beads. For example, when toluene was not included in the formulation, the particles obtained were translucent. On the other hand, when toluene was used, the particles obtained were white and opaque (the presence of pores may disperse the light through the beads turning them opaque). Similar effects of some of the reaction parameters investigated in the experiments reported in Table 2 (concentration of the stabilizing agent and reaction

temperature) on the average particle size of polymer beads synthesized by suspension polymerization have been reported in the literature.<sup>[3]</sup>

It is known that the agitation speed has an important effect on particle size in suspension polymerization reactions.<sup>[3]</sup> From the experiments performed in this work using the two different experimental set-ups shown in Figure 2, it was also found that the type of agitation influences the particle size and stability of the suspensions. For instance, in the experiments reported in Table 1 (magnetic agitation was applied to the laboratory-scale reactor shown in Figure 2A), larger average particle sizes were obtained in comparison to those achieved in the experiments reported in Table 2 (note that the experiments reported in Table 1 were aimed at investigating the WSILs of Scheme 1 as stabilizing agents in suspension polymerization reactions under fixed reaction conditions). On the other hand, in the experiments reported in Table 2 (mechanical agitation was used in the experimental set-up shown in Figure 2B), polymer beads with sizes in the nanometer range could be obtained by using a low concentration of stabilizing agent ([C<sub>4</sub>MIM][Cl]). This was the case for Experiment 11, which showed an average particle size of 250 nm in solution, as revealed by DLS, and around 100 nm, as determined by AFM in dry conditions (Figure 4).

It has been reported that polymers containing imidazole groups are able to bind different transition metals to their surface, finding applications in the removal of transition-metal ions from waste streams<sup>[8,13]</sup> and as supports for palladium-catalyzed reactions.<sup>[14]</sup> An important property of these polymeric materials is their surface area, since this factor determines to a large extent the amount of chemical species that can be loaded. Other polymer architectures with large surface areas and an intrinsic porosity have also found applications as replacements of inorganic materials such as zeolites and/or activated carbon used as heterogeneous catalytic supports<sup>[15]</sup> and more recently in hydrogen storage.<sup>[16]</sup> Even though the incorporation of a pore former (toluene in this work) is essential to promote the synthesis of polymer beads with large surface areas,<sup>[8]</sup> it has been found in this study that the incorporation of a WSIL ([C<sub>4</sub>MIM][Cl]) into the aqueous continuous medium of the suspension also has an important effect on the creation of surface area in the particles, as shown in Table 3. The results given in Table 3 show the surface area values (as determined by nitrogen gas adsorption) for different polymer beads synthesized in the experimental set-up shown in Figure 2A and under reaction

Table 2. Experimental design performed in the automated parallel synthesizer (Figure 2B) for the synthesis of cross-linked beads by suspension polymerization using a water-soluble ionic liquid as stabilizing agent.<sup>[a],[b]</sup>

Expt	$x_1$	$x_2$	$x_3$	$x_4$	Remarks	Average particle size
8	–	–	–	–	collapsed translucent beads	large (3 mm)
9	+	–	–	–	collapsed translucent beads	medium (1.5 mm)
10	–	+	–	–	stable suspension, translucent beads	medium (1.4 mm)
11	–	–	+	–	white stable suspension	nanometer scale (250 nm)
12	–	–	–	+	collapsed white beads	large (2.8 mm)
13	+	+	–	–	stable suspension, translucent beads	small (0.65 mm)
14	–	–	+	+	stable suspension, white beads	small (0.8 mm)
15	+	–	–	+	cloudy stable suspension	nanometer scale (600 nm)
16	–	+	+	–	white stable suspension	nanometer scale (525 nm)
17	–	+	–	+	stable suspension, white beads	small (0.7 mm)
18	+	–	+	–	yellow stable suspension	nanometer scale (405 nm)
19	+	+	+	–	yellow swollen gel-like	n.a.
20	+	+	–	+	white stable suspension	nanometer scale (650 nm)
21	+	–	+	+	white stable suspension	nanometer scale (400 nm)
22	–	+	+	+	stable suspension, white beads	small (0.75 mm)
23	+	+	+	+	white stable suspension	small (0.35 mm)

[a] Mechanical stirring speed was 400 rpm. [b] Four reaction parameters were analyzed as follows:  $x_1$  = content of ionic liquid [C<sub>4</sub>MIM][Cl] in the aqueous phase (– = 20 wt %, + = 70 wt %),  $x_2$  = reaction temperature (– = 75 °C, + = 90 °C),  $x_3$  = content of *N*-vinylimidazole in the polymer beads (– = 50 mol %, + = 87.5 mol %), and  $x_4$  = content of porogenic agent (toluene) in the organic phase (– = 0 % vol., + = 30 % vol.).

Table 3. Surface area properties, as determined by the nitrogen gas adsorption technique, of cross-linked polymer beads.<sup>[a]</sup>

Expt	Content of [C <sub>4</sub> MIM][Cl] in the aqueous phase [wt %]	Average particle size [mm]	Langmuir surface area [m <sup>2</sup> g <sup>-1</sup> ]	Porosity	Pore shape	BET average pore diameter [nm]
24	100	0.5	57.6	nonporous	–	–
25	70	1.6	191.9	mesopores	ink bottle	3.8
26	50	1.9	208.8	mesopores	ink bottle	3.7
27	30	2.4	268.8	mesopores	slit	4.4
28	10	2.7	303.8	mesopores	slit	4.6
29	0 (90°C)	2.7	158.8	mesopores	cylindrical	7.7
30	0 (90°C, no toluene)	1.3	1.7	nonporous	–	–

[a] The cross-linked polymer beads were synthesized under similar reaction conditions to those used in experiments reported in Table 1.

conditions similar to those used in the experiments reported in Table 1. The pores have been classified according to the shape of the adsorption isotherms<sup>[17]</sup> obtained for each sample and according to the IUPAC classification. Figure 6 shows nitrogen adsorption/desorption isotherms for some of the experiments reported in Table 3. According to the shape of the isotherms, the materials can be classified with regard to pore shape.<sup>[17]</sup> The results in Table 3 show that beads with a “large” average particle size (>1.5 mm) can be classified as good porous materials. More important, the results in

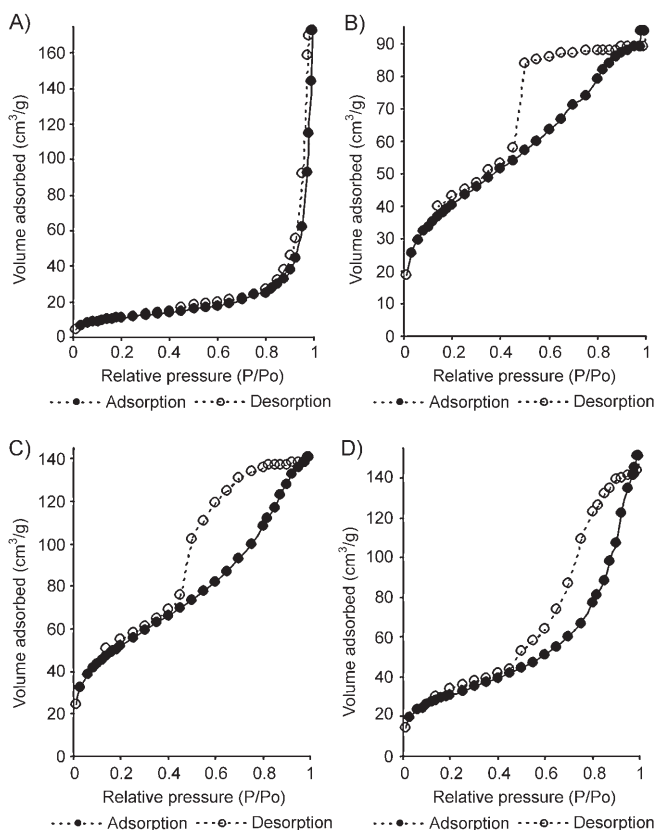


Figure 6. Shape of the nitrogen adsorption/desorption isotherms at 77 K of some of the experiments reported in Table 3. The materials can be classified according to the shape of the adsorption isotherms. A) Expt 24, nonporous beads, B) Expt 26, mesoporous beads with ink-bottle-like pores, C) Expt 27, mesoporous beads with slit-shape pores, and D) Expt 29, mesoporous beads with cylindrical pores.

Table 3 also reveal a strong influence of the content of [C<sub>4</sub>MIM][Cl] on the formation of surface area. First, when both [C<sub>4</sub>MIM][Cl] and pore former (toluene) are included in the synthetic formulation of the beads (Expts. 24–28) and the amount of toluene remains constant, the creation of surface area is strongly related to the content of IL in the aqueous continuous medium of the suspension and therefore to

the size of the beads obtained, as explained before. These results reveal that a low content of WSIL in the reaction medium yields particles with large sizes and surface areas whilst a high content of WSIL promotes the synthesis of beads with small sizes and surface areas. Second, the inclusion of a pore former has been found to be essential to create surface area in the beads, as revealed by additional experiments in which toluene was not used, and even in presence of WSILs, nonporous materials were obtained. In general, the absence of WSILs or stabilizing agents in the reaction system leads to unstable systems or coalescence of the beads in suspension polymerization reactions. However, to investigate the pure effect of toluene as a pore former and in the absence of any stabilizers, Experiments 29 and 30 (Table 3) were performed. These suspension polymerization reactions were carried out at 90°C owing to the fact that at lower reaction temperatures the suspension may be unstable and show coalescence. From these results, it is again confirmed that the absence of toluene yields nonporous materials with a small surface area (Expt 30). In the case of Experiment 29, beads with a relatively large surface area were formed as expected with the inclusion of toluene. However, when comparing results of Experiments 28 and 29, it is clear that the combination of pore former and a relatively small amount of WSILs (10 wt%) in the reaction mixture promotes a more efficient formation of surface area (around twice as large) for beads with similar average particle sizes (2.7 mm). The morphology of some of the synthesized polymer beads was also investigated by scanning electron microscopy (SEM) to gain an insight into the formation of pores. Images of the morphologies obtained are shown in Figure 7, which shows the presence of pores in the beads. Moreover, from the results in Table 3 and the shape of the adsorption/desorption isotherms of Figure 6 it can also be observed that the shape of the pores formed in the beads can be modified by varying the concentration of the WSIL during synthesis. From these findings one can conclude that, at least for the investigated reaction system, the combination of a pore former and the use of a WSIL as a stabilizing agent in suspension polymerization reactions may allow the surface area of polymer beads to be “tuned” during their synthesis.

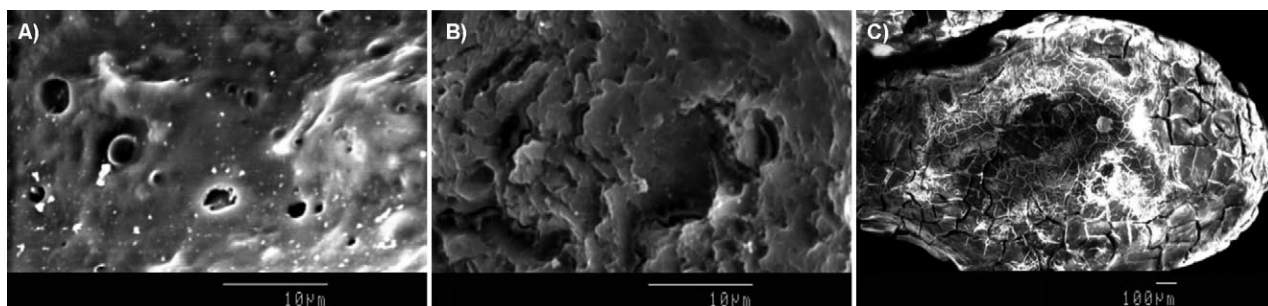


Figure 7. Morphology of some of the synthesized polymer beads as investigated by SEM. Images of polymer beads A) and B) obtained from Expt 28 and C) obtained from Expt 25.

## Conclusion

This contribution shows, for the first time, that WSILs have potential as stabilizing agents in the synthesis of polymers by suspension polymerization as a result of their surface active properties. This approach allows “tuning” of the average particle size (from the macro- to the nanoscale) of the synthesized polymer beads by adjusting the concentration and the aliphatic side-chain length of the investigated ILs in the aqueous phase of the suspension. Furthermore, the surface area of the beads can also be “adjusted” with a combination of a pore former and a WSIL used as a stabilizing agent during their synthesis. Moreover, the IL aqueous solutions used could be recovered and reused to carry out further reactions in a completely “efficient” synthetic approach.

## Experimental Section

**Materials:** 1-Methylimidazole and *N*-vinylimidazole (Aldrich) were distilled under reduced pressure and stored at room temperature prior to use. Ethylene glycol dimethacrylate (Aldrich) was purified by passing it through active alumina (Merck) and was stored at 4°C prior to use. All other materials were used as received.

**WSILs by microwave-assisted synthesis:** WSILs were synthesized by microwave heating in a similar way to those methods reported in the literature,<sup>[18]</sup> by reacting 1-methylimidazole with a molar excess (1.1 mol) of the corresponding chloroalkane (1-chlorobutane, 1-chlorodecane, or 1-chlorohexadecane; Aldrich). The reactions were performed in sealed reaction vials (10 mL) specially designed for the single-mode microwave system Emrys Liberator (Biotage, formerly Personal Chemistry). These vials were filled with the reagents, sealed, and degassed with argon for 2 min. The reaction volume for every batch was 5 mL (per vial). The reagents were mixed during the microwave-assisted reaction by using a magnetic stirring system included in the microwave apparatus. Optimal reaction conditions for the synthesis of these ionic liquids in the aforementioned microwave platform were found to be 170°C and a reaction time of 6–7 min under a high absorption reaction mode (150 Watts). At the end of the reaction time the vials were decapped and any unreacted material (upper organic phase) was decanted. Note that under the reaction conditions described, the lower organic phases in the reaction vials (WSILs) were almost colorless liquids in the case of [C<sub>4</sub>MIM][Cl] and [C<sub>10</sub>MIM][Cl], and a white solid in the case of [C<sub>16</sub>MIM][Cl]. The synthesized WSILs (Scheme 1) were further purified to remove traces of unreacted starting materials as follows: [C<sub>16</sub>MIM][Cl] was recrystallized from acetone and dried under vacuum at 40°C, [C<sub>10</sub>MIM][Cl] was

washed several times with ethyl acetate before drying under vacuum at 40°C, and [C<sub>4</sub>MIM][Cl] was just dried under vacuum at 40°C since the yield of this reaction was close to 100%. The <sup>1</sup>H NMR spectra of the synthesized WSILs confirmed their chemical structure (Scheme 1) and the purity of the materials. The long aliphatic chain WSIL, [C<sub>16</sub>MIM][Cl], was obtained as a white powder at room temperature. Even though its melting point was found to be 41°C, as revealed by DSC measurements, it can still be classified as a room-temperature IL (melting point below 100°C). The melting point of [C<sub>10</sub>MIM][Cl], found by DSC, was around 4°C. Although [C<sub>4</sub>MIM][Cl] was obtained as a liquid substance at room temperature from the microwave-assisted synthesis, after some days it started to crystallize; its melting point was determined to be around 40°C. The rest of the experiments in this work involving [C<sub>4</sub>MIM][Cl] were performed using the liquid substance before crystallization (as obtained from the synthesis and purification procedures).

**Synthesis of cross-linked polymer beads by suspension polymerization in IL aqueous solutions:** Typical suspension polymerization experiments were performed using a similar formulation to that reported in the literature for the synthesis of poly(ethylene glycol dimethacrylate-*N*-vinylimidazole) cross-linked beads.<sup>[8]</sup> The main difference between this latter synthetic approach and the one used here lies in the preparation of the aqueous phase. In order to study the stability of the suspensions using WSILs as stabilizing agents, the aqueous phases were prepared by dissolving predetermined amounts of the corresponding IL [instead of poly(vinyl alcohol)]<sup>[8]</sup> in purified water (demineralized). The organic phase was formulated (on the basis of 50 g of aqueous phase) with ethylene glycol dimethacrylate (6 mL, 32 mmol), toluene (4 mL, 38 mmol) (pore former), *N*-vinylimidazole (3 mL, 33 mmol), and 2,2'-azobisisobutyronitrile (100 mg, 0.6 mmol). The aqueous phase was placed in the corresponding experimental set-up (as described below) at the desired reaction temperature. Subsequently, the organic phase was dispersed into the aqueous medium by vigorous stirring. This moment was considered to be the beginning of the polymerization process, which was conducted for 0.5 h to obtain almost 100% yield of polymer beads based on the initial amount of monomer (as determined by gravimetry). The beads obtained were separated from the aqueous phase by filtration, washed with water and ethanol to remove unreacted monomer and pore former (toluene), dried, and stored at room temperature.

To determine the stability of the suspension polymerization reactions in the presence of WSILs, two different experimental set-ups were employed. A typical laboratory-scale reactor (Figure 2A) consisting of a round-bottomed flask (50 mL) placed in an oil bath (80°C) and stirred (400 rpm) with a cylindrical PTFE-coated magnetic stirring bar. The experimental scale for this laboratory set-up was 25 mL based on the aqueous phase. This set-up was utilized to evaluate the potential of WSILs as stabilizing agents in the suspension polymerization system described and therefore the rest of the reaction conditions remained unmodified (under the previously mentioned conditions). The reaction conditions utilized in the suspension polymerization experiments performed with the experimental set-up of Figure 2A are summarized in Table 1.

A second experimental set-up consisting of an automated parallel synthesizer<sup>[12]</sup> (A-100 minipilot plant, Chemspeed Technologies) (Figure 2B)



was used to perform a qualitative study involving the variation of more reaction conditions simultaneously. In this way, the influence of reaction temperature and the content of one of the utilized WSILs ([C<sub>4</sub>MIM][Cl]), co-monomers, and pore former on the stability of the suspension polymerization reactions could be qualitatively investigated. The advantage of performing experiments in parallel (using the same type of reactors, the same stock solutions of reagents, etc.) is that the reaction conditions can be varied systematically and that the results are, therefore, easily comparable. The main characteristic of this experimental set-up is the mechanical agitation that can be afforded to the reaction systems, which is, next to the stabilizing agent, one of the most important variables influencing the stability of monomer-polymer drops in suspension polymerization reactions. An anchor-type impeller and an agitation speed of 400 rpm were found to be suitable for performing the required suspension polymerization experiments. The experimental scale for this set-up was 50 mL based on the aqueous phase. The reaction conditions of the suspension polymerization experiments carried out in this synthesizer are summarized in Table 2.

**Characterization techniques:** <sup>1</sup>H NMR spectra of the synthesized WSILs were recorded at room temperature on a Varian Gemini 300 spectrometer using deuteriated dimethyl sulfoxide (Cambridge Isotopes Laboratories).

The melting points of the synthesized WSILs were determined by DSC on a Netzsch DSC 204 F1 instrument calibrated with indium. Multiple heating and cooling scans (20, 40, and 10 °C min<sup>-1</sup> scan rates) were generated over a temperature range of -100 to 250 °C using nitrogen as the purge gas. The melting point temperatures were noted at the maxima of the heat capacity peaks during the heating scans.

Surface and interfacial tension parameters were measured with a Krüss K10T tensiometer with a Wilhemy plate and by the Du Nouy ring method, respectively. From the surface tension measurements the critical micellar concentrations were determined.

Particle sizes and particle-size distributions were determined using digital image analysis techniques.<sup>[9]</sup> Images of large- and medium-sized particles (>1 mm) (for the particle sizes see Table 1 and Table 2) were obtained with a conventional digital camera. Images of small-sized particles (<1 mm) (for the particle sizes see Table 2) were obtained with an optical microscope (Optem, zoom 125) equipped with a digital camera (Sony Exwave HAD). In both cases, the images obtained were analyzed using

the image processing toolbox incorporated into the MATLAB software to obtain the average particle size and particle-size distribution (see the results given in Table 1 and Table 2). Figure 8 shows an overview of this characterization technique for two selected experiments reported in Table 1 and Table 2.

Some of the experiments reported in Table 1 and Table 2 yielded particles with average sizes in the nanometer range (Expts 5, 7, 11, 15, 16, 18, 20, and 21). In these cases, the materials obtained had a similar appearance to those synthesized in other pure ionic liquids (gel, waxy solid, and/or chalky solid compounds).<sup>[6,7]</sup> In all the experiments described, the composites were dispersed in water (~0.1 g L<sup>-1</sup>) under vigorous stirring until stable emulsion-like dispersions were obtained. The resulting dispersions were analyzed by DLS; the average particle sizes are reported in Table 1 and Table 2. DLS experiments were performed at 25 °C at 90° on a Malvern 4700 DLS Particle Size Analyzer apparatus equipped with a 488 nm laser. The values of the refractive index and viscosity of water used were 1.331 and 0.89 cPoise (1 cPoise ≈ 0.001 Kg m<sup>-1</sup> s<sup>-1</sup>), respectively. Imaging of one selected sample (Expt 11) in dry conditions was performed by AFM<sup>[9]</sup>, as shown in Figure 4. For this measurement, a sample from Experiment 11 used during the DLS measurements was additionally diluted with water (100-fold) and spin-cast (to obtain near monolayer coverage) onto a clean silicon wafer substrate. Imaging was performed in intermittent contact mode with a Multimode SPM (Digital Instruments, Santa Barbara, CA) using NSC36-type tips (~1 Nm<sup>-1</sup>, Mikromasch, Spain). The heights of the beads were determined from histograms after zero-order leveling of the images.<sup>[9]</sup>

Surface area, pore size, and pore-size distribution of the synthesized polymer beads were determined using nitrogen adsorption (TriStar 3000 apparatus of Micromeritics) at 77 K. Samples were dried under vacuum at 40 °C for three days just prior to measurement.

The surface morphology and porosity of the polymer beads was examined using scanning electron microscopy (SEM) (JEOL JSM-840 A). The samples were initially dried under vacuum at 40 °C for three days before being analyzed. Dried beads were mounted on a SEM sample holder, sputter coated with gold for 2 min, and scanned at the desired magnification.

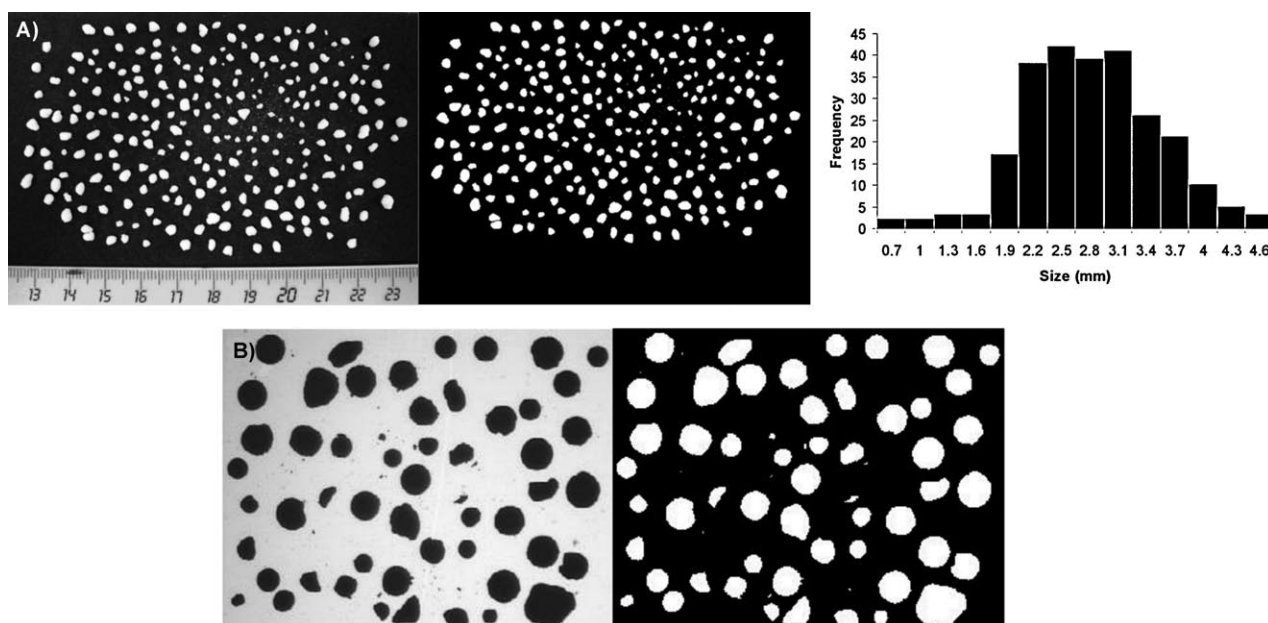


Figure 8. Overview of the determination of the average particle size and particle-size distribution of the synthesized cross-linked polymer beads by a digital image analysis technique. A) Digital images of large-sized particles (Expt 1) and their respective particle-size distribution, as obtained after the corresponding statistical analysis. B) Digital images of small-sized particles (Expt 22) obtained with an optical microscope.

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