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Liposomes by Polymerization of an Imidazolium Ionic Liquid: Use as Microreactors for Gold-Catalyzed Alcohol Oxidation

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Abstract: The bipodal ionic liquid N,N'-bis(10-undecenyl)-2-methylimidazolium underwent polymerization in aqueous media with potassium persulfate to form submicrometric liposomes. A TEM study indicated that the liposomes are the result of several morphological transformations of the polymer particles. Photopolymerization at room temperature led to spherical particles with some internal voids and polymer chains. We took advantage of the positive charge on the imidazolium rings and used a photocuring agent to form in a single step starting from the imida-

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zolium monomer and NaAuCl₄ spherical polymer particles containing gold nanoparticles (10–15 nm) in their interior. This system was found to promote the selective aerobic oxidation of 2-hydroxybenzyl alcohol to salicylaldehyde.

Introduction

The spontaneous self-assembly and spatial structuring of ionic liquids and liquid crystals form the basis of many fundamental phenomena that have been exploited in numerous applications.^[1-4] The special features and amphiphilic character of molecules comprising polar and apolar parts tend to be reflected at the supramolecular level by the appearance of intermolecular aggregations that maximize the favorable and minimize the unfavorable interactions.^[5] This self-assembly is generally better expressed in media that have a strong bias towards one type of polarity, water being the most studied solvent. The strong hydrogen bonds present in pure water are disturbed when apolar chains and substituents are introduced into the medium and the phenomena observed under these conditions, particularly aggregation, are generally described as arising from the hydrophobic nature of these groups in a hydrophilic medium.^[6,7] The interplay between hydrophilicity and hydrophobicity has ap-

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Supporting information for this article is available on the WWW peared as a general and powerful tool for the creation of spatial inhomogeneities and spatial organization. The forces arising between the solvent and the solute have been applied, for instance, in the synthesis of micro-/mesoporous silicates using a structure-directing agent.^[8-11]

As a particular example of the use of amphiphilic molecules in producing spatially structured objects, in this report we describe the synthesis and polymerization of an imidazolium ionic liquid bearing two long alkenyl chains with terminal C=C bonds. Ionic liquids with imidazolium heads and long alkyl chains have been used as templates for the preparation of mesoporous silicas because of their ability to selfassemble in aqueous media.^[12,13] In this case, the terminal C=C bond should allow cross-linking of the chains, freezing the shape of self-assembled monomer particles. The length and conformational freedom of the alkyl chains should still permit after polymerization a considerable flexibility and even reshaping of the polymeric particle. The presence of two alkyl chains may favor preferentially the formation of vesicles and liposomes with a defined membrane and an empty space with respect to spherical particles.^[14,15] It has frequently been observed that surfactants with a single alkyl chain form micelles, whereas those surfactants bearing two long alkyl chains tend to self-assemble to form liposomes.[16-19] Liposomes with porous walls can allow mass transfer from the exterior to the interior of the membrane for substrates smaller than the pore diameter and this spatial organization allows the location and immobilization in the

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interior of the liposomes guests that can be responsible for some of the properties of the particle. In the case presented herein we will show that the positive charge on the imidazolium head can be advantageously used to attract $AuCl_4^$ through ion pairing and this monoatomic complex can act as a precursor to gold nanoparticles. As a consequence of the preferential location of $AuCl_4^-$, the resulting nanoparticles will be mostly located in the interior of the polymeric particle. Gold nanoparticles can exhibit catalytic properties for aerobic oxidations and other organic reactions.^[20–23] In this way, the system comprising encapsulated gold nanoparticles inside porous polymeric particle of micrometric length resemble in a certain way the reported microreactors formed by nanoscopic zeolite cavities containing catalytic sites.^[24–26]

Results and Discussion

Synthesis and characterization of the liposomes: In the first stage of our work we synthesized N,N'-bis(10-undecenyl)-2-methylimidazolium bromide (1^+Br^-), a surfactant molecule with a polar head and two hydrophobic tails long enough to favor self-organization to form vesicle-like structures. The synthesis was carried out in a straightforward manner by treating 2-methylimidazole with 11-bromo-1-undecene in toluene at reflux (Scheme 1).



Scheme 1. Synthetic procedure followed to obtain N,N'-bis(10-undecenyl)-2-methylimidazolium bromide (1^+Br^-) .

The purity of monomer 1^+Br^- was checked by reversedphase HPLC, which showed that the peak corresponding to 1^+Br^- was 77% of the total area and that it was accompanied by three other peaks (see Figure S1 of the Supporting Information). A second peak (5%) close to 1^+Br^- was attributed to the imidazolium 1^+ associated with a counteranion different to Br-, for example, OH-, on the basis of its similar retention time and optical spectrum. On the basis of the synthetic route followed to obtain 1⁺Br⁻, the other two peaks (15 and 3%) were assigned to monopodal imidazolium associated with Br- or the other counterion. Careful integration of the ¹H NMR signals showed a 10% deficiency with respect to the imidazolium protons in the area of the vinylic signal corresponding to the undecenyl chain (see Figure S2 of the Supporting Information), which supports the assignment of the second largest HPLC peak to the monosubstituted protonated imidazolium. We anticipate that the ability of compounds 1^+ to self-assemble will not be much disturbed by the presence of a proportion of monoundecenyl derivatives, although sometimes the presence of co-surfactants can play a role in the self-assembly.^[27]

The rationale behind the synthesis of imidazolium 1^+ was to obtain a surfactant with ω -alkenyl moieties that have the possibility, after spontaneous self-organization in an aqueous medium, of polymerizing through the terminal C=C double bonds and thus form cross-linked, structurally defined micrometric particles that could be separated from solution by filtration or centrifugation.

To obtain the liposomes, the as-prepared imidazolium ionic liquid 1^+ was dissolved in water and stirred for 1 h to allow self-assembly of the precursor before the addition of potassium persulfate as the radical polymerization initiator. Potassium persulfate is a typical radical initiator and is widely used to promote the thermal polymerization of styrene and other alkenes in aqueous media.^[28] To study the influence of the polymerization temperature on the shape, dimension, and homogeneity of the liposomes, polymerization was performed at 40, 80, and 100 °C. Under these conditions, in all cases the signals typical of C=C double-bond hydrogen atoms were shifted from 5.8 to 5.0 ppm in the ¹H NMR spectra, which clearly indicates that polymerization has occurred to a significant extent, even at the lowest temperature. For the cross-linking reaction performed at 80°C, the area of the residual vinylic signals was about 12% of the initial peaks.

Transmission electron microscopy (TEM) images obtained from the polymeric material after centrifugation of the suspension showed that all the particles have the same cell-like system with a morphology defined by a hollow liposome with a polymeric wall of 20–30 nm thickness and an internal void. This characteristic morphology arises from the spontaneous self-organization of our bipodal ionic monomers, the structure of which is reminiscent of natural phospholipids (Scheme 2).



Scheme 2. Structure of the vesicles obtained by the self-assembly and polymerization of *N*,*N*-dialkenylimidazolium.

After statistical analysis of the vesicle size distribution by TEM it was concluded that the most size-homogeneous vesicles are formed at 40 °C and at this temperature the diameter ranges from 400 to 600 nm (see Figure 1, left). At higher temperatures we obtained vesicles with dimensions ranging from 400 nm to 1 μ m with a significantly broader liposome size distribution. The yield of liposomes obtained in terms

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Figure 1. TEM images of the vesicles prepared by heating the reaction mixture containing 1^+Br^- at 40 °C (left) and the particles present in the aqueous phase after sedimentation of the larger vesicles upon polymerization at 100 °C (right).

of the percentage of the initial monomer recovered as liposomes when the reaction was carried out at 40 °C was 65%, which indicates that the C=C double-bond cross-linking promoted by potassium persulfate is not complete at this temperature.

In the case of the polymerization performed at 100 °C, we also observed that the liquid phase contains small spheres (Figure 1, right) with diameters of 20–40 nm and an internal polymeric structure. However, owing to their small dimensions, these nanoparticles do not sediment under our centrifugation procedure, remaining in solution and being a part of the 28% of the monomer 1^+Br^- that is not recovered as vesicles under these conditions.

The monomer 1^+Br^- polymerizes by the common radical chain mechanism initiated by homolytic O-O bond rupture of the persulfate to form oxyl radicals. These oxygen-centered radicals attack the C=C double bond to generate carbon-centered radicals that will propagate the chain.^[29] Under similar conditions, latex spheres of fairly homogeneous particle size have been obtained.^[30] The spherical shape of the polystyrene latex is believed to arise from hydrophobic interactions that lead to a geometrical body that offers the least contact interface between water and the hydrophobic styrene.^[31] The principle feature arising from the use of the monomer 1^+Br^- is the spatial self-assembly of this molecule to form hollow spheres in water rather than thick spheres.^[32] There are precedents reported in the literature using silanes that have clearly shown the formation of rigid silica hollow spheres rather than thick spheres when appropriate precursors are used.^[33] The origin of this internal space is the imbrication of the alkyl chains with the formation of a bilayer arrangement, as indicated in Scheme 2. Vesicles and liposomes are well known in biological systems, the individual component phospholipids structurally resembling compound **1⁺Br**⁻.

Concerning the influence of the polymerization temperature on the morphology and structure of the particles, we interpret the results by considering that at 100 °C the forces effecting the self-assembly of the monomer are largely disturbed and that, on the other hand, the radical polymerization is considerably faster. These factors have a detrimental influence on the size homogeneity of the vesicles. On the other hand, the use of potassium persulfate as initiator requires a threshold temperature to promote a high degree of double-bond polymerization.

To circumvent the problems associated with the use of thermal activation to promote the polymerization using persulfate we considered the possibility of synthesizing the spheres at room temperature using a photocuring agent, namely 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (2), as the radical source; compound 2 decomposes into radicals upon irradiation with UV light. Thus, by keeping the same concentration of the organic precursor as used in the thermal cross-linking, we performed the polymerization of the ionic liquid 1^+Br^- by adding the water-soluble compound 2 to the aqueous solution and irradiating the samples through quartz tubes (Scheme 3).



Scheme 3. Alternative procedures for the formation of polymeric particles from the imidazolium ionic liquid 1^+ .

As in the previous case, the course of the polymerization was conveniently followed by ¹H NMR spectroscopy, periodically taking small aliquots of the liquid phase. We observed that the polymerization was almost complete in 12 h. To remove traces of unreacted compound **2** as well as some radical recombination byproducts, the sample was extracted with dichloromethane until the complete disappearance of organic compounds, as indicated by GC–MS.

TEM images of the extracted suspension revealed some morphological differences in the resulting polymeric particles, which appear as thick spheres rather than vesicles (Figure 2a). We attribute this change in the polymer morphology to the mildness of the room-temperature photochemical polymerization procedure. It appears that the spheres are metastable intermediates in the formation of vesicles.

The particle size distribution of the spherical polymer particles ranges from 100 to 900 nm with an average of 400 nm (Figure 2b). It seems that photocuring gives a somewhat broader size distribution than the polymerization with potassium persulfate. A careful inspection of the TEM images after various intervals of time reveals the mechanism through which vesicles are formed and provides a rationale for the different morphologies obtained by thermal and photochemical polymerization. Thus, the TEM images reveal that at short reaction times the particles still contain small polymeric chains in the interior of the particles. These inter-

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Figure 2. a) TEM (left) and SEM (right) images of the spherical particles obtained by room-temperature polymerization of imidazolium 1^+ through UV photocuring using water-soluble 2. b) Size distribution of the spheres obtained by room-temperature polymerization of imidazolium 1^+ promoted photochemically by compound 2.

nal chains exhibit some structuring and are not completely dense. At this stage the external membrane has already developed. A representative image is shown in Figure 3a. If at



Figure 3. Selected TEM images showing the changes in the polymer particle morphology towards the formation of vesicles under the effect of a focused electron beam recorded a) almost immediately and after b) 2, c) 4, and d) 8 min exposure time (scale bars = 200 nm). The instrument operating voltage was 100 keV.

this moment, at which the presence of internal polymeric chains in the spherical particles is clearly visible, we take TEM images at different exposure times using a sufficiently high-power electron beam, changes in the morphology of the particles can be observed with the internal polymeric material migrating towards the wall to create an empty internal space and thicker external walls. The results of this in situ experiment are shown in Figure 3. From this experiment it can be deduced that the electron beam causes the migration of the internal polymeric chains towards the peripheral wall, an effect that we suggest also occurs spontaneously by capillary forces during the thermal evolution and aging of the particles. This migration of the internal polymer chains promoted either by focalized electrons in a few minutes or spontaneously during the thermal curing of the system leads to the formation of the thick external walls of the vesicles. This reorganization produces the empty internal volume of the liposomes.

The different stages through which the vesicles are formed also explains why, for sufficiently cured samples, images such as those presented in Figure 1, left show vesicles with a clearly defined internal void, whereas for insufficiently cured samples, such as those shown in Figure 3a and b and even Figure 1, right, the polymer particles still contain polymer chains inside their volume.

Gold nanoparticles inside polymeric spheres: One of the aims of our work was to show that particles obtained by the self-assembly of imidazolium 1^+ can be used to organize spatially nano objects. With this in mind, and after studying the polymerization of monomer 1^+ , the next step was to show that it is possible to prepare gold nanoparticles inside the polymeric particles derived from 1^+ (P1) and even to show the catalytic application of our systems in gold-catalyzed oxidation reactions.

We thought that the cationic head of the imidazolium ionic liquid precursor would interact with anionic tetrachloroaurate through coulombic forces during all the stages of polymer formation and that, later, the location of the gold nanoparticles in the polymeric particles would be largely determined by the position of the imidazolium heads. Thus, due to ion pairing with the imidazolium units, tetrachloroaurate should occupy the same positions as the imidazolium heads. Subsequently, the reduction of $AuCl_4^-$ and metal nanoparticle formation would lead to gold nanoparticles that should associate with the polymer particles and be located inside and outside of the polymeric particles.

However, when persulfate polymerization of imidazolium monomer 1^+ was attempted in the presence of AuCl₄⁻, it was observed that the presence of this metal complex severely interferes with the mechanism of the radical polymerization and samples of polymeric vesicles like those described in the absence of AuCl₄⁻ could not be obtained satisfactorily under the same conditions.

We circumvented this problem by performing the polymerization of monomer 1^+ and the formation of gold nanoparticles from tetrachloroaurate photochemically rather than thermally. It has previously been reported that the formation of gold nanoparticles up to a particle size 10 nm can be promoted efficiently by UV light irradiation by employing the same photocuring agents as those used in the radical polymerization of alkenes.^[34-36] Thus, it could be that the same photochemical process is able to effect simultaneously the formation of gold nanoparticles and the polymerization of the double bonds of monomer 1^+ . This was confirmed ex-

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perimentally and we were able to obtain an **Au-P1** sample in which the gold nanoparticles are embedded in the micrometric polymer particles. Scheme 4 summarizes the process-



Scheme 4. Concurrent process leading to the formation of gold nanoparticles inside the vesicles on irradiation of a mixture of $1/AuCl_4/2$.

es that occur simultaneously upon irradiation of $1/\text{AuCl}_4/2$ mixtures in water. To effect this polymerization, we adapted the procedure used for the preparation of the polymeric nanoparticles by adding, after stirring for 1 h, a solution of NaAuCl₄ and then the photocuring agent **2** to give a mixture of $1/\text{AuCl}_4/2$ in a molar ratio of 0.16:0.064:0.32. The mixture was then irradiated with UV light ($\lambda > 300$ nm) at room temperature. Also in this case, the polymerization was conveniently followed by ¹H NMR spectroscopy by monitoring the disappearance of the signals of the vinylic protons. At the end of the reaction we observed the characteristic color of gold nanoparticles. Figure 4 shows photographs before and





BEFORE IRRADIATION

AFTER IRRADIATION

Figure 4. Photographs showing the color of solutions of the imidazolium ionic precursor 1^+ in the presence of photocuring agent 2 before and after irradiation in the presence and absence of NaAuCl₄. Left- and right-hand images correspond to solutions with and without NaAuCl₄, respectively.

after irradiation of solutions of the imidazolium ionic precursor 1^+ in the presence of photocuring agent 2 with and without tetrachloroaurate.

In accord with the formation of spheres in the polymerization of 1^+Br^- by photocuring, the **Au-P1** samples also consisted of submicrometric polymeric particles. TEM images of **Au-P1** samples obtained by photochemical curing recorded after extraction with dichloromethane show the formation of the expected spherical polymer particles of submicrometric diameter containing in their interior a considerable number of small-sized gold nanoparticles. The image shows that the synthesis solution does not contain any gold nanoparticles that are not associated with the polymeric particles.

Figure 5 shows some selected images that illustrate the type of polymer-encapsulated gold nanoparticles that can be obtained. As can be seen, the density of the gold nanoparti-



Figure 5. Selected TEM images showing the **Au-P1** structure before (top and bottom left) and after (bottom right) their use as a catalyst in the aerobic oxidation of 2-hydroxybenzyl alcohol (see below).

cles increases significantly as we approach the center of the polymer particle. We even notice that the gold nanoparticles in **Au-P1** are almost exclusively formed inside the polymeric particles and not on the external surface. The average size of the gold particles is about 10 ± 5 nm, which is in the range of values previously reported for the photochemical formation of gold nanoparticles using compound **2** as the photocuring agent.^[34-36]

The reasons for this preferential internal location of the gold nanoparticles are most probably the previously commented morphology of the polymeric spheres and the mechanism of aggregation and shaping of the monomer 1^+ . Thus, the internal polymer chains observed in the TEM images of the spheres indicate that most of the imidazolium rings occupy internal positions. As a result of ion pairing, most of the gold atoms in AuCl₄⁻ should therefore be located inside the polymer particle and as the gold nanoparticles evolve, their formation should occur inside the polymer particles, as is observed.

Thus, the incorporation of gold nanoparticles in the polymer particle by preassociation between $AuCl_4^-$ and imidazolium is a simple and highly efficient methodology for obtaining these entities in a single step without dedicated polymer synthesis.

To address the effects of monomer structure and the cross-linking process on the morphology of the resulting **Au-P1** particles, we performed an analogous experiment using cetyltrimethylammonium bromide (CTAB) instead of 1^+Br^- as the surfactant. CTAB is a widely used structure-directing agent and its ability to form micelles is firmly estab-

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lished. Ion pairing should work similarly for both 1^+Br^- and CTAB, and this phenomenon should control the location of the gold nanoparticles. The differences between the particles derived from 1^+Br^- or from CTAB should arise from the differences in the self-assembly and the chain cross-linking of these two complexes.

When a micellar solution of CTAB containing $AuCl_4^-$ was submitted to photocuring using compound **2** to generate the gold nanoparticles under identical conditions to those used for **Au-P1**, TEM images revealed that gold nanoparticles (10–15 nm particle size) were present throughout the solution and mostly unassociated with the CTAB micelles. Figure 6 shows an image of the resulting Au–CTAB sample.



Figure 6. TEM image obtained after the photocuring of a micellar solution of CTAB containing $AuCl_4^-$. The image shows small gold nanoparticles (10–15 nm) in high contrast and the larger CTAB micelles (5–150 nm) in low contrast. The scale bar corresponds to 200 nm.

It is reasonable to assume that the rigid membrane of the liposomes and the internal location of $AuCl_4^-$ should trap the gold nanoparticles after their formation in the liposomes. However, in the micelles derived from CTAB, the gold nanoparticles are free to diffuse into the aqueous solution, where they are predominantly observed. This control experiment illustrates well the advantages of using a strategy similar to that used with the ionic liquid **1**⁺**Br**⁻.

Catalytic activity of Au-P1 samples in the aerobic oxidation of 2-hydroxybenzyl alcohol: Numerous studies have shown that metal nanoparticles can be dispersed in imidazolium ionic liquids and that these solutions are efficient, reusable homogeneous catalysts for hydrogenation reactions.^[37-39] In a certain way, **Au-P1** is a polymeric analogue of these liquid systems because the gold nanoparticles in **Au-P1** will also be surrounded by imidazolium rings. Thus, the catalytic properties of **Au-P1** are of general interest in the context of extending the use of ionic liquids in solid systems.

To explore the activity of our **Au-P1** system as a heterogeneous catalyst for selective oxidation reactions, we selected the aerobic oxidation of the primary alcohol 2-hydroxybenzyl alcohol (HBA). The current demand for environmentally friendly processes requires the development of green oxidation methods that employ clean oxidants and reaction media and do not generate waste.^[40-42] HBA was oxidized at neutral pH by using molecular oxygen in water at 90 °C. Under these conditions, the **Au-P1** nanoparticles obtained by photocuring were directly used without any additional process.

As anticipated, after 24 h salicylaldehyde was obtained with a selectivity of 99% and a yield of 33%. The total mass balance was 64%, which indicates that some residual material is adsorbed on the polymeric spheres, which were not analyzed. Extraction showed additional amounts of HBA to close the mass balance. In addition, we did not observe the formation of the corresponding hydroxybenzoic acid and, therefore, the process is highly selective for the oxidation to aldehyde without over oxidation to the carboxylic acid. TEM images of the catalyst before and after the reaction show that the structure and morphology of the Au-P1 particles remain unaltered during the reaction (Figure 5). Au-P1 can be easily separated from the reaction medium and recycled for two consecutive runs without a decrease in its activity. Even though the present process gives a moderate yield, the results obtained demonstrate that our system can be used as a heterogeneous catalyst for the oxidation of primary alcohols.

Conclusion

An imidazolium ionic liquid bearing two C_{11} alkenyl chains with terminal C=C double bonds is a versatile monomer that undergoes self-assembly in water and after thermal or photochemical polymerization gives cell-like or spherical particles. We have shown that the spherical particles transform into cell-like polymeric liposomes. We have taken advantage of the internal location of the majority of the imidazolium units and their ion pairing with AuCl₄⁻ ions to form gold nanoparticles inside the polymeric structure. The resulting material, which consists of gold nanoparticles ($10 \pm$ 5 nm average size) embedded within the polymer structure, exhibits notable catalytic activity for the selective aerobic oxidation of 2-hydroxybenzyl alcohol to salicylaldehyde.

Experimental Section

General: All the materials used in the present investigation were commercially available and used as received. Combustion chemical analyses to determine the organic content was performed in a FISONS CHNOS analyzer. FTIR spectra were recorded with a Nicolet 710 spectrometer with the samples prepared in KBr disks. ¹H and ¹³C NMR spectra were recorded with a Varian Gemini 3000 spectrometer at 300 and 75 MHz, respectively. The reactions were monitored by NMR spectroscopy by taking an aliquot of 5 mL from the quartz tube at 3 h time intervals. The water was evaporated and the remaining solid was redissolved in CDCl₃ to record the ¹H NMR spectra. The TEM experiments were carried out using a Philips CM300 FEG system with an operating voltage of 100 kV. SEM images were obtained with a JEOL JSM-5410 instrument operating at 20 kV.

Synthesis of the monomer $N_{,N'}$ -bis(10-undecenyl)-2-methylimidazolium bromide: Triethylamine (1.2 equiv, 7.3 mmol, 0.738 g, 1.017 mL) and 11bromoundecene (2 equiv, 12.2 mmol, 2.84 g, 2.66 mL) were added to a solution of 2-methylimidazole (6.1 mmol, 0.5 g) in toluene (50 mL). The mixture was stirred at 90 °C for 48 h and filtered to remove the ammonium salt formed during the course of the reaction. Then the toluene was evaporated and the resulting oil was washed several times with hexane until a yellowish powder was formed (0.282 g, 56.5%). The purity of 1⁺

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 ${\bf Br}^-$ was checked by reversed-phase HPLC using a C-18 column and a mixture of methanol/acetonitrile (3:1) as eluent and a diode array as detector.

¹H NMR (300 MHz, DMSO): δ = 7.733 (s, 2H), 5.877–5.716 (m, 2H), 5.024–4.878 (dd, J_1 =5.017, J_2 =4.952, 4H), 4.156–4.039 (t, J_1 =4.138, J_2 = 4.114, J_3 =4.090 Hz, 4H), 2.624 (s, 3H), 2.069–1.952 (m, 4H), 1.775–1.658 (m, 4H), 1.363–1.128 ppm (m, 24H); ¹³C (75 MHz, D₂O): δ =138.284, 121.575, 113.82, 48.007, 33.498, 29.34, 28.968, 28.695, 25.758, 9.732 ppm; elemental analysis calcd (%) for C 64.0, H 10.40, N 6.15; found: C 63.1, H 10.35, N 6.29.

Synthesis of liposomes

Thermal polymerization: The as-prepared imidazolium ionic liquid (0.2 mmol, 0.0775 g) was dissolved in water (50 mL) and stirred for 1 h to allow the self-organization of the monomer. After this time, a catalytic amount of potassium persulfate (30 mg) was added to the solution. The solution was stirred for 24 h at three different temperatures: 40, 60, and 100 °C. Under these conditions, the polymerization was confirmed by ¹H NMR spectroscopy since the signals corresponding to the C=C double bonds decrease. The solution was allowed to cool to room temperature and centrifuged at 9000 rpm for 30 min. The supernatant liquid was removed and after lyophilization of the remaining solid, a white powder was obtained (yields: 65, 68, and 72 % for polymerization at 40, 60, and 100 °C, respectively).

Photopolymerization: Polymerization by the photochemical pathway was carried out by irradiating the samples with UV light through quartz tubes under nitrogen. In this procedure the imidazolium ionic liquid (0.16 mmol, 0.062 g) was dissolved in water (20 mL) and stirred at room temperature for 1 h. The water-soluble 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (**2**; 0.32 mmol, 0.066 g) was dissolved in water (20 mL) and added to the monomer solution after completion of the monomer self-organization. The solution was irradiated for 12 h and the polymerization was monitored by ¹H NMR spectroscopy until the signals corresponding to the C=C double bond had almost disappeared. Once irradiation was complete, the solution was washed with dichloromethane (3×40 mL) and the aqueous layer was reduced to 10 mL. The remaining solution was lyophilized to give a white powder (0.0332 g, 53.5%).

Synthesis of gold nanoparticles inside the polymeric spheres

Thermal method: The imidazolium ionic liquid (0.2 mmol, 0.0775 g) was dissolved in water (40 mL) and stirred under nitrogen for 1 h. Tetrachloroauric acid (0.04 mmol, 0.016 g) dissolved in water (10 mL) was added to this solution, which was stirred for 30 min. Then potassium persulfate (30 mg) and ascorbic acid (70 mg) were added to the above solution and the temperature was maintained at 40 °C for 24 h. The solution was then centrifuged followed by lyophilization to give the corresponding polymeric spheres as the final material (0.0362 g, 42 %).

Photochemical method: The photochemical polymerization was carried out by irradiating the samples with UV light through quartz tubes under nitrogen. The imidazolium ionic liquid (0.16 mmol, 0.062 g) was dissolved in water (15 mL) and stirred at room temperature for 1 h. Next, tetrachloroauric acid (0.016 mmol, 0.008 g) dissolved in water (5 mL) was added to this solution, which was stirred for 30 min. Then the water-soluble 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (2; 0.32 mmol, 0.066 g) was dissolved in water (20 mL) and added to this solution. The solution was irradiated for 12 h and the polymerization was monitored by ¹H NMR spectroscopy until the signals corresponding to the C=C double bond had almost disappeared. Once irradiation was complete, the solution was washed with dichloromethane (3×40 mL) and the aqueous layer was reduced to 10 mL. The remaining solution was lyophilized to give a powder with a color characteristic of gold nanoparticles (0.035 g, 45.2%). Another two samples were prepared with molar ratios of 1⁺/AuCl₄ of 0.016:0.032 and 0.016:0.064, keeping the concentrations of 1^+Br^- and 2 constant. The exact molar ratio of $1^+Br^-/HAuCl_4/2$ was 0.16:0.032:0.32 or 0.16:0.064:0.32. The catalyst employed for the oxidation of 2-hydroxybenzyl alcohol was the one prepared with 0.064 mmol of HAuCl.

An analogous procedure was performed using an aqueous solution (20 mL) of cetyltrimethylammonium bromide $(10^{-3}\,\rm M),~HAuCl_4~(10^{-4}\,\rm M),$

and 2 (10^{-3} M). The irradiation was carried out through quartz under nitrogen for 12 h.

Procedure for the catalytic oxidation of 2-hydroxybenzyl alcohol: 2-Hydroxybenzyl alcohol (50 mg) was dissolved in a solution of potassium phosphate (170 mg) and the catalyst in water (40 mL) under oxygen in a 50 mL round-bottomed flask fitted with a silicone septum. The reaction mixture was maintained at 90 °C on a hot plate for 24 h. After the required time, the solution was extracted with dichloromethane (2×10 mL) and the combined extracts were dried over anhydrous sodium sulfate. Then the percentage conversion and yield were determined by gas chromatography on a Hewlett-Packard 5890 series II instrument equipped with a FID detector and using a known amount of nitrobenzene as the external standard.

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