One-Pot Synthesis: Polymers, Hydrogel and Nanoparticles from Natural Extracted Green Materials

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Abstract: The development of green nanomaterials from renewable resources is the utmost importance in a context of sustainable development. In this work, we describe the preparation of green nanomaterials of polymer, nanoparticles and hydrogel that arise from the natural extraction of β-myrcene and ocimene using air/water as a catalyst in one pot. Interestingly, we noticed the polymerization of myrcene in situ condition with attaining high molecular mass and low polydispersity index. The explanation of the polymerization kinetics that were investigated through nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC). Importantly, we elucidated the preparation of green hydrogel by using water as a crosslinking agent. Further, we also described green nanoparticle formation by using emulsion method. The nanoparticles that obtained were 130 ±10 nm in terms of size and were found to be monodispersed. With these novel 'green nanomaterials', we project that they will be beneficial to multiple nanotechnological applications.

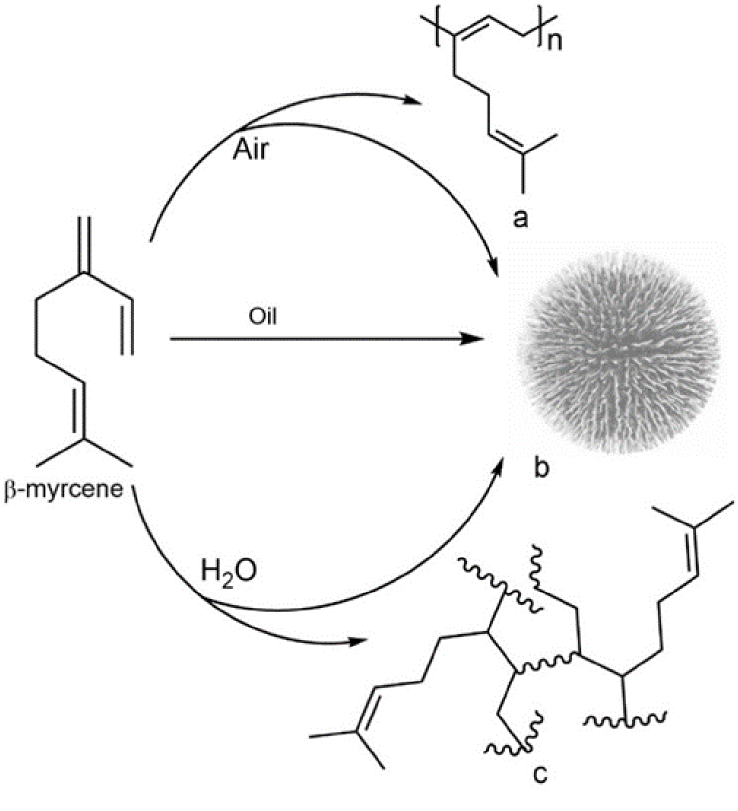
Introduction

Over the last few years, nanomaterials have achieved superior performance in many applications, such as in medicine, advanced manufacturing, and energy technologies[1-3]. The only disadvantage currently is that most of the materials and processes are restricted to just nonrenewable resources, and they also create wastes that are hazardous[2-5]. Taking these factors into consideration, green nanotechnology, a union of nanotechnology and principles together with the practices of green chemistry can be of great assistance in ensuring the safe environment in the 21st century. Green chemistry is defined as a set of principles or a chemical philosophy that enhances the design of given products and also processes that lower or completely eliminate the usage and creation of substances that are hazardous[6,7]. In today's society, green nanotechnology practices mostly incorporate the use of nonhazardous solvents, natural sources, and energy efficient processes that help in the establishment of nanomaterials. Over the past several years, sustainable development has become one of the main focuses in the field of macromolecular science and technology[8-11]. Renewable sources of energy are seen as useful in both academia and industry, notwithstanding the bleak demonstration of future materials that are fossil-derived[12-15]. There have been several attempts to arrive at new polymers so as to replace fossil-derived polymers with alternatives that are sustainable. Recently, terpenes have been demonstrated as robust building blocks for sustainable polymers as they are also extracted in large quantities and are available from many plants. In recent publications, a conjugate diene structure, β-myrcene (7-methyl-3-methylene-octa-1,6-diene), that is part of the extensive terpene family, has been investigated. One example is illustrated by Liu et al,[16] who described the homo- and copolymerization of β-myrcene by incorporating a catalyst, known as lutetium, that is highly active. On the other hand, Bolton et al. prepared a triblock polymer that employed β-myrcene and α-methyl-p-methylstyrene in a specific living polymerization process[17-20]. Others who have carried out similar investigations are Georges et al. and Loughmari, who both reported stereoselective polymerization with β-myrcene utilizing a lanthanide catalyst. They also examined microstructure with an accurate high-field Nuclear Magnetic Resonance (NMR) spectroscopy [21-24].

To the best of our knowledge, the formation of nanoparticles and hydrogels in relation to the green materials from ocimene and myrcene is minimum. There was still a challenge in the preparation of the naturally extracted monomers, hydrogel, and nanoparticles as they are reactive and have long chains. Here, we describe the preparation green nanomaterials, polymers, nanoparticles and hydrogel formation in one pot synthesis using air and water which act as a catalyst and crosslinking agent, respectively. It was noted that myrcene is very reactive and will even oxidize when exposed to air at room temperature, and this influenced the polymerization process under mild conditions. Myrcene was an important factor during the preparation of hydrogels. 10% of ocimene and 85% of myrcene was an optimum composition in the formation of hydrogel and nanoparticles. The nanoparticles that obtained were 130 ±10 nm in terms of size and were found to be monodispersed. A confirmation that the nanoparticles were spherical in shape and the size through DLS and FESEM established that the crosslinked precursor was situated externally. These results clearly show that the new green materials can be utilized in novel nanotechnology applications.

Results and Discussion

In nanotechnology, there is a combination of green chemistry techniques and nanotechnology applications that are the major components of this area and quite vital. In the field, natural materials are being used to synthesize nanomaterials and also, the design of the benign synthetic processes are required to be environmentally acceptable. View of this, we describe the preparation of green nanomaterials, polymers, nanoparticles and hydrogel in one pot synthesis, see Scheme 1 and Figure 1.



Scheme1. Synthesis of green polymeric materials and hydrogel from β-mercene monomer.

Firstly, myrcene and ocimene were exposed to air for up to 60 minutes with stirring, during this time the monomers completely polymerized, see the, Figure 2a.

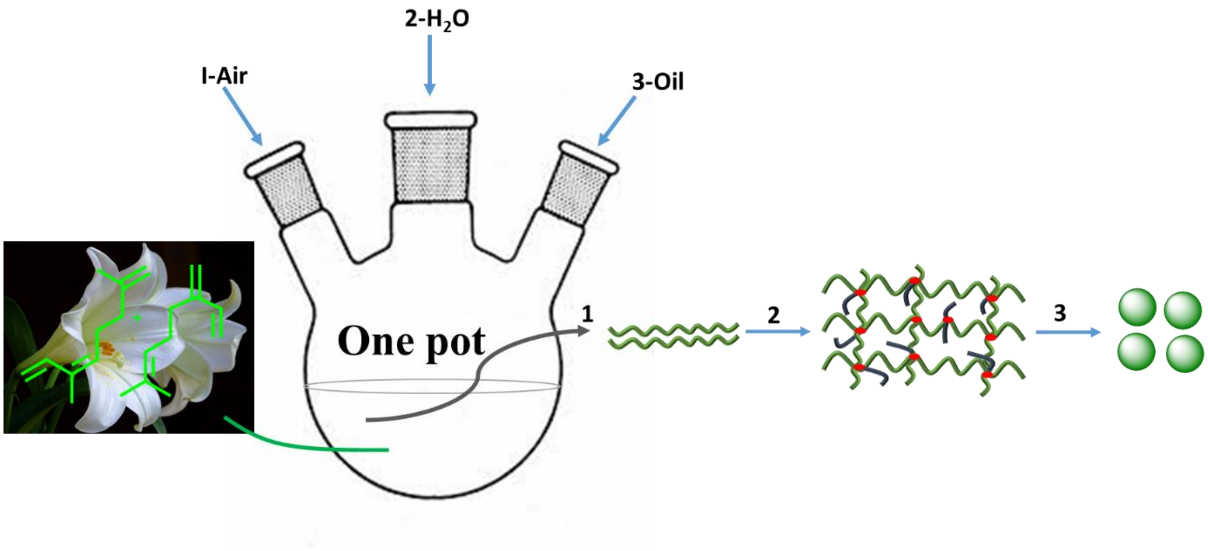


Figure 1. Graphical representation of one pot synthesis of myrcene with different nano-structures. 1- air catalyzed formation of polymer chain, 2-H_2O oxidation development of crosslinking gel and 3- oil emulsification producing nanoparticles.

These monomers are highly reactive to air and can polymerize under such conditions, see Scheme 1 and Figure 2. Myrcene is one of the oxygenated terpenes, this oxygenated derivative actually came from the initial terpenes, more specifically from a photo-oxidation process. In this way, terpene photo-oxidation leads to the formation of allylic hydroperoxides, which will soon generate alcohols when losing an oxygen atom. Terpenes forms linear alkanes, esters, fatty acids or alcohols, as a result of isomerization of processes, dehydration, cyclisation and photo-oxidation during the manufacture of hashish, see Scheme S1.

In the preparation, myrcene and ocimene were kept open so as to be exposed to air for about 60 minutes while stirring, and in the process, the monomers polymerized completely. In monitoring the polymerization kinetics, NMR was GPC employed. Taking NMR analysis into account, we established that myrcene is more reactive compared to ocimene in air. After exposing both the monomers to air for roughly 60 min, it was noted that myrcene had completely polymerized. Analysis of the sample was carried out between 5 to 60 minutes of stirring. Myrcene is known to be very reactive when exposed to air, and so it begins to polymerize with five min of stirring time. In 30 min time, approximately 50% of the myrcene was polymerized. Confirmation came from NMR based on the vinyl bonds disappearing at 6.3 ppm and 4.9 ppm, see Figure 2a.

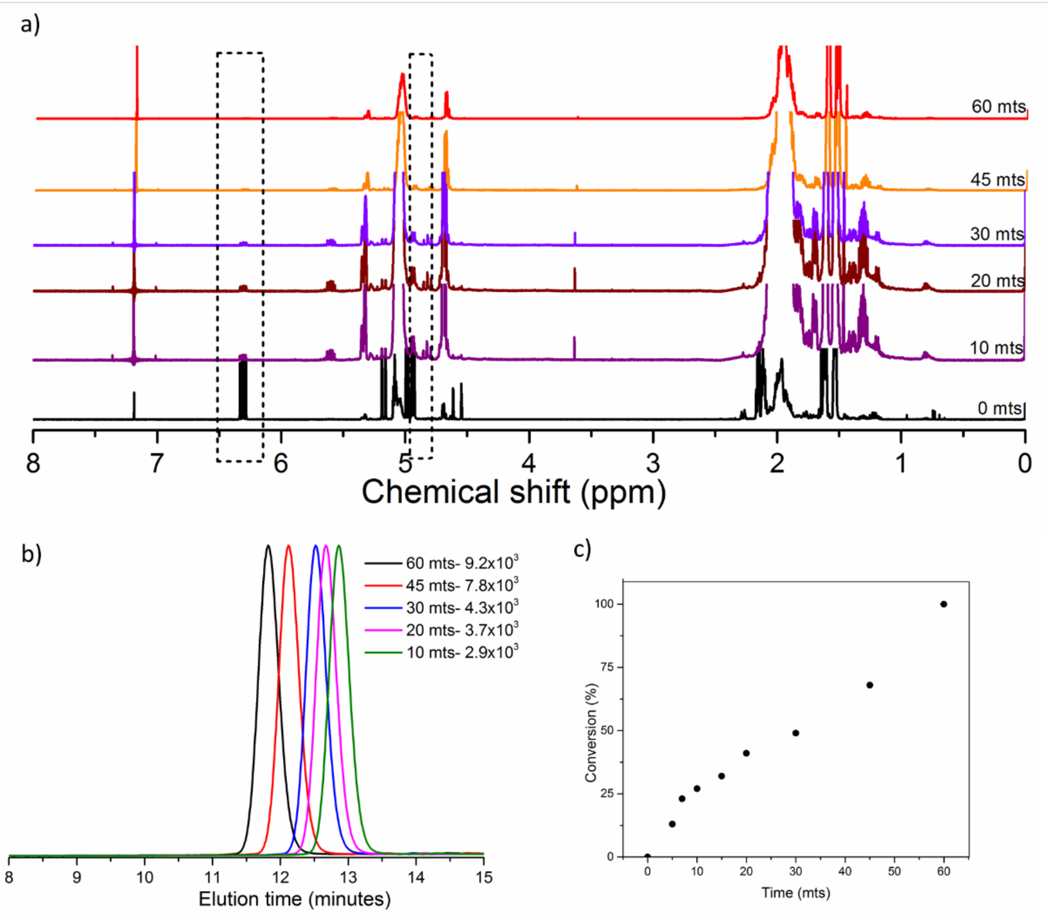


Figure 3. NMR and GPC spectra of polymerization kinetics. a) 1HNMR spectra of poly(myrcene-ocimene) with different intervals of time. b) GPC chromatogram of copolymer and c) conversion of copolymer composition with time intervals.

In the characterization of gel permeation chromatography (GPC) of the copolymer, THF was utilized as a standard eluent and polystyrene (PS) as a standard. Over the course of the reaction, it was noted that the molecular weight varied from 2900 g/mol to approximately 9200 g/mol. In the first 10 minutes, the molecular weight was roughly 2900 g/mol, which meant that only 15% was converted while air was being used as a catalyst in the polymerization process, see Figure 2b. When 30 minutes of reaction time had been reached, 53% of the conversion was completed and the molecular weight was found to be 4300 g/mol. Later, after 60 min of stirring time, the monomer was polymerized entirely, and the molecular weight was established to be 9200 g/mol (see Figure 2b). The results from these reactions show the kinetics of myrcene and ocimene copolymerization with air acting as a catalyst.

In another instance, the Fourier Transform Infrared (FTIR) spectroscopy affirmed the disappearance of the double bond that existed in the copolymer. Thus, it is important to note that the poly(myrcene-ocimene) copolymer was produced in both of the two cases as validated by FTIR and NMR spectroscopy. Previous reports have shown that once myrcene is exposed to air, it undergoes the process of oxidation and later forms a structure which is cyclic, though this condition takes a period of three days. As observed, the characteristic C=O vibration maximum that arises from the ester bond was established to be 1730 cm^{-1} as portrayed in Figure 3. The myrcene monomer was included and that is why there is a retention in the peak of the poly(myrcene-ocimene) copolymer.

Hydrogel preparation

Next, continuation in the same pot (after 10 minutes of stirring), when the myrcene monomer was just added into water and quacked for five min, we observed hydrogel formation without any crosslinking agent (Figure 3a). In FTIR we observed the disappearance of the two-vinyl bond of monomers A and B (1187 cm^{-1} and 1143 cm^{-1}), see Figure 3b.

To get a clear understanding of the process, we resorted to testing various conditions. As a result of the oxidation levels of myrcene, it was noted that at low temperatures (5°C), the formation of the gel was slow after myrcene/ocimene had been added to water, but when the conditions were at room temperature, gel formation was immediate. It is worth commenting that myrcene has no stability in air and thus will only polymerize if there is no oxidation.[25-29] As the weight of the β-myrcene moiety increased, so did the gel content of the copolymers.[29,30] The double bond that was present in the β-myrcene unit enhanced and promoted formation of micro-crosslinks that were in between the polymer chains, hence leading to an increase in the proportion of the gel. To put forth, the yield of the copolymer ranged from 80% to 93% and it rose as a result of an increase in the myrcene content present in the copolymer gel. Using field emission scanning electron microscopy (FESEM, see Figure S3a), the gels nature was established.

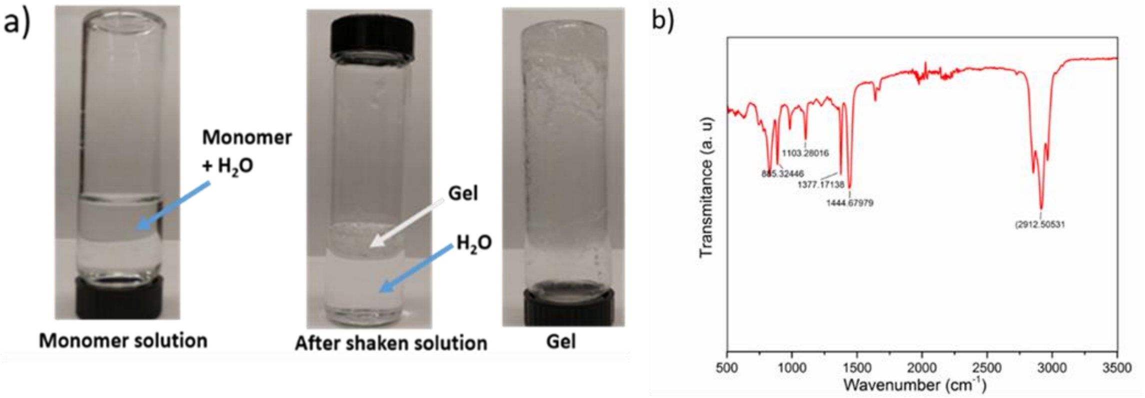


Figure 4. Synthesis of gel without cross-linking agent and initiator, monomer solution and water was just shaken and the gel crosslinked separated from system. And b) FTIR spectra of the hydrogel.

Nanoassembly /nanogel preparation

Finally, In the same flask (after shaking with water for 5 minutes), we added tetra butyl ammonium bromide surfactant dissolved in toluene (oil phase). The reaction was heated to 70˚C for 6 hours. The ethanol was used to remove surfactant and water from the system, centrifuged and finally freeze-dried. FESEM reveals that nanoassmbly were spherical in shape but size was not uniform, see Figure S3b. Hence, we decided to perform UV crosslinking microemulsion process to get homogeneous nanoparticles. In the formation of nanoparticles, we decided to introduce a bis-acrylamide as a crosslinker. It was a surprise to witness nanofibers forming after just an hour when there was an exposure to UV light. When the stirring time was increased to three hours, nanoparticles were formed. In obtaining the crosslinks AB monomers (A- myrcene and B-ocimene), the ratio of the monomers A to B is crucial. In examining, myrcene is reactive and will always form a gel through linking with bis-acrylamide, but we make a particular note that ocimene at room temperature is not reactive. During the process, monomer A was subjected to heating to a temperature of 50°C for roughly 15 min, after which monomer B was added to this mixture. We carried out a variation of monomer B from 5% to nearly 50%. As the concentration of B was adjusted to a higher level, we observed that the formation of nanoparticles was difficult. Various tests were performed, but we came to the conclusion that having 10% monomer B with 4% bis-acrylamide crosslinker, 85% monomer A, and 1% of photo initiator were the optimal conditions for crosslinking of the AB, resulting in the formation of a nanoparticles, see Figure S3b. The nanoparticles were monodispersed with the size of 130 nm. FESEM confirms that nanoassembly were in spherical shape and DLS confirm the size and homogeneity of the nanoparticles, see Figure S3. Emulsion copolymerization involves several processes and it is always controlled by many factors, though the process appears easy to regulate.[2,30,31] Factors such as the partitioning nature, polarity, and water solubility, which involve the monomers play a vital role in the emulsion copolymerization criteria. We also tried by simple emulsion technique to fabricate polymer nanoassembly. In this situation, we used sodium dodecyl sulfate as a surfactant. Here, we observed that we could also prepare polymer nanoassembly but the size was not homogeneous, see Figure S3.

This illustration symbolizes a reliable way of preparing a bio-based hydrogel and nanoparticles that are pegged to β-myrcene, ocimene, and renewable synthons during the initial processes. In the establishment of the hydrogel and nanoparticle preparation, the weight ratio that involved the monomers became an important factor. However, to get high molecular weight (more than 10 k g/mol) emulsion or radical polymerization needs to be considered.

Conclusions

In conclusion, we report a simple and novel method to prepare a green material of polymer, nanoparticles and hydrogel in a one-pot synthesis. The polymerization of myrcene and ocimene was achieved using air as a catalyst and the attained molecular mass was high with low PDI. In the establishment of the hydrogel and nanoparticle preparation, the weight ratio that involved the monomers became an important factor. It was noted that myrcene is very reactive and will even oxidize when at room temperature and this influenced the polymerization process under mild conditions. However, when a good polydispersity index and a high molecular weight is needed, emulsion polymerization ought to be considered. Myrcene was an important factor during the preparation of hydrogels. 85% of myrcene and 10% of ocimene was an optimum composition in the formation of hydrogel and nanoparticles. The nanoparticles that obtained were 130 ±10 nm with spherical in shape was confirmed by DLS and FESEM technique. The results clearly show that these new green materials can be utilized in the new nanotechnological applications.

Experimental Section

Experimental Methods. All chemicals and solvents were purchased from Sigma-Aldrich at the highest purity available and used without further purification.

General procedure to One pot synthesis of green materials. 1 g (0.12 mmol) of β-myrcene and 0.5 g (0.06 mmol) ocimene were stirred at 35°C in an open atmosphere for one h. The viscous solution was characterized by NMR and FTIR. Next, the synthesis of myrcene ocimene gel was carried out with 0.8 mmol of myrcene and 0.08 mmol of ocimene was added to 10 ml vial. 5 ml of water was added to the monomer vial and shaken for a couple of minutes. Viscous gel was then separated from the homogeneous solution mixture (a small sample was taken out and water was removed from the system with the lyophilized). Finally, 0.8 μmol of ammonium persulfate and 1.5 μmol of bisacrylamide was added to this solution. 5 mmol of dodecylsuphate (DDS) was added to the mixture and heated for 70°C for 24 h. Anothe process via 5 mmol of tetrabutylammonium bromide in toluene was added to the mixture and stirred for 4 h under UV light at 365 nm was executed. The organic solvent was evaporated, centrifuged, and washed with ethanol. The centrifuged particles were lyophilized for SEM characterization.

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Keywords: Green Chemistry • Myrcene • Ociemene • Natural monomers • Air sensitive monomers.

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