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Investigation of emulsion gel polymerization of polystyrene using Saponin-based biosurfactants

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Abstract

Emulsion gel polymerization offers an efficient approach to enhance polymerization processes by allowing lower processing temperatures, resulting in both environmental and industrial advantages. This research employed biosurfactants, particularly crude soapnut extract (SE), which contains saponin-based surfactants as a replacement for traditional synthetic surfactants such as cetyltrimethylammonium bromide (CTAB), used in the emulsion gel polymerization of styrene. Polymerization involved styrene as the monomer, azobisisobutyronitrile (AIBN) as the initiator, fumed silica (FS) as the gelling agent, and SE as the surfactant. Saponin-based biosurfactants were obtained through maceration extraction of soapnut fruit (*Sapindus sp.*), and polymerizations were performed at room temperature for 24 h. The polymerizations were carried out in two stages: first, a crude SE solution was used to evaluate the feasibility of polymerization using saponins in emulsion gels; subsequently, freeze-dried SE (FD-SE) powder was utilized to optimize the surfactant concentration. In both stages, monomer-to-polymer conversions exceeded 80%, with optimal surfactant amounts identified as 1.5 mL crude SE and 0.4 g FD-SE in 0.5 mL of water for 2.0 mL of styrene. Scanning electron microscopy (SEM) and ImageJ analysis showed that PS prepared with SE formed polydisperse, agglomerated particles (6–26 μm), likely due to the complex composition of crude SE affecting droplet stabilization. Differential scanning calorimetry (DSC) analysis showed a glass transition temperature (T_g) of 96 °C, which was lower than that of polystyrene synthesized using CTAB-based surfactants. Gel permeation chromatographic (GPC) analysis confirmed that all samples possessed sufficiently high molar masses for T_g to be independent of molecular mass, suggesting that the reduction likely arises from residual impurities or structural variations affecting chain packing. Despite this, the study successfully demonstrated the potential for synthesizing polystyrene at ambient temperature using saponin-based surfactants extracted from soapnut, highlighting the promise of exploring other natural surfactants for emulsion gel polymerization.

Keywords: Biosurfactants, Emulsion gel polymerization, Low-temperature polymerization, Polystyrene, Saponins.

Introduction

Emulsion gel polymerization has been extensively studied as an effective method for polymerizing vinyl monomers at reduced temperatures.[1-5] Emulsion gels are soft, solid-like materials containing emulsions within a gel network structure, exhibiting stable mechanical properties.[6] When it comes to industrial applications, synthetic considerations extend beyond temperature reduction to include factors such as polymer conversion efficiency, ease of polymer extraction, toxicity, and cost-effectiveness. In light of these considerations, the emulsion gel technique offers several desirable characteristics.[6] The polymerization process takes place within emulsion droplets embedded in a gel matrix.[6-8] The primary components of emulsion gel polymerization include the monomer, initiator, gelling agent, and surfactant.[1-6]

The emulsion gel polymerization technique has been predominantly applied to vinyl monomers.[1-5] This method has shown particular promise in producing well-defined composite particles, as demonstrated through the synthesis of polystyrene (PS) using high internal phase gels and cetyltrimethylammonium bromide (CTAB)-catalyzed in situ polymerization at room temperature.[1] Notably, polymerization conversions exceeding 90% have been achieved within one or a few days, depending on the composition of the emulsion under ambient conditions when using styrene in emulsion gel systems also containing, azobisisobutyronitrile (AIBN), CTAB, and fumed silica.[2] While styrene polymerizes efficiently at room temperature using this method, other monomers may require elevated temperatures to reach practical reaction rates. For example, methyl methacrylate (MMA) showed significantly slower polymerization at room temperature and required a temperature of 40 °C to achieve desirable conversion levels.[3] Similarly, the polymerization of vinyl acetate (VAc) using emulsion gel polymerization at 40 °C resulted in over 90% monomer conversion within 9 h.[4] The resulting poly(vinyl acetate) exhibited high molar mass and elevated glass transition temperatures compared to those produced through conventional bulk polymerization. These findings highlight the versatility of the emulsion gel polymerization approach, offering efficient pathways for synthesizing a variety of vinyl polymers with enhanced thermal and molecular properties under relatively mild conditions.[1-5]

Various types of synthetic surfactants have been employed in previous studies involving emulsion gel polymerization, with CTAB, a cationic surfactant, being the most widely used. One key study of room-temperature decomposition of azobisisobutyronitrile (AIBN) in emulsion gels yielded fundamental insights into polymerization at reduced temperatures for the development of novel materials with tailored properties.[9] That work highlighted the significant role of surfactants such as sodium dodecylsulfate (SDS) and CTAB in facilitating AIBN decomposition within the emulsion gel medium. When CTAB was used, the polymerization process was enhanced compared to systems without surfactant, which showed minimal polymerization activity. To explain the strong dependence of the polymerization rate on surfactant concentration, a model was proposed involving a surfactant-initiator complex in conjunction with standard free radical polymerization.[2] The observed decrease in overall activation energy with increasing surfactant concentration was identified as a key factor driving the enhanced reaction rate. It was also noted that the presence of the gelling agent, fumed silica, alone was insufficient to initiate or accelerate polymerization without the presence of a surfactant. Moreover, CTAB was found to play a critical role in gel formation, further underscoring its multifunctional importance in the emulsion gel polymerization process.[1-5]

Although research on synthetic surfactants in emulsion gel polymerization has shown promising results, the use of natural surfactants in this context remains largely unexplored. While there are a few studies which have investigated saponin-type biosurfactants in

conventional polymerization, their application in emulsion gel polymerization has not yet been reported. One notable study demonstrated the successful use of crude, microwave-assisted saponin extracts in the emulsion polymerization of styrene latex.[10] Without any further purification, the saponin-containing aqueous solution functioned effectively as a surfactant, stabilizing the emulsion and yielding monodisperse polystyrene latex particles. This highlighted the potential of saponins as natural, biodegradable, and sustainable alternatives to conventional synthetic surfactants, offering a reduced environmental footprint.[10] To the best of our knowledge, despite the broad utility of saponins in various fields, no studies have reported their use in emulsion gel polymerization systems. Therefore, the primary objective of the present study is to investigate the feasibility of using biosurfactants as substitutes for conventional synthetic surfactants like CTAB in emulsion gel polymerization at room temperature. Additionally, the study aims to identify the optimal concentration of the biosurfactant and evaluate the properties of the resulting polymers.

Experimental

Materials

Styrene (DAEJUNG Chemicals & Metals, South Korea) was used as the monomer. Basic alumina (Sisco Chemical Laboratories, India) was used to purify the monomer. The initiator was 2,2'-azobis (isobutyronitrile)-AIBN (Paras Polymer and Chemicals, India). The recrystallization process with methanol was carried out to purify AIBN. Purified styrene and AIBN were stored in a refrigerator. The gelling agent was fumed silica (CAB-O-Sil, M-5P-hydrophilic fumed silica from Cabot Corporation, Tuscola, IL, USA). Cetyltrimethyl ammonium bromide (CTAB, HiMedia Laboratories, Pvt. Ltd, India) was utilized as the reference surfactant. As for the source of biosurfactant, "saponin" extracted from soapnut fruit (purchased from a local Ayurveda Herbal shop, Sri Lanka) was used.

Saponin Surfactant Extraction

The outer pericarp of soapnut fruit (*Sapindus sp.*) was washed and dried at 40-60 °C for 48 h and then ground into a powder, followed by drying in a hot air oven for 5-6 h to remove moisture.[11] Maceration extraction was carried out using a 1:10 ratio of soapnut powder to distilled water. The mixture was continuously stirred using a magnetic stirrer for 4 h to facilitate the extraction process.[11] The mixture was vacuum filtered to obtain the crude saponin extract (SE) solution. This extract was stored under cold conditions and later freeze-dried (FD-SE) to yield the crude saponin powder.

Preparation of polymer samples

Styrene was purified using a basic alumina column to remove inhibitors and ensure suitability for polymerization. The initiator, azobisisobutyronitrile (AIBN), was purified via recrystallization in methanol. Both the purified styrene and AIBN were stored in a refrigerator to maintain a cool, dark environment and to prevent premature photo-initiation. To evaluate the quality and consistency of the purified reagents, a bulk polymer sample was prepared alongside a reference/control sample for comparison. The compositions of these samples are detailed in Table 1.

Table 1. Bulk, Reference, and Control Sample Compositions.

Sample and polymerization conditions	**Styrene (mL)**	**AIBN (g)**	**CTAB 0.25M**	**Fumed Silica (g)**
Bulk PS sample (70 ºC for 4 h)	2.0	0.04	-	-
Reference - Emulsion gel sample with CTAB as the surfactant (room temperature (RT) for 24 h)	2.0	0.04	0.5 mL	0.105
Control sample - (RT for 24 h)	2.0	0.04	-	0.105

Bulk polymerization was carried out by mixing purified styrene and AIBN in a glass vial and heating the mixture at 70 °C for 4 h. Following polymerization, the sample was dried under ambient conditions for 24 h to remove water and unreacted monomers and then dried in a desiccator for another 24 h. For the reference sample, an emulsion gel polymerization method was employed using CTAB as a surfactant. The reference emulsion gel samples were prepared

by adding 2.00 mL of purified styrene, 0.040 g of purified AIBN, and 0.105 g of fumed silica into a glass vial. The contents were mixed using a vortex mixer for 1 min. Then, 0.50 mL of 0.25 M aqueous CTAB solution was added, followed by an additional 1 min vortex mixing. The mixture was then kept in a dark environment at room temperature for 24 h to allow polymerization to proceed. Afterward, the sample was dried. A control sample was prepared using the same procedure, except the surfactant was omitted, in order to evaluate the effect of the surfactant on the polymerization process.

Preparation of polymer samples using crude saponin extract and crude saponin powder

The compositions of the samples prepared using crude SE and FD-SE are detailed in Tables 2A and 2B. The samples were prepared following the same procedure used for the reference emulsion gel sample. To determine the optimal surfactant concentration, the volume of crude SE solution varied from 0.50 mL to 2.50 mL (Table 2A). Due to practical difficulties in obtaining a stable emulsion at higher crude SE volumes, the crude SE solution was freeze-dried (FD-SE). Subsequently, several samples were prepared by varying the mass of FD-SE powder (0.1 g to 0.5 g) which was dissolved in 0.50 mL of water (Table 2B). Each sample was prepared in triplicate to ensure reproducibility and to calculate average polymerization conversion values.

Table 2A. The compositions of the samples prepared using crude SE solution. Each sample contained 2 mL of styrene, 0.04 g of AIBN, and 0.105 g of fumed silica.

Sample name	Surfactant	Volume of Crude SE solution
SE-0.5	Crude SE solution	0.50 mL
SE-1.0	Crude SE solution	1.00 mL
SE-1.5	Crude SE solution	1.50 mL
SE-2.0	Crude SE solution	2.00 mL
SE-2.5	Crude SE solution	2.50 mL

Table 2B. The compositions of the samples prepared using FD-SE powder. Each sample contained 2 mL of styrene, 0.04 g of AIBN, and 0.105 g of fumed silica.

Sample name	Surfactant	Mass of FD-SE*
FD-SE-0.1	FD-SE powder	0.1 g
FD-SE-0.2	FD-SE powder	0.2 g
FD-SE-0.3	FD-SE powder	0.3 g
FD-SE-0.4	FD-SE powder	0.4 g
FD-SE-0.5	FD-SE powder	0.5 g

* Expressed as the mass of crude FD-SE powder dissolved in constat amount of water (0.50 mL).

Determination of Polymerization Conversions

Polymerization conversions were determined based on mass measurements. Prior to the experiment, all glass vials were thoroughly cleaned and air-dried. The empty vials were first weighed, followed by weighing after the addition of styrene and other components, with each addition carefully recorded. After polymerization and subsequent drying in a desiccator, the final weight of each vial was measured. The polymerization conversion was then calculated using Equation 1.

$$\% \text{ Conversion} = \frac{\text{Yield mass} - \text{AIBN mass} - \text{FS mass} - \text{SE dry mass}}{\text{Mass of styrene}} \times 100 \quad (1)$$

where, yield mass = dry mass of the polymerized sample – mass of the empty vial

Polymer Isolation and Characterization

Scanning electron microscopy (SEM) was performed on the polymerized samples using a Carl Zeiss evo 18 instruments operated at an acceleration voltage of 10 kV. Prior to imaging, the samples were sputter-coated with a thin layer of gold to enhance conductivity and image quality. Particle size was measured by analyzing approximately 50 particles using ImageJ software.

A portion of the polymerized sample was dissolved in toluene and centrifuged at 4000 rpm for 20–40 min until a clear supernatant was obtained, allowing for the removal of fumed silica. The resulting supernatant was then poured into distilled water to precipitate the polystyrene (PS). The precipitated polymer film was thoroughly washed with distilled water to remove residual surfactant and subsequently dried under ambient conditions for 24 h.

Fourier-transform infrared (FTIR) spectroscopy was performed on the isolated polystyrene (PS) using a Bruker Alpha Spectrometer (Model: 1 003 1705) equipped with an attenuated total reflectance (ATR) accessory. Spectra were recorded in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}.

Thermal properties were analyzed using temperature-modulated differential scanning calorimetry (TMDSC) on a TA Instruments Q2000 DSC. Samples were heated from 0 °C to 160 °C at a rate of 3 °C/min, with a modulation amplitude of ±1 °C every 120 s. Each sample underwent two heating cycles and one cooling cycle to evaluate thermal transitions.

Molecular mass analysis was performed using gel permeation chromatography (GPC) via size-exclusion chromatography (SEC) with dimethylacetamide (DMAc) as the mobile phase. Measurements were carried out on a PSS SECurity² system, which included a SECurity Degasser, a SECurity TCC6000 column oven maintained at 60 °C, and a PSS GRAM column set comprising an 8 × 150 mm (10 µm) precolumn and three 8 × 300 mm (10 µm) analytical columns (1000 Å and 30 Å pore sizes). High-performance liquid chromatography (HPLC)-grade DMAc containing 0.01 M LiBr was used as the eluent at a flow rate of 1 $mL \cdot min^{-1}$. Calibration was performed using narrow-disperse linear polystyrene (M_n: 266 $g \cdot mol^{-1}$ to 2.52 × 10^6 $g \cdot mol^{-1}$) and poly(methyl methacrylate) (M_n: 202 $g \cdot mol^{-1}$ to 2.2 × 10^6 $g \cdot mol^{-1}$) standards (PSS ReadyCal). Prior to analysis, all samples were filtered through 0.22 µm PTFE membrane filters. Data analysis, including determination of molecular mass and dispersity, was conducted using PSS WinGPC UniChrom software (version 8.2).

Results and Discussion

Saponin Surfactant Extraction

Saponins extracted from the pericarps of soapnut fruits (*Sapindus sp*.) were chosen as the biosurfactant due to their strong surface activity, effective foaming properties, and low toxicity.[12] Although the crude extract from *Sapindus sp*. contains not only saponins but also a variety of other compounds, including cyanogenic glycosides, cyclitols, oleic acid (in some cases), and various phytochemicals such as flavonoids, triterpenoids, carbohydrates, fatty acids, phenols, and fixed oils, the extract was used without further purification.[13,14] This approach was intended to assess the feasibility of polymerization using the unrefined natural surfactant. Figure 1 depicts the images of (a) soapnut fruits (*Sapindus mukorossi*) (b) ground

soapnut fruit powder (c) extracted and filtered crude soapnut solution (SE) and (d) freeze-dried powder of crude extract of soapnut (FD-SE).

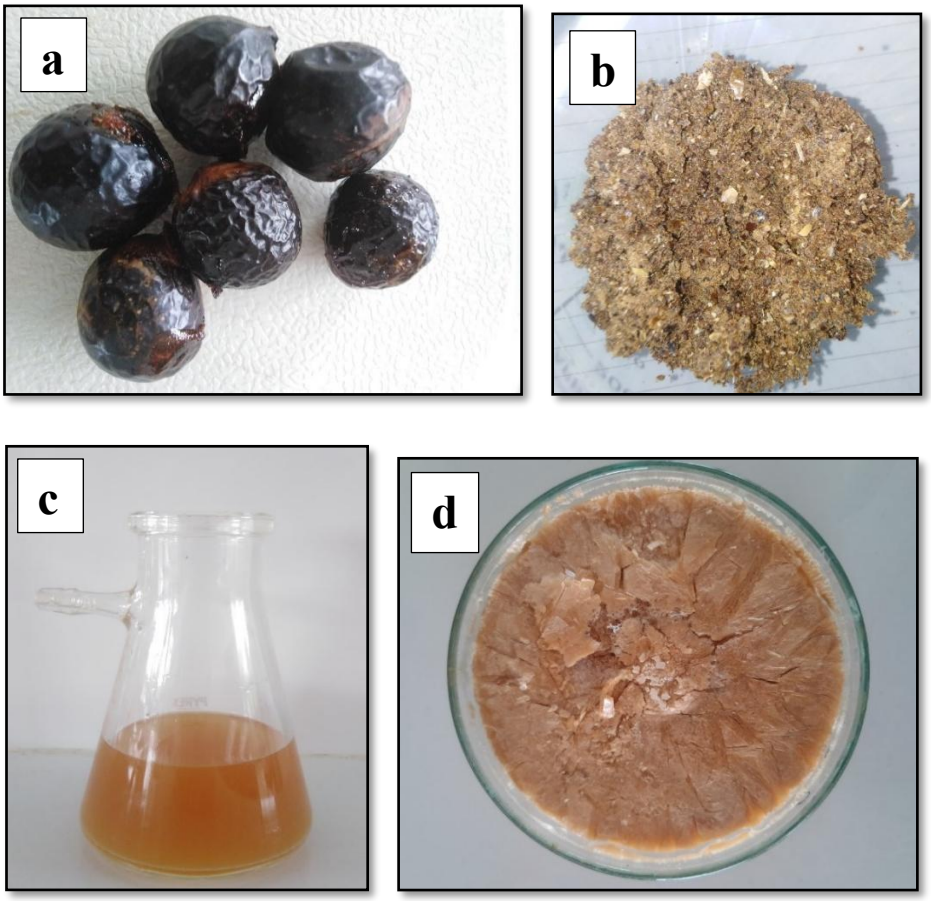


Figure 1. (a) Soapnut fruits (*Sapindus mukorossi*), **(b)** ground soapnut fruit powder, **(c)** extracted and filtered crude soapnut solution (SE), **(d)** freeze-dried powder of crude extract of soapnut (FD-SE).

Polymerizations were conducted using crude SE as the surfactant, with varying amounts added to determine the optimal amount required for effective styrene polymerization. Figure 2 shows the samples obtained using varying amounts of crude SE, while Figure 3 shows a representative sample after polymerization.

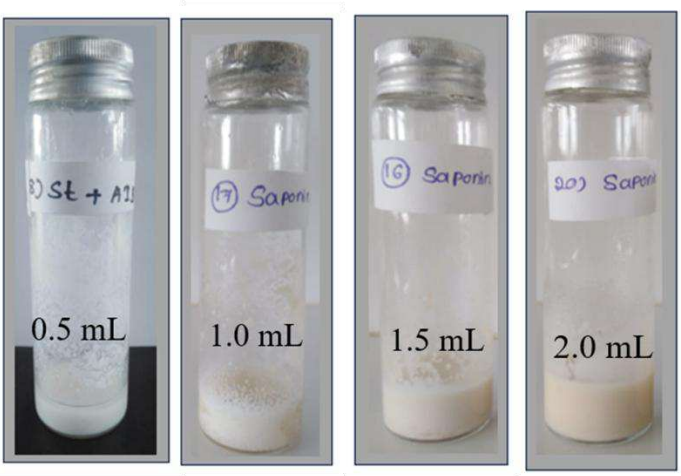


Figure 2. Samples with different amounts of crude SE (before polymerization). The volume labels denote the volume of crude SE added. See Tables 1 and 2 for complete compositions.



Figure 3. Representative sample after polymerization.

Gel stability is a crucial factor in emulsion gel polymerization. It was observed that increasing the volume of the crude SE solution to enhance surfactant concentration led to a decline in gel stability. Specifically, stable gels could not be formed when the crude SE solution volume exceeded 1.5 mL. To address this issue, the crude SE solution was freeze-dried to obtain a solid powder form of the extract (FD-SE). This enabled the preparation of a series of samples by varying the amount of FD-SE while maintaining a constant water volume. Figure 4 shows a representative sample before and after the polymerization using FD-SE.

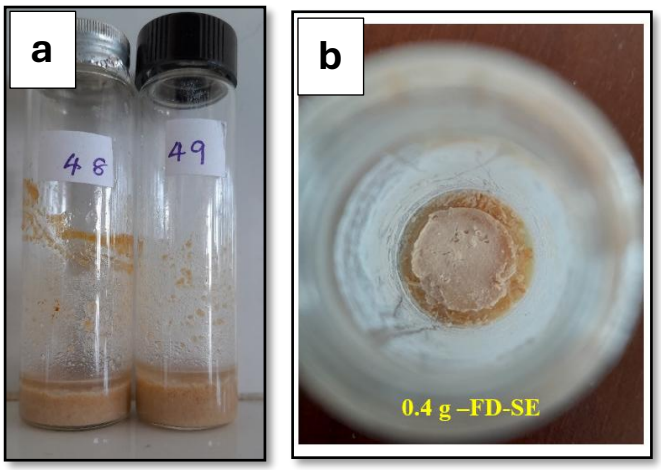


Figure 4. Representative sample using FD-SE, before (a) and after (b) polymerization.

Determination of Polymerization Conversions

Bulk polymerization of polystyrene (PS) was carried out at 70 °C, as the reaction does not proceed effectively at room temperature. The bulk PS sample achieved a polymerization conversion of 98%. In contrast, the reference sample was polymerized at room temperature using the emulsion gel technique. CTAB, a well-known surfactant, was previously reported to yield promising results in emulsion gel polymerization of styrene,[1,2,5] was selected as the reference surfactant for comparison with biosurfactant-based systems. The CTAB-containing sample yielded a polymerization conversion of 84%, demonstrating not only the effectiveness of CTAB as a surfactant but also confirming the role of fumed silica as a suitable gelling agent in the emulsion gel polymerization process. Additionally, a control sample without any surfactant was prepared to evaluate the impact of surfactant presence on the polymerization. This control, also performed at room temperature, resulted in a significantly lower polymerization conversion of just 7%, indicating that the absence of a surfactant drastically hinders the efficiency of emulsion gel polymerization of styrene under ambient conditions. In the emulsion gel technique, the surfactant facilitates the initiator decomposition due to the complex formation, reducing the temperature of the polymerization process.[2] The significantly lower conversion observed for the control sample without surfactant indicates that the gelling agent, fumed silica, alone cannot promote emulsion gel polymerization of styrene. This confirms that the presence of a surfactant is essential for achieving efficient polymerization under ambient conditions.

The polymerization conversions were calculated for the samples prepared using varying volumes of crude SE solution (0.5 mL to 2.5 mL), and masses of freeze-dried SE (FD-SE) powder (0.1 g to 0.5 g) are shown in Tables 3 and 4, respectively. This was carried out to determine the optimal concentrations of crude biosurfactant. The corresponding graphical representations are shown in Figures 5 and 6. The results indicate that polymerization conversion increased with increasing crude SE volume and FD-SE mass, reaching maximum values at 1.5 mL and 0.4 g, respectively. Previous studies have shown that surfactant concentration plays a critical role in emulsion gel polymerization.[2] At low concentrations, the surfactant does not facilitate AIBN decomposition or to effectively block surface silanol groups on fumed silica, which inhibit radical activity. As the surfactant concentration increases, more initiator–surfactant complexes form, promoting radical generation, while silanol groups are increasingly blocked, minimizing surface inhibition, both contributing to enhanced polymerization conversion.[2] However, exceeding the optimal surfactant concentration can

have adverse effects.[15] An excess of surfactant can lead to the formation of micelles that encapsulate monomer and initiator species, reducing their availability in the continuous phase.[1,16] Additionally, large surfactant amount may disrupt the emulsion gel structure, alter viscosity, and compromise system stability.[1,15] As a result, polymerization conversion decreases beyond the optimal concentration, underscoring the importance of fine-tuning surfactant levels for maximum efficiency in emulsion gel polymerization.

Table 3. Calculated average polymerization conversions for the series of SE solutions.

SE solution volume (mL)	Average polymerization conversion (%)
0.5	38±8
1.0	68±1
1.5	85±5
2.0	81±6
2.5	70±1

Table 4. Calculated average polymerization conversions for the series of FD-SE powder.

FD-SE powder mass (g)	Average polymerization conversion (%)
0.1	45±0
0.2	66±5
0.3	77±3
0.4	83±0
0.5	79±12

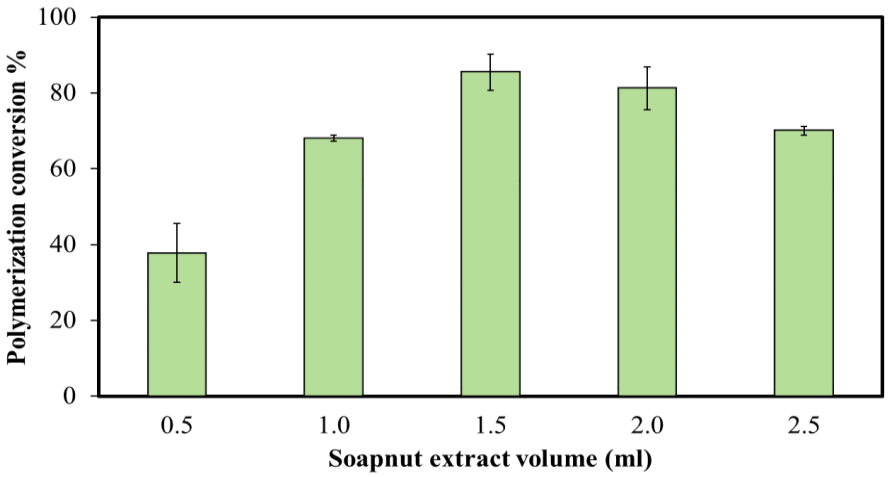


Figure 5. Polymerization conversions as a function of crude SE volume.

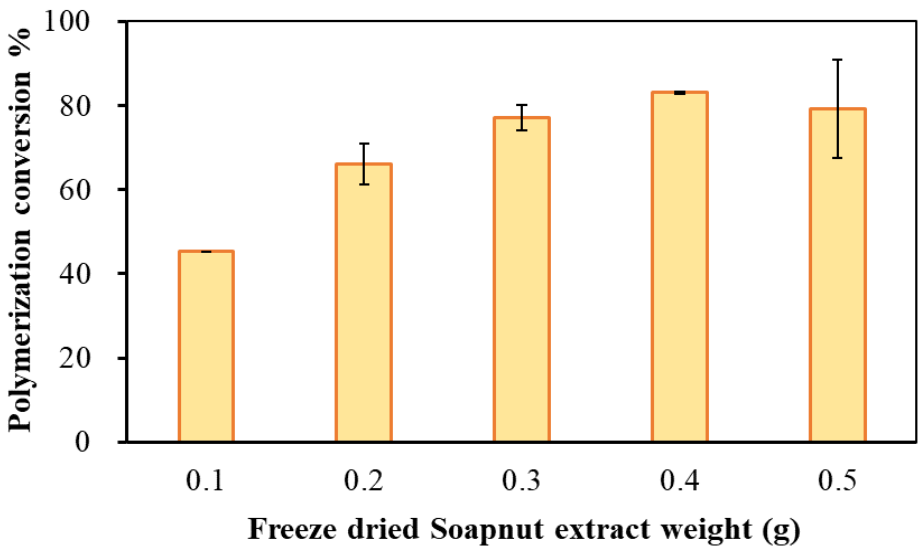


Figure 6. Polymerization conversions as a function of FD-SE mass.

As previously noted, stable gel formation was not achieved when the volume of crude SE solution exceeded 1.5 mL. The additional water introduced with higher SE volumes resulted in unstable gels and prolonged drying times beyond the standard 24 h due to excess water. This extended drying period also allowed additional time for polymerization to occur, potentially inflating conversion values and making these samples unsuitable for direct comparison with those prepared using smaller SE volumes.

To overcome the above limitations, the SE solution was freeze-dried to obtain a solid powder form of the soapnut extract (FD-SE). This approach enabled the preparation of SE solutions by varying the weight of FD-SE while maintaining a constant water volume, thereby avoiding the excess water issue.

The optimal amount of FD-SE for emulsion gel polymerization was found to be 0.4 g as illustrated in Figure 6. Significantly lower polymerization conversions were observed in the 0.1 g and 0.2 g samples, primarily due to smaller surfactant concentrations. Conversely, at 0.5 g, a practical issue arose: the FD-SE did not readily dissolve, leading to inconsistent surfactant dispersion and substantial deviations in the conversion estimates. This further supports the selection of 0.4 g FD-SE as the optimal amount for effective and reliable emulsion gel polymerization.

The polymerization conversions for the control, bulk, reference (CTAB), and soapnut-based (SE and FD-SE) samples are summarized in Table 5 and Figure 7. The bulk polymerization carried out at 70 °C yielded the largest conversion, primarily due to the elevated temperature required for efficient AIBN decomposition in the absence of a catalytic surfactant. In contrast, bulk polymerization at room temperature was not feasible under these conditions. The control sample, prepared without any surfactant, exhibited the least conversion, clearly demonstrating that the presence of a surfactant significantly enhances the efficiency of emulsion gel polymerization of styrene at ambient temperature. Notably, the polymer samples prepared using crude SE and FD-SE achieved polymerization conversions comparable to those obtained with CTAB, a widely used synthetic surfactant in emulsion gel systems. These results underscore the promising potential of using soapnut-derived saponin as a natural, eco-friendly alternative for polymerizing styrene under mild conditions.

Table 5. Average polymerization conversions for the control, bulk, reference, and soapnut samples.

Sample No	Sample	Composition	Average % conversion
S-01	Soapnut (Optimum SE volume)	AIBN-0.04 g/styrene 2 mL/SE -1.5 mL/FS-0.105 g (RT for 24 h)	85%
S-02	Soapnut (Optimum FD-SE mass)	AIBN-0.04 g/styrene 2 mL/FD-SE-0.4 g in 0.50 mL of water/FS-0.105 g (RT for 24 h)	83%
B-01	Bulk PS	AIBN-0.04 g/styrene 2 mL (70 ^{0}C for 4 h)	98%
C-01	Control	AIBN-0.04 g/styrene 2 mL/FS-0.105 g (RT for 24 h)	7%
R-01	Reference	AIBN-0.04g/styrene 2mL/CTAB(0.25M)-0.5mL/FS-0.105g (RT for 24 h)	84%

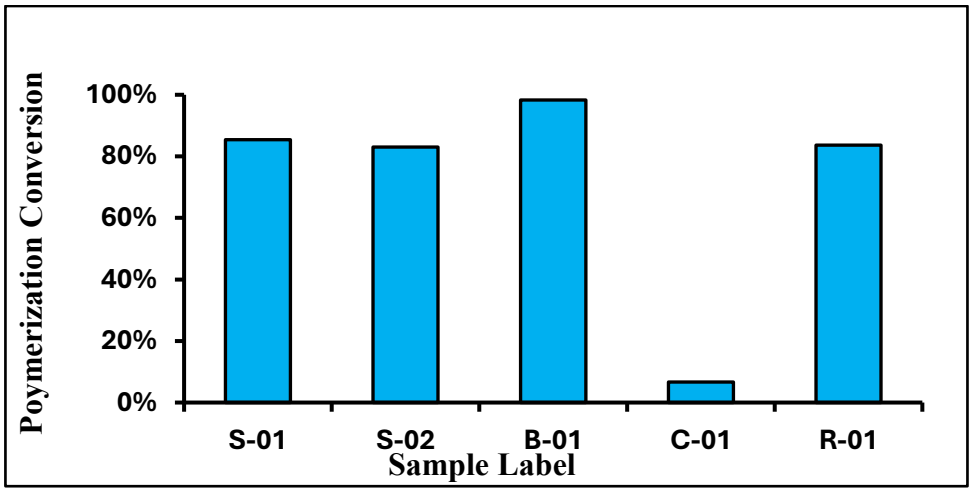


Figure 7. Average polymerization conversions for the control, bulk, reference, and soapnut samples.

Characterization

Before extracting PS from the polymerized samples, the morphology of the PS/SE/AIBN/FS system was analyzed using scanning electron microscopy (SEM) and the SEM images are shown in Figure 8. Since PS is a non-conducting polymer, a thin gold coating was applied to prevent charge accumulation and image distortion during electron beam exposure. Previous studies on PS samples polymerized via emulsion gel polymerization with AIBN as the initiator, fumed silica as the gelling agent, and CTAB as the surfactant have shown spherical, monodispersed nanostructures.[1,5] In contrast, the polymer samples prepared using SE exhibit a polydisperse nature, with particle sizes ranging from 6 µm to 26 µm and an average particle

size of 11 µm, as determined through ImageJ analysis. The particles appear agglomerated, and the surfaces of these agglomerates display a distinctly rough texture. This difference may arise from the complex composition of crude soapnut extract, which, in addition to saponins, contains other phytochemicals that could interfere with surfactant packing or stabilization mechanisms. Such components may influence the emulsification process, droplet stabilization, or interactions with monomers and initiators, ultimately leading to the observed polydisperse structures.

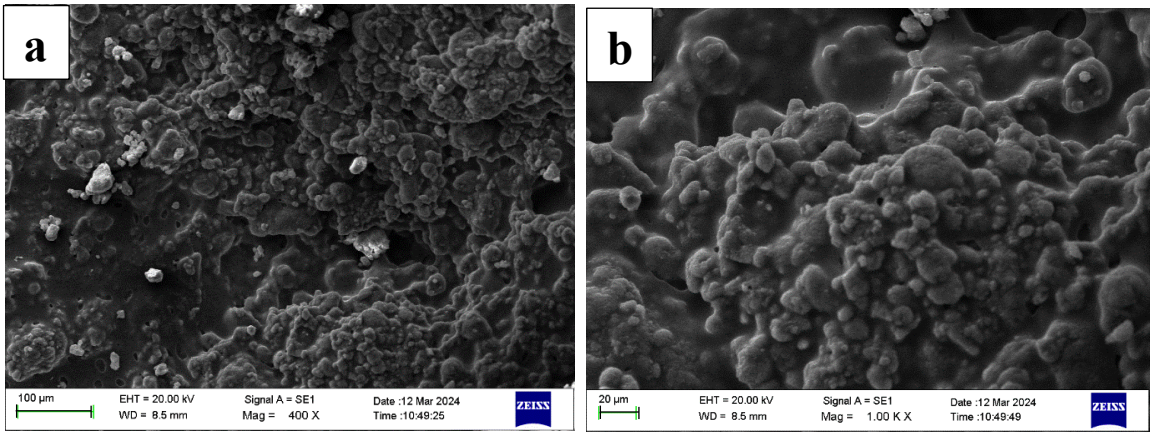


Figure 8. SEM image of PS/SE/AIBN/FS sample at (a) 400x magnification (b) 1.00kx magnification.

For further characterization, PS was selectively extracted from the PS/SE/AIBN/FS samples by dissolution in toluene followed by precipitation in water. Figure 9 shows the FTIR spectra of extracted PS samples obtained from both bulk polymerization and SE-mediated emulsion gel polymerization. The presence of all characteristic bands associated with PS confirms the successful synthesis of the polymer using SE as the surfactant.[17]

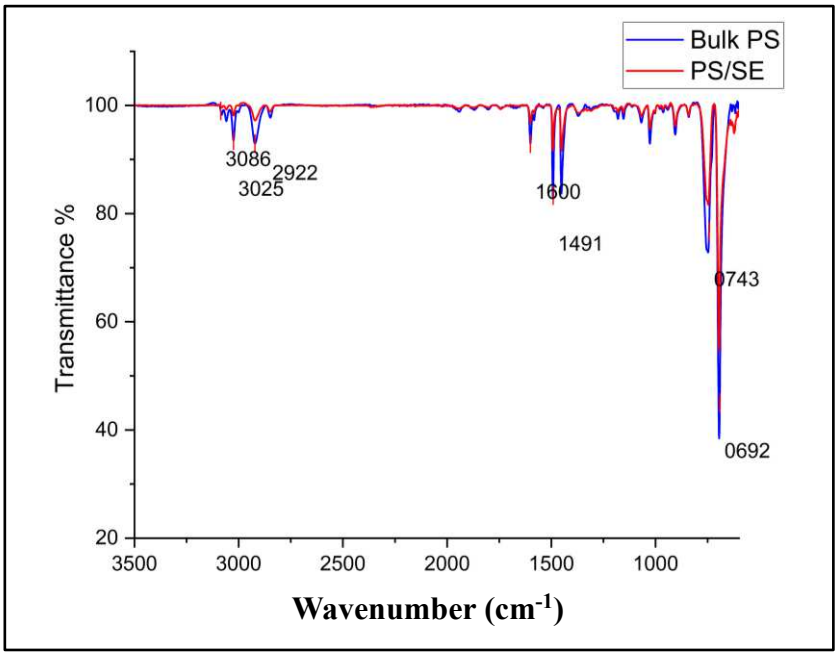


Figure 9. FTIR spectra of extracted PS samples obtained from both bulk polymerization and SE-mediated emulsion gel polymerization.

Temperature-modulated differential scanning calorimetry (TMDSC) was employed to investigate the thermal transitions of the samples, and the resulting thermograms are shown in Figure 10. PS generally exhibits a glass transition temperature (T_g) around 100 °C when synthesized at sufficiently high molar mass.[18] Among the samples tested, the PS synthesized using SE showed a lower T_g than the PS obtained from bulk polymerization and PS obtained from emulsion gel polymerization using CTAB. The T_g of polymers can be influenced by factors such as chemical structure, chain flexibility, crystallinity, molecular mass, side groups, composition, moisture content, and the presence of plasticizers.[18,19]

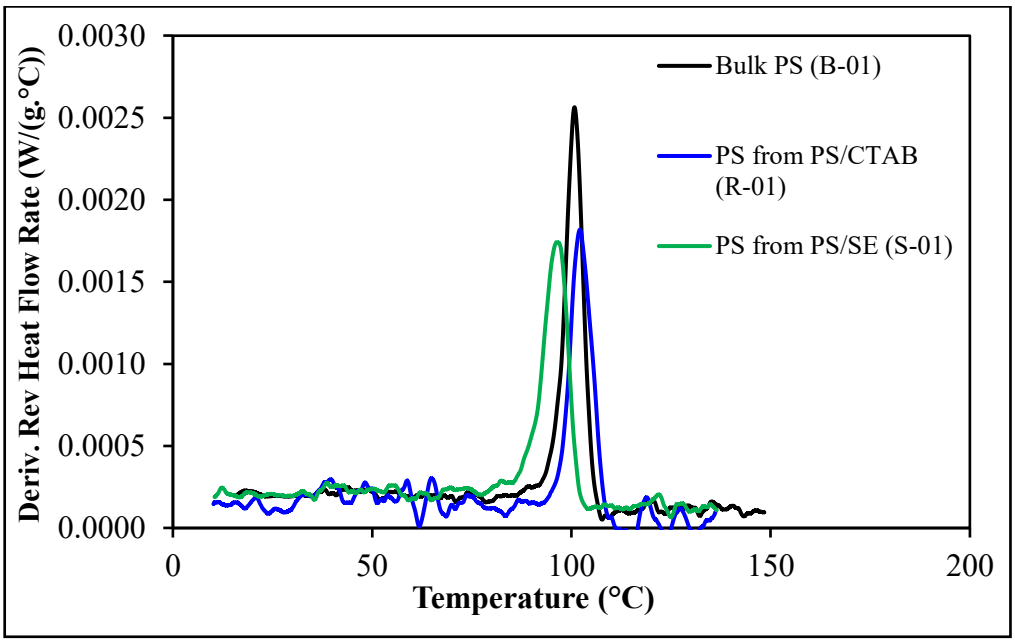


Figure 10. DSC thermograms of Bulk PS sample, PS from R-01 sample, and PS from S-01 sample.

GPC analysis was conducted for PS samples obtained via bulk polymerization (B-01), emulsion gel polymerization using CTAB (R-01), and emulsion gel polymerization using SE (S-01). The corresponding GPC chromatograms are shown in Figure 11. Table 6 provides a summary of the average molar masses, T_g, and polydispersity index (PDI) of the respective polymer samples.

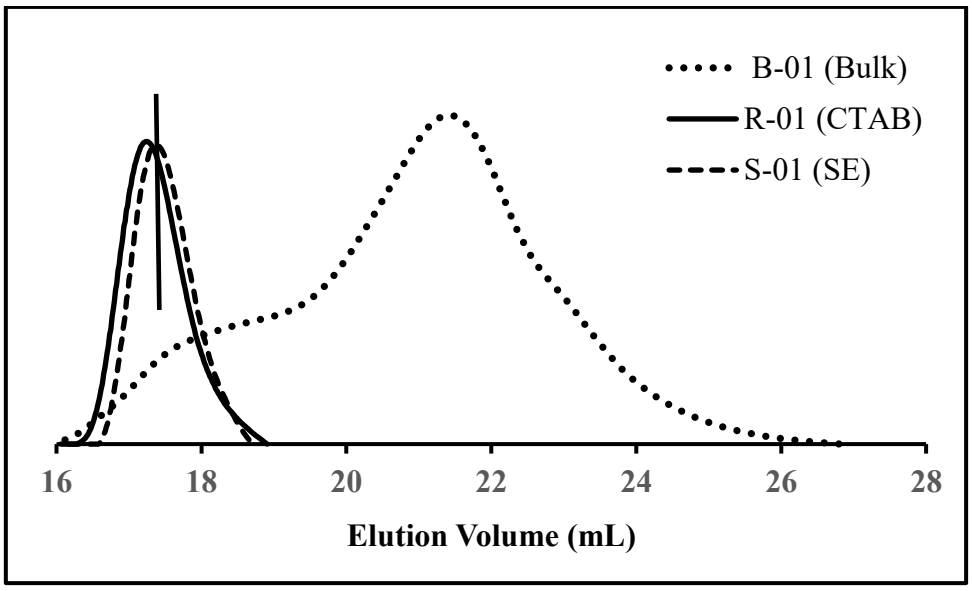


Figure 11. GPC traces for the PS obtained from bulk polymerization (B-01), emulsion gel polymerization using CTAB (R-01), and emulsion gel polymerization using SE (S-01).

Table 6. Average molar masses, T_g, and PDI values for the PS obtained from bulk polymerization (B-01), emulsion gel polymerization using CTAB (R-01), and emulsion gel polymerization using SE (S-01).

Sample no	Number average molar mass (g/mol)	Weight average molar mass (g/mol)	T_g (°C)	PDI
B-01 (Bulk)	3.3×10^4	1.6×10^5	101	5.0
R-01 (Ref)	2.4×10^6	2.7×10^6	102	1.1
S-01 (SE)	2.2×10^6	2.5×10^6	96	1.1

As illustrated in Figure 11 and Table 6, the PS samples synthesized using both CTAB (R-01) and SE (S-01) exhibited relatively monodisperse molecular mass distributions, with PDI values close to 1. The PS sample obtained from bulk polymerization (B-01) showed a much broader molecular mass distribution, resulting in a higher PDI indicating greater heterogeneity in chain lengths. However, as evident from the GPC data, all samples possess sufficiently large molar masses where T_g becomes independent of molecular mass. Therefore, the observed variations in T_g are likely influenced by other factors such as differences in microstructure, chain packing, or the presence of residual components such as surfactants or plasticizers in the crude saponin extract used during soapnut-extract-based polymerization.

Conclusion

This study explored the feasibility of performing emulsion gel polymerization of styrene at ambient temperature using biosurfactants as sustainable alternatives to conventional synthetic surfactants such as CTAB. Saponin extracted from the pericarp of *Sapindus sp*. (soapnut) fruit was employed as the biosurfactant in polymerizing systems comprising styrene, fumed silica, AIBN, and soapnut extract (SE). The results demonstrated that room-temperature polymerization of styrene is indeed achievable using saponin-type surfactants. The polymerization conversion observed for the SE as the surfactant was 85%, with an optimum SE volume of 1.5 mL for 2 mL of styrene. When using freeze-dried soapnut extract (FD-SE), the best average polymerization conversion was 83%, with an optimal concentration of 0.4 g per 0.5 mL of water for 2 mL of styrene. FTIR spectroscopy confirmed the successful synthesis of PS with SE as the surfactant, while temperature-modulated DSC revealed a T_g of 96 °C, slightly lower than those of PS samples obtained from bulk polymerization and CTAB-mediated systems. GPC analysis showed that all samples possess sufficiently high molar masses where T_g is independent of molecular mass. The slightly lower T_g observed for the SE-based PS is therefore likely influenced by residual components, such as surfactants or plasticizers present in the crude saponin extract, or subtle differences in chain packing and microstructure. Overall, this study demonstrates that soapnut-derived saponin surfactants are viable candidates for producing low-PDI polystyrene under mild, room-temperature

conditions. This approach holds significant potential for developing greener and more sustainable polymerization processes.

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Data Availability

The data used to support the findings of this study are included within the article.

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