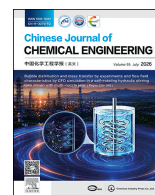




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Review

Preparation of polystyrene microspheres by suspension polymerization: A review

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ABSTRACT

Polystyrene microspheres are widely utilized in automobiles, electronics and packaging due to their diverse characteristics, which are highly dependent on particle size. Traditionally, with the manipulation of suspension polymerization parameters, different sizes of microspheres ranging from 10 to 1000 μm can be prepared, with the coefficient of variation (CV) of particle size distribution ranging from 20% to 50%. However, emerging application fields such as pharmaceuticals and biotechnology have high demands for stability and require a narrow particle size distribution. To address this, researchers have proposed novel approaches. This review summarizes both well-developed traditional methods and emerging techniques for particle size control, analyzing their underlying mechanisms. The aim is to provide a reference for the development of preparation methods with controllable particle size. Firstly, the mechanisms of traditional particle size control methods, including optimization of stirring parameters, design of dispersant systems, regulation of oil-to-water ratio, utilization of salt effects and temperature control, are analyzed, and the mechanism of these methods in modulating microspheres size is concluded. Secondly, novel techniques such as membrane emulsification, microfluidic technology and acoustic field-assisted methods in controlling particle size distribution and enhancing reaction efficiency are introduced, mainly focused on their principle characteristics and potential application prospects. Finally, the future development of suspension polymerization technique in preparation of polystyrene microspheres is discussed.

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1. Introduction

Polystyrene (PS), a synthetic aromatic polymer derived from styrene monomers via free radical polymerization [1–10], is widely utilized in automobiles, electronics and packaging due to its excellent transparency, low density and favorable processing characteristics [1–10]. A specialized form, polystyrene microspheres, typically defined as spherical particles ranging from 20 nm to 1000 μm in diameter [10–12], have garnered significant interest for their functionalizable surface properties and potential in drug delivery and diagnostic applications [7]. Crucially, microsphere

performance is highly size-dependent, as illustrated in Fig. 1. Especially, driven by increasing demands in materials engineering, diagnostics and biomedical applications for high-performance microsphere materials, there is a pressing need to prepare PS microspheres with controllable particle size in high uniformity.

In industry, PS microspheres are prepared by suspension polymerization, a heterogeneous technique developed in the mid-20th century, enabling the direct preparation of polymer microspheres through monomer-to-polymer phase transformation [13–20]. However, in current industrial practice, microsphere particle sizes are mainly in the range of tens to hundreds of micrometers (e.g., around 100 μm), with coefficient of variation (CV) varying from 20% to 50%, which fails to meet the stringent requirements of applications such as drug delivery and bionanotechnology that demand extremely narrow particle size distributions (typically $\text{CV} < 10\%$) [21–28]. To address these

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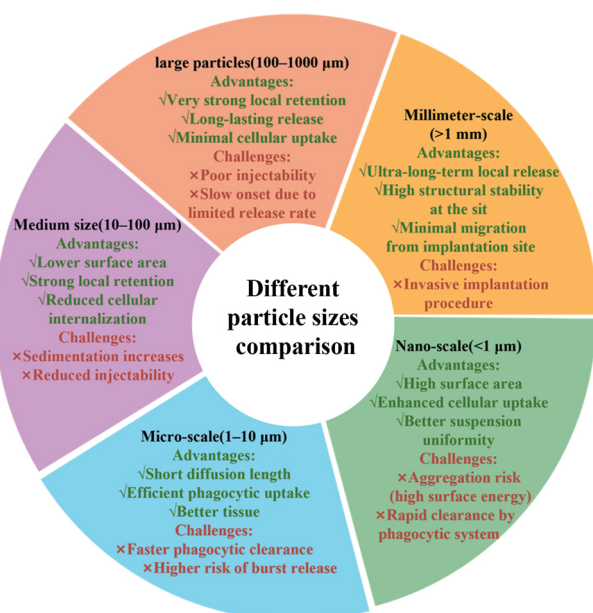


Fig. 1. Comparison of different particle size ranges in pharmaceutical drug delivery systems. Each sector represents advantages (✓) and challenges (✗) associated with specific particle size ranges, highlighting the trade-offs between therapeutic efficacy, manufacturing complexity and clinical applications.

limitations, researchers have pursued dual approaches: optimizing traditional process parameters (e.g., stirring, dispersant, phase ratio and temperature) or/and integrating novel intensification technologies (such as membrane emulsification, micro-channel technology and acoustic field-assisted techniques) into suspension polymerization processes [20–25]. Optimization of traditional suspension polymerization technology employs strategies such as increasing stirring speed to reduce droplet size, optimizing dispersant concentration to minimize coalescence and controlling oil-to-water ratio, salt effects and temperature to regulate particle size. Nevertheless, these approaches remain constrained by droplet coalescence and Ostwald ripening, resulting in particle size CV values typically ranging from approximately 20% to 50% or even higher [24–26]. The integrated approaches with novel technologies aim to enhance droplet size precision, reduce shear variability and strengthen interfacial stability, demonstrating considerable potential. However, these technologies remain primarily at laboratory or pilot-scale stages, with industrial adoption facing challenges related to scalability and cost considerations.

This review systematically reviews the regulatory principles and strategies for preparing microspheres via suspension polymerization. Firstly, traditional particle size control methods (including optimization of stirring parameters, dispersant system design, oil-to-water ratio regulation, salt effects and temperature control) and their limitations in achieving high monodispersity are analyzed. Secondly, process intensification techniques such as membrane emulsification, microfluidic technology and acoustic field-assisted methods, focusing on their mechanisms, characteristics and application prospects are introduced. Finally, future developments in suspension polymerization technology for microsphere preparation, particularly toward micron and submicron sizes with ultra-narrow particle size distributions are discussed, thereby providing theoretical guidance and strategic direction for related research and industrial applications.

2. Suspension Polymerization Mechanisms

Suspension polymerization is a well-established heterogeneous process to prepare micron-sized polymer particles in industry. As schematically presented in Fig. 2, a monomer phase with an initiator, dispersed into an aqueous continuous phase to form droplets (droplet stage), within which polymerization subsequently occurs to yield spherical polymer particles (polymerization stage) [26]. After separation from the aqueous phase, washing and drying, the polymer microsphere product is obtained.

The initial generation of droplet and evolution of droplets during polymerization are identified as key factors that influence the final microsphere particle size and its distribution width [19,27–32]. Multiple studies have indicated that the final particle size is primarily determined by the size of the initial monomer droplets [29–32]. Maggioris *et al.* [29] and Brooks [30] noted that in industrial suspension polymerization, droplet break-up was accompanied by droplet coalescence, and thus the particle size distribution of the resulting polymer dispersion was controlled by droplet coalescence and break-up. Alexopoulos *et al.* [31] explicitly stated that a balance between the rate of droplet breakage and coalescence determined the size of droplet in suspension polymerization. Gritskova *et al.* [22] emphasized that droplet stage uniformity was an important prerequisite for achieving narrow-distribution microspheres. Minor variations in droplet generation and stabilization can be amplified during subsequent polymerization: if the initial droplet size distribution is broad or coalescence and breakup phenomena occur, the final polymerized microsphere size distribution will also be broad [22,33]. Conversely, if the droplet size distribution is narrow and coalescence and breakup are suppressed, the polymerized microspheres are more likely to exhibit a narrow size distribution [33]. From a mechanistic perspective, the sequence of droplet generation → stabilization → polymerization constitutes the core chain that constrains the final PS microsphere particle size distribution including CV and polydispersity index (PDI) [31,32]. If the droplet stage is poorly controlled subsequent polymerization, regardless of how strictly controlled, will be unable to significantly narrow the final particle size distribution [22,33,34].

Several theories have been developed to estimate droplet generation size. Classical turbulence theory describes droplet breakup and coalescence mechanisms during dispersion stage that govern droplet size [34,35]. According to Kolmogorov theory, the maximum stable droplet diameter ($d_{\max}$) is related to energy dissipation rate (ϵ) and interfacial tension (σ) by the formula $d_{\max} = C(\sigma/\rho)^{0.6}\epsilon^{-0.4}$ [35]. The Weber number ($We = \rho v^2 d/\sigma$) is used to assess droplet stability, with droplets tending to break up when We exceeds a critical value (typically 1–10) [22]. These theories provide guidance for designing operational parameters such as stirring speed, energy input, interfacial tension and viscosity ratio in traditional technique and intensified strategies integrated with novel technique to manipulate droplet size [33–35].

From the principle of suspension polymerization, the size and distribution of the formed droplets most significantly influence the microsphere size and distribution. Therefore, to achieve controllable microsphere size and distribution, it is necessary to start by regulating the size and distribution of the droplets during their formation.

3. Well-developed Methods for Particle Size Control

According to the known suspension polymerization mechanisms, several strategies were developed to modulate droplet generation size through hydrodynamic regulation by stirring,

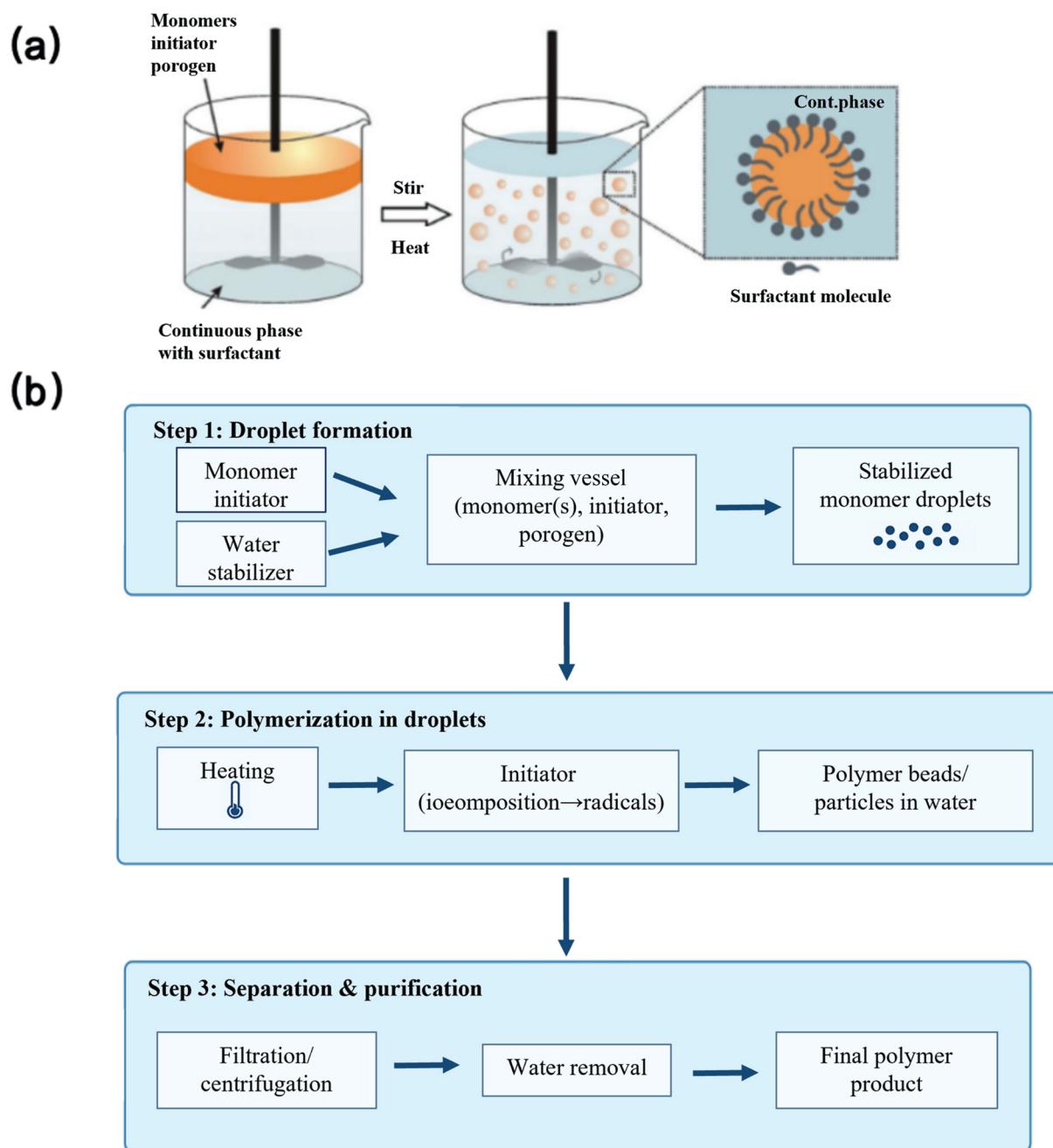


Fig. 2. Basic depiction of the suspension polymerization technique.

interfacial stabilization with the addition of dispersants, dispersion density modulated with phase ratio or the addition of salts, or kinetic/physicochemical tuned by temperature. Despite decades of development, conventional strategies that rely on empirical optimization struggle to produce monodisperse PS microspheres, typically yielding particle size distributions with span indices >1.5 ($CV > 50\%$) [34–36]. Quantitative analysis reveals significant limitations, including substantial energy inefficiency, where intensive stirring can consume 20% to 50% more power for only marginal PS size reductions, and inherent process instability, with PS microsphere coagulation rates escalating 5–10 fold under suboptimal conditions [37–45]. While fundamental mechanisms such as shear-induced breakage and steric hindrance are well-described by population balance equations (PBEs), unexplained

phenomena persist, such as sudden emulsion transitions occurring when dispersant excesses exceed 3% (mass) in PS systems, and localized hot spots that contribute to particle size distribution (PSD) broadening by up to 30%, highlighting critical gaps in comprehensive process understanding [44–49].

3.1. Control mechanism of stirring parameters on particle size

Stirring parameters play a pivotal role in balancing the breakage and coalescence of styrene monomer droplets through turbulence induction, aiming for mean PS microsphere sizes between 50 and 500 μm with uniform dispersion. While much quantitative data originates from polyvinyl chloride (PVC) or methyl methacrylate (MMA) polymerization studies, these

principles are directly relevant and applicable to PS synthesis [50–60]. Industrial research indicates that increasing stirring speed from 480 to 1800 $\text{r} \cdot \text{min}^{-1}$ can reduce mean microsphere diameter by up to 50% (e.g., from 1.2 mm to 0.6 mm in PS-relevant systems), with the Sauter mean diameter (d_{32}) decreasing 8% to 14% for every 10% stirring speed increment [61–68]. This reduction is attributed to elevated energy dissipation rates (ϵ , reaching $10^4 \text{ m}^2 \cdot \text{s}^{-3}$ near impellers). Although higher shear enhances droplet breakage efficiency (rates 2–5 times higher), it can also broaden the PS microsphere PSD by 20% to 30% via over-fragmentation and bimodal distributions [61–66]. Conversely, lower stirring speeds tend to yield larger PS particles with monomodal PSD but result in lower conversions due to inadequate mass/heat transfer [62–68].

The geometric design of stirring equipment significantly influences particle size control effectiveness by producing distinct flow field characteristics that dictate droplet breakup and dispersion behavior [62–70]. As depicted in Fig. 3, turbine-type stirrers are particularly suited for small particle size microsphere preparation, leveraging their high shear and intense turbulent mixing capabilities to generate localized high-intensity shear zones near the impeller, thereby effectively breaking up larger droplets and promoting favorable macroscopic mixing. In contrast, propeller-type stirrers primarily generate axial flow with relatively low shear intensity, making them more appropriate for larger particle size microsphere preparation or systems requiring gentle mixing. Anchor-type stirrers, also shown in Fig. 3, generate a combination of tangential and radial flow with blades conforming to vessel walls, excelling in processing high-viscosity fluids by promoting bulk flow, preventing wall fouling, and enhancing heat transfer to ensure uniformity. However, anchor stirrers typically provide lower and more distributed shear rates compared to turbine impellers, rendering them less effective for generating extremely small particle sizes through high-intensity droplet breakup, and are thus more frequently utilized in processes demanding consistent conditions in a viscous matrix or handling larger particles with less aggressive shear [61–71].

Flow field distribution and energy transfer efficiency are influenced by parameters such as the impeller diameter-to-reactor diameter ratio, clearance height and blade angle. Researches have demonstrated that impeller diameter ratios between 0.3 and 0.5 provide optimal particle size control effects [29,72–75]. Impeller diameters that are too small lead to insufficient mixing, while excessively large diameters generate unnecessary vortices and increase energy consumption. Clearance height is affected by other geometric parameters [76–78]. Insufficient clearance promotes solid deposition, whereas excessive clearance reduces bottom mixing efficiency. Flow field distribution is optimized when clearance heights are maintained at approximately 1/3 to 1/2 of the reactor diameter [76–78].

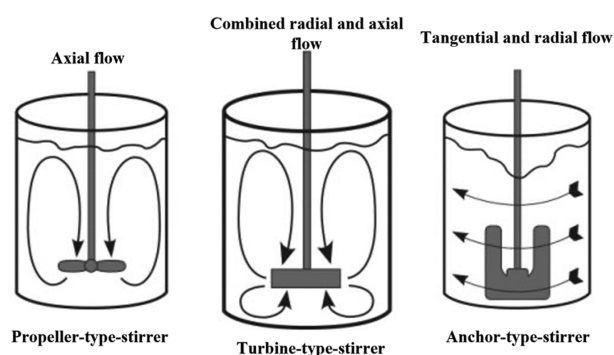


Fig. 3. Different flow patterns generated by various types of stirrers [63].

3.2. Design and optimization of dispersant systems

Dispersant systems are designed to stabilize the interface of styrene monomer droplets, effectively preventing coalescence and enabling precise control of PS microsphere sizes through steric or electrostatic barrier mechanisms [17,79,80]. Budenheim's industrial investigations and Taghizadeh's comprehensive reviews have pointed out that for expandable polystyrene (EPS) production requiring larger bead sizes of 0.3–5 mm, inorganic stabilizers are preferred due to their superior thermal stability, mechanical robustness and cost-effectiveness under high-temperature and high-shear processing conditions compared to organic alternatives [81]. Polyvinyl alcohol (PVA) at 0.5% to 2% (mass) is highly effective in styrene systems, reducing the mean PS microsphere size by up to 67% (from 150 μm to 50 μm) and significantly sharpening the PSD (span from 1.5 to 1.1) [82]. This effect is achieved through Marangoni influences and the formation of adsorbed layers with a thickness greater than 10 nm when the molecular weight exceeds 70000 [83–85]. Composites like PVA-SDS (sodium dodecyl sulfate), often in 3:1 to 5:1 ratios, further enhance stability under high solids holdup, up to 40%, yielding sub-100 μm PS microspheres with 15% to 25% narrower distributions. This is attributed to dual mechanisms: SDS lowers interfacial tension to $4 \text{ mN} \cdot \text{m}^{-1}$, while PVA provides robust steric hindrance, with a shear stress limit of $0.95 \text{ mN} \cdot \text{m}^{-1}$ [86–88].

General Aniline and Film Corporation's pioneering work demonstrated that polyvinylpyrrolidone (PVP) at 0.025% to 1% (mass) functions as an effective primary dispersant, often synergized with secondary agents like sorbitan monolaurate to prevent agglomeration [89]. Their studies showed that PVP formed protective colloid layers promoting uniform, porous particles with bulk densities of $410\text{--}480 \text{ kg} \cdot \text{m}^{-3}$, achieving 95% to 96% conversion rates with superior clarity, strength and thermal stability. Optimal molecular weights of 40000–300000 with water-to-monomer ratios of 1.9–2.25:1 ensure granular, non-agglomerated products, providing finer porosity control than PVA though requiring secondary dispersants in high-viscosity systems [89]. BASF's research established that styrene-maleic anhydride (SMA) sodium salts at 0.1% to 1% (mass) serve as effective anionic dispersants, with amphiphilic properties that increase polymerization rates and enhance interfacial dynamics, yielding homogeneous particles with improved clarity [90]. Cymit Química's studies revealed SMA's hydrophobic styrene segments anchor to droplets while hydrophilic maleic acid groups provide steric and electrostatic stabilization, complementing organic dispersants by accelerating reactions without significant PSD broadening.

Kadi [91] systematically investigated tricalcium phosphate (TCP) at 3% to 9% (mass) in multi-stage EPS production, demonstrating that TCP functions via Pickering stabilization by adsorbing onto droplet surfaces while increasing aqueous viscosity, resulting in smaller spherical particles with narrower PSD and enhanced mechanical properties. Their work showed that TCP reduced polymerization time by 60% in multi-stage initiator dosing methods, with artificial neural network models accurately predicting optimal conditions at 9% TCP for balancing PDI, pentane absorption (5% to 8% (mass)) and residual monomer ($<500 \text{ mg} \cdot \text{kg}^{-1}$) [91]. Vivaldo-Lima et al. [19] confirmed TCP's advantages including superior stability and low residuals, but noted over-stabilization risks at excessive concentrations, with TCP remaining the most widely adopted inorganic stabilizer due to optimal cost-efficiency balance. Other inorganics like barium sulfate and magnesium pyrophosphate offer similar benefits [19].

Quantitative optimization studies reveal that excessive dispersant concentrations, specifically exceeding 2% (mass) PVA,

can induce emulsion shifts, leading to PS microsphere sizes smaller than 1 μm , and reduce the styrene polymerization rate by 50% to 60% [30,92–94]. Conversely, water-insoluble polydimethylsiloxane (PDMS) at 0.11% to 4.32% (mass) has been shown to produce PS particles of 0.40–0.51 μm with a very narrow PSD (span 1.01–1.08), maintaining stability up to 100% conversion via the formation of thixotropic layers with an elastic modulus of 9.8 $\text{mN}\cdot\text{m}^{-1}$ [73,94]. Advantages of PDMS systems include superior PS microsphere uniformity, with coagulum less than 1%, and environmental benefits due to minimal soluble residues; PDMS demonstrates 2–3 times better stability than PVA at low styrene monomer loads (less than 25%). However, drawbacks include that high PDMS concentrations can decrease styrene polymerization rates, from 5.5% to 2.2% per minute, and PS molecular weight, from 4.5×10^5 to 1.8×10^5 . Additionally, economic considerations involve a 20% to 30% higher cost, and there is limited scalability for PS microspheres larger than 0.9 μm . Unresolved desorption dynamics at dispersant excesses underscore the need for molecular rheology studies.

Frontier directions involve artificial intelligence (AI)-optimized hybrids [30,94–97], such as PDMS with polylactides, for core-shell PS microsphere structures, enabling PSD indices less than 1.05 and biomedical tunability. Experimental evidence has confirmed these efficiency improvements. For instance, Zhang *et al.* [96] demonstrated that Bayesian optimization successfully simplified the dispersion polymerization process, enabling the preparation of uniform microspheres (with particle sizes $>10 \mu\text{m}$) in only four experimental steps. Additionally, Takasuka *et al.* [97] employed machine learning to develop mathematical models of the polymerization process, thereby reducing the need for time-consuming and costly experiments. Using a generative AI approach, they screened over 2000 candidate polymer materials and identified 10 viable formulations. This validated the potential of machine learning to reduce the number of experimental trials required for optimizing PS formulations by over 40%. Notably, the machine learning process achieved the ideal ratio of styrene to MMA in just five computational cycles [97].

3.3. Effects of oil–water ratio and salt type

The phase ratio (styrene monomer to water) and salt type are crucial parameters that modulate dispersion density and ionic strength, aiming to produce PS microspheres sized 0.1–2 mm by controlling droplet collision and repulsion rates [98–102]. A 1:9 monomer–water ratio (styrene:water) has been shown to yield 0.4–0.56 μm PS microspheres in PS systems, where stability is achieved through reduced holdup [99–103]. Conversely, higher ratios, for example, 1:4, can increase microsphere size by 20% to 50%, potentially up to greater than 1 mm, due to elevated coalescence [101,102]. Monovalent salts, such as NaCl at 0.5% to 2% (mass), can moderately fine-tune PS microsphere sizes to 100–500 μm . Divalent salts, such as Na_2SO_4 at 0.1% to 0.5% (mass), achieve more significant size reductions, to less than 0.5 mm, at 50% lower concentrations through enhanced electrostatics, but risk inducing aggregation (salting-out thresholds are around 1% (mass)) for PS particles [54–60].

Data from PS models indicate that changes in PVA concentration by $\pm 50\%$, often linked to phase ratio adjustments in PS systems, can alter the d_{32} of PS microspheres by 7% to 19%, with low monomer–water ratios minimizing droplet interactions. Advantages of this strategy for PS production include simple and effective implementation, where salt addition can improve stability in high-holdup systems, increasing styrene conversion by 10% to 15%. However, disadvantages include unresolved ion-specific effects, such as 2–3 times higher aggregation rates for multivalent salts,

which can lead to broad PS microsphere PSDs (span greater than 1.5) and entail economic penalties from wastewater. Gaps in understanding electrochemical interactions within PS systems necessitate advanced probes. Enhancements via microfluidic technology for adaptive ratios could refine PS microsphere sizes to less than 100 μm , integrating with AI for accurate density predictions [98–104]. Zhang *et al.* [100] has demonstrated that an AI-based dynamic light scattering system successfully achieved high-precision measurement of PS microsphere diameters within the range of 100–1500 nm. Malashin *et al.* [101] used deep neural networks (DNNs) for predicting density-related properties of polymer composites, the coefficient of determination (R^2) reached as high as 0.89, providing a reliable foundation for extending this AI framework to the prediction of PS density.

3.4. Effect of temperature

Temperature is a vital parameter that simultaneously governs styrene polymerization kinetics and the system's physicochemical properties [52,105]. Precise temperature control aims to achieve narrow PS microsphere PSDs, with a span around 1.1, at optimal conditions, for instance, 70 $^\circ\text{C}$ [84]. At this temperature, a balance is struck between increased initiator decomposition rates, which are 2–3 times higher than at 60 $^\circ\text{C}$, and a reduction in styrene monomer droplet viscosity, dropping 20% to 30%, which effectively mitigates coalescence [54–57,106,107]. Here, the comparisons refer specifically to azobisisobutyronitrile (AIBN)-initiated systems (typically 0.2% to 0.5% (mass) relative to styrene); for AIBN, the 10-h half-life shifts from 65 $^\circ\text{C}$ to 70 $^\circ\text{C}$, corresponding to a 2–3 times increase in the decomposition constant (k_d) between 60 $^\circ\text{C}$ and 70 $^\circ\text{C}$, which governs the observed acceleration in polymerization. However, further temperature elevation to 80 $^\circ\text{C}$ can broaden the PS microsphere PSD by 30% to 40%, with coalescence frequency increasing twofold, through the intensification of the gel (Trommsdorff) effect, leading to a 50% broadening of PS molecular weight [108–111]. It can be observed that in benzoyl peroxide (BPO)-initiated recipes, albeit shifted to slightly higher characteristic temperatures, which is consistent with BPO's higher activation energy and different half-life profile. Localized hot spot formation at high temperatures can also induce size irregularities, with $\pm 20 \mu\text{m}$ variations, in the microspheres [66,110–112].

Quantitative studies show that 70 $^\circ\text{C}$ effectively stabilizes the D_{50} of PS microspheres at approximately 100 μm [52,66,105–112]. While higher temperatures can shorten stabilization duration to less than 30 min, they simultaneously promote instability, with coalescence rates increasing 3–5 fold [105–112]. A dual impact is observed: chemical effects, such as an increased styrene polymerization rate, under AIBN initiation (similarly under BPO at higher setpoints), where faster radical generation elevates R_p , interact with physical effects, including interfacial tension reduction to 25–30 $\text{mN}\cdot\text{m}^{-1}$. Advantages of temperature control include precise control windows. For example, optimal temperature profiles in PS production yield desired viskositätszahl values of 57–67 $^\circ\text{C}$. Disadvantages lie in incompletely understood thermal thresholds; for instance, gelation at temperatures above 80 $^\circ\text{C}$ risks runaway reactions and decreases styrene conversion by 5% to 10%. Frontier PINN simulations integrate thermal imaging for hot spot mitigation in PS reactors, thereby enhancing microsphere size uniformity by 25% [108–112].

These strategies, while individually effective in PS microsphere production, for example, stirring for coarse size control and dispersants for fine tuning, demonstrate peak performance when synergistically integrated. However, non-intuitive outcomes, such as a fivefold increase in coalescence with condensers, underscore the necessity for holistic models specifically tailored to PS systems.

3.5. Effect of gel fraction

The particle size and its distribution of suspension polymerization products, particularly precursors for ion exchange resins (IER), not only depend on external parameters such as stabilizer concentration and agitation rates but also significantly on internal polymer properties, most notably the gel fraction. The gel fraction reflects the degree of crosslinking within the polymer network, which dictates the rheological behavior of the dispersed phase during the reaction. Generally, a higher gel fraction mitigates particle swelling and promotes an earlier transition from a viscous liquid to a solid state (gelation). This rapid fixation stabilizes smaller droplets and effectively suppresses coalescence during the later stages of polymerization, resulting in a narrower size distribution and smaller average particle diameters.

The gel fraction is mainly derived from the insoluble crosslinked fraction in the polymer network. The higher the dosage of crosslinking agents (e.g., divinylbenzene (DVB) and ethylene glycol dimethacrylate (EGDMA)), the greater the crosslinking density and the higher the gel fraction. Rahmatpour *et al.* [113] investigated the effect of DVB concentration on the product. They observed that increasing the DVB content from 4% to 15% significantly shifted the particle size distribution toward finer ranges (e.g., 0.18 μm or smaller) and improved the product yield to over 70% due to enhanced morphological stability. Analogous results were reported in related seeded polymerization processes. Kim and Suh [114] demonstrated that the crosslinking density of the seed particles was pivotal for controlling final particle size. They found that a higher seed crosslinking density limited the absorption and swelling of monomers, thereby facilitating the production of highly monodisperse particles with sizes exceeding 10 μm . Additionally, in the preparation of phenolic beads, Singh and Lal [115] showed that reaction parameters tied to crosslinking—such as the formaldehyde/phenol ratio—modulate particle sizes by altering the viscosity and stability of the dispersed phase.

From a mechanistic perspective, increasing the gel fraction essentially shortens the time window in which the polymerization system remains in a low-viscosity fluid state. Vivaldo-Lima *et al.* [19] emphasized that the viscosity changes associated with gelation govern particle evolution. It is noted that early gel points, resulting from high degrees of crosslinking, “freeze” the droplet structure, thus preventing the broadening of size distribution caused by prolonged fluid phases. Therefore, the precise regulation of gel fraction is a critical strategy for tailoring particle properties, and this approach is of great significance for ensuring the uniformity of particle size in suspension polymerization products.

4. New Processes and Technologies

Traditional suspension polymerization methods, while mature for industrial PS microsphere production, exhibit limitations in achieving high monodispersity, typically characterized by a CV above 20% to 50%, precise micron-level size control, and the creation of complex functionalized structures [116–120]. To overcome these challenges, recent technological advancements, such as membrane emulsification, microchannel and acoustic field-assisted methods, focus on enhancing droplet formation and stabilization specifically for styrene-based systems during the monomer dispersion stage, aiming to improve uniformity and reproducibility while retaining the fundamental process of dispersing styrene monomers in aqueous phases for *in-situ* polymerization. These approaches lead to small microspheres, typically ranging from 10 to 300 μm and narrower particle size distributions, frequently with CV below 5%, and with the potential to prepare nano-scale spheres when porogens are incorporated. At

present, these technologies are confined to laboratory or pilot scales by cost and scalability issues. High-value niche applications, driven primarily by biomedical separations, drug delivery and chromatography, constitute a significant and growing segment within the broader global polymer emulsion market, a sector exhibiting continuous expansion.

4.1. Membrane emulsification technology

Membrane emulsification significantly improves droplet uniformity during the emulsification stage for PS microspheres. This process involves forcing styrene monomer phases through porous membranes, such as Shirasu porous glass (SPG) membranes known for their narrow pore size distributions with a CV below 5%, into aqueous phases containing stabilizers [7,121–129]. This technique achieves precise size control with droplet-to-pore diameter ratios typically between 3 and 10, enabling the production of uniform PS particles ranging from 700 nm to 7 μm , or TiO_2 –PS composites sized between 20 and 25 μm . As illustrated in Fig. 4, highly uniform droplets form in aqueous stabilizer solutions when organic dispersed phases, comprising styrene monomers and initiators, are passed through membrane pores under controlled transmembrane pressure. Droplet size is primarily dictated by the membrane pore diameter, with the observed droplet diameter-to-pore diameter ratios (typically 3–10 times) providing a theoretical basis for precise microsphere particle size control [121,122].

The selection of membrane material profoundly influences droplet formation and the stability of the polymerization reaction in suspension polymerization. SPG membranes have demonstrated unique advantages in styrene suspension polymerization systems due to their extremely narrow pore size distributions (CV below 5%) and excellent chemical stability, offering versatility for preparing PS microspheres of diverse specifications [121,122]. Ceramic membranes, including alumina and aluminum oxide [122–125], despite their higher cost, maintain stable pore structures under high-temperature suspension polymerization conditions owing to their exceptional high-temperature and corrosion resistance. Metal membranes have exhibited excellent performance under high-pressure operations [126]. Membrane surface wettability is critical for the stability of suspension polymerization systems, with the hydrophilic characteristics of SPG membranes being ideally suited for aqueous continuous systems. The uniformity of membrane pore diameter directly translates to droplet size uniformity, ultimately resulting in excellent microsphere monodispersity and serving as a technical guarantee for high-quality preparation [125–128]. The mechanical strength and chemical stability of membrane materials determine their service life during suspension polymerization processes, which holds significant economic importance for industrial applications.

Transmembrane pressure is identified as the primary driving force for dispersed phases passing through membrane pores, and its magnitude directly affects the droplet formation rate and size uniformity. Insufficient pressure leads to unstable droplet formation, whereas excessive pressure can cause oversized droplets or membrane pore blockage. Research on polymethyl methacrylate microsphere preparation indicated that increasing transmembrane pressure from 0.05 to 0.3 MPa resulted in an increase in droplet size, though excessive pressure potentially had a negative impact on uniformity [129]. This conclusion is equally applicable to PS microsphere preparation, emphasizing the necessity of optimizing transmembrane pressure. The continuous phase flow rate and composition significantly influence droplet stability and the progression of the suspension polymerization reaction. Appropriate shear at the membrane surface facilitates timely

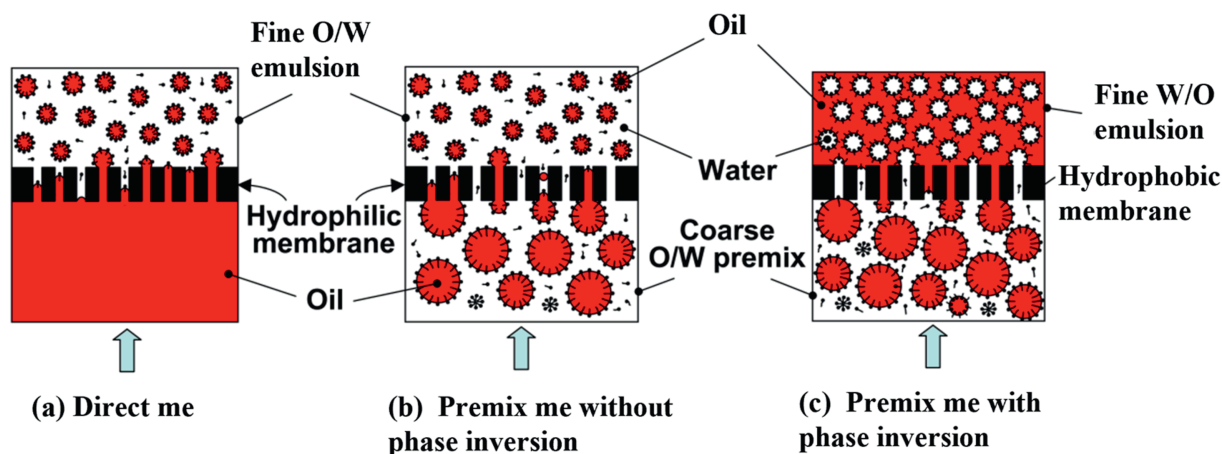


Fig. 4. Schematic diagram of membrane emulsification methods [130].

droplet detachment, preventing droplet coalescence. Consistent with Fig. 5 [130], an increased continuous phase flow rate leads to a reduction in droplet size and an improvement in uniformity. This effect is achieved through enhanced shear forces acting at the membrane-continuous phase interface, with cross-flow systems (Fig. 5(a)) exhibiting superior performance compared to other configurations.

Compared to traditional shearing methods, membrane emulsification offers low energy consumption and high controllability, enabling the production of ultra-monodisperse PS microspheres with tailored porosity for enhanced adsorption and post-modification [131].

Industrial scaling of this technology remains limited to pilot levels, with reactors typically producing quantities in the

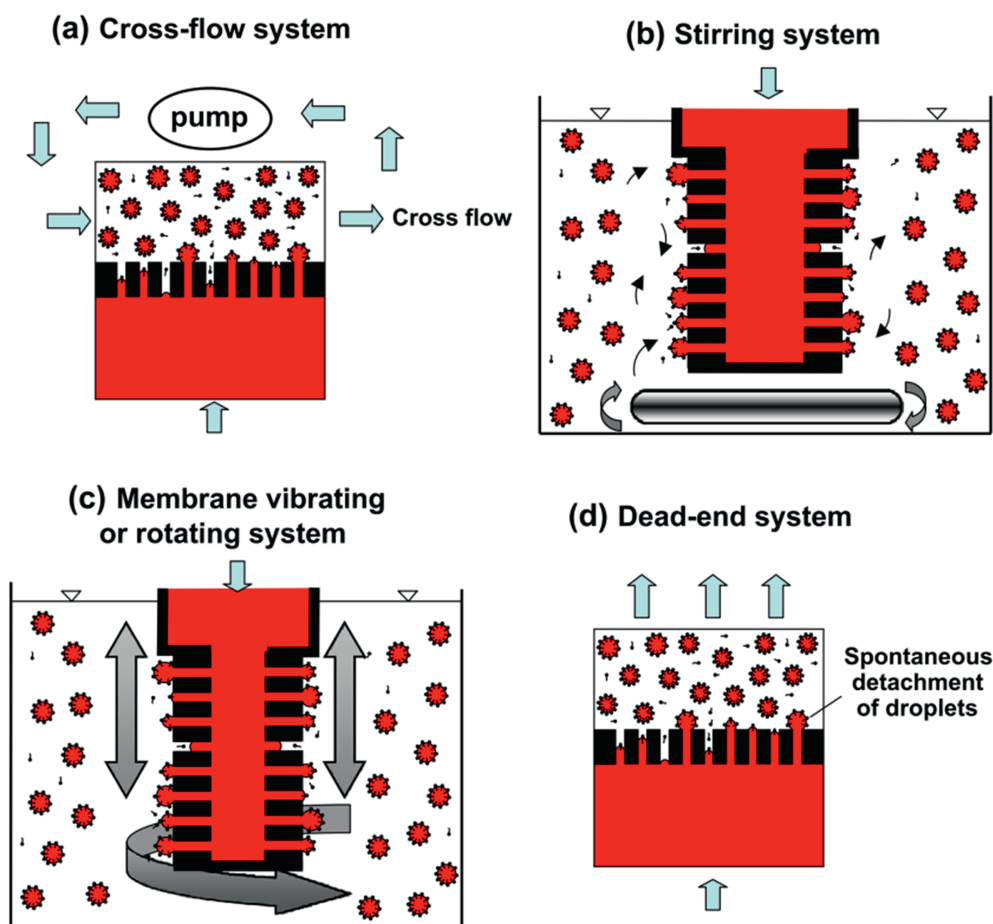


Fig. 5. Membrane emulsification systems for controlling hydrodynamic conditions near the membrane surface [130].

milligram to gram range within 1–10 L volumes. Challenges include achieving high-throughput due to membrane blockage, particularly with viscous styrene mixtures and high costs, with SPG and ceramic units costing thousands of dollars. These factors restrict market penetration despite the potential for high-value PS microparticles in biomedical applications [123–133]. Disadvantages also encompass fouling during extended runs, for example, from styrene residue buildup, high initial capital expenditure and pressure-induced instability at scales beyond laboratory settings, which can increase the CV to 5% to 10% in unoptimized systems. Future research efforts should focus on developing cost-effective membrane regeneration techniques, anti-fouling surface modifications, such as tuning hydrophilic/hydrophobic properties for styrene compatibility, and parallel systems for scale-up to meet industrial demands for uniform PS in chromatography and drug carriers. As shown in Fig. 6, membrane emulsification technology demonstrates significant technical advantages in suspension polymerization systems compared to traditional high-shear emulsification methods [130,134–144]. It enables the preparation of ultra-monodisperse microspheres with particle size

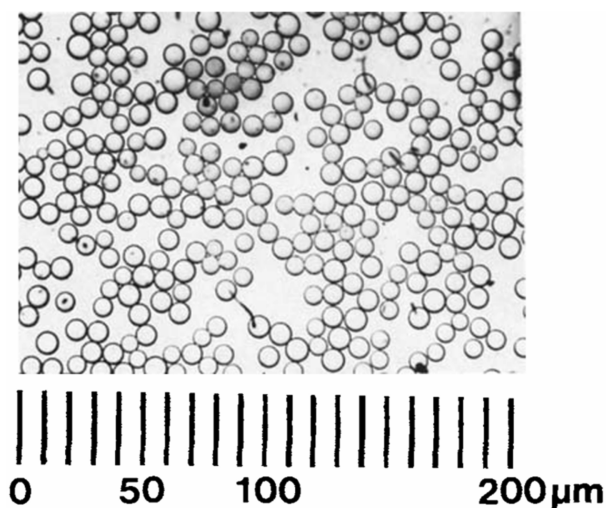


Fig. 7. Photograph of emulsion droplets taken by optical microscope [131].

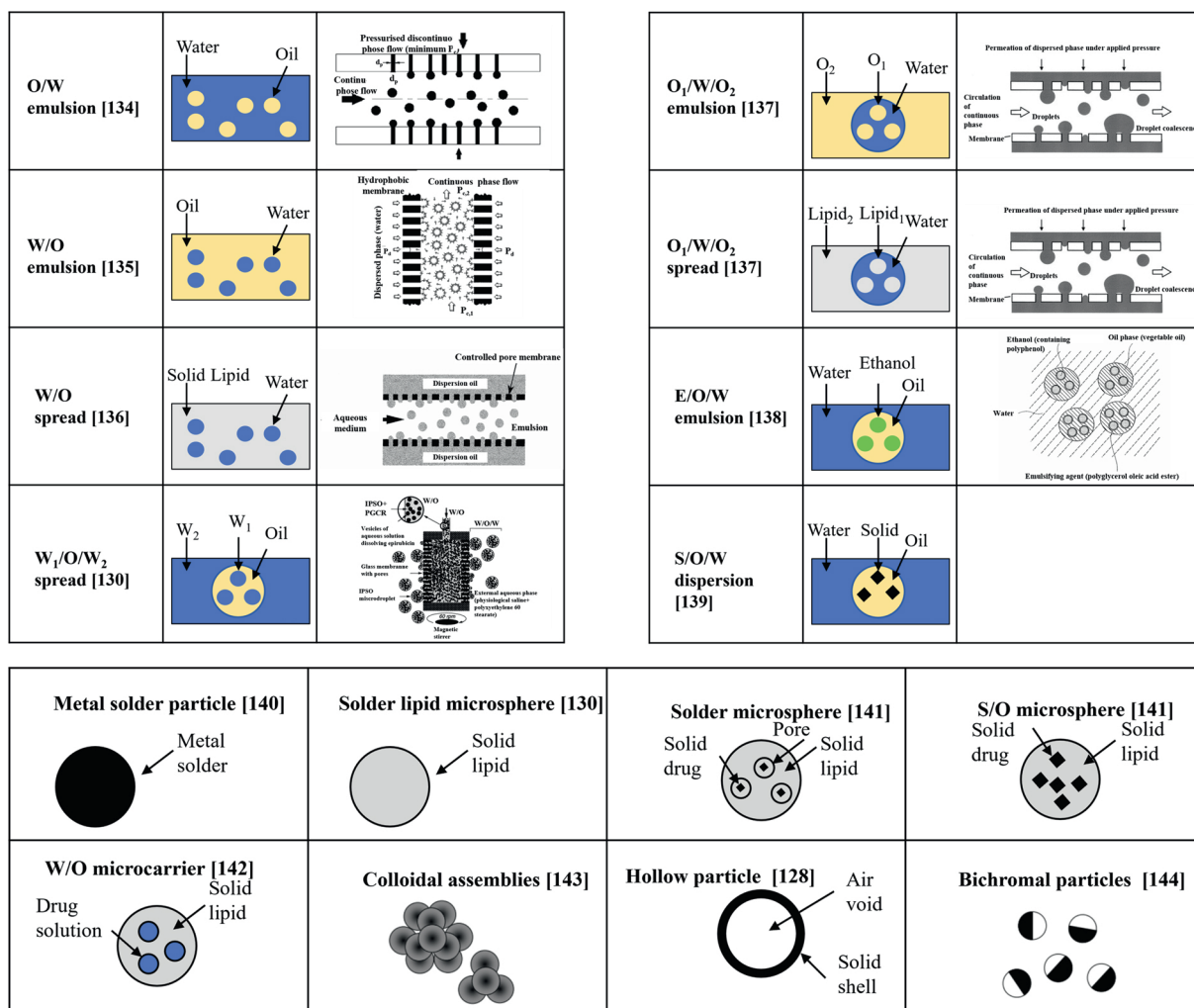


Fig. 6. Some products of membrane and microchannel emulsification [128,130,134–144].

distribution CV below 5%, characterized by low energy consumption and high controllability (Fig. 7) [131].

4.2. Microchannel technology

Microchannel technology, particularly microfluidic technology, is recognized as an advanced polymerization process that achieves precise droplet size control through accurate fluid flow management within microchannels. This precision results in uniform microspheres with extremely narrow particle size distributions during suspension polymerization [118,132,133]. The underlying mechanism leverages microscale fluid dynamics to precisely control droplet formation, which directly determines the uniformity of the final PS microspheres. In microfluidic devices, organic dispersed phases containing styrene monomers and initiators, such as BPO, are brought into contact with aqueous continuous phases containing stabilizers. Highly uniform droplets are formed at channel junctions by meticulously controlling the flow rate ratios of the dispersed and continuous phases, as well as the channel geometry. Droplet size is primarily determined by channel width and fluid flow rates, with typical droplet diameters ranging from 10 to 300 μm and a CV achievable below 5% [133,145–147]. The droplet formation mechanism within microchannels involves a complex balance of interfacial tension, shear forces and viscous forces. As the dispersed phases enter the continuous phases, droplets form under the shear action at channel junction points and are subsequently carried by the continuous phases. The high repeatability of this process ensures that each droplet possesses similar initial conditions, thereby facilitating the formation of uniform PS microspheres in suspension polymerization reactions [118,145–147]. Fig. 8 illustrates a schematic diagram of mono-disperse microsphere preparation using microchannel technology.

Microchannel (microfluidic) technology enhances droplet precision during the formation stage for PS microspheres by controlling fluid flows in channels with widths typically between 10 and 300 μm . This process utilizes shear and interfacial forces to generate uniform styrene droplets, achieving a CV below 5% and sizes ranging from 10 to 300 μm , which translate to post-polymerization particles of 16.9–23.5 μm , often stabilized by PVA or SDS [118,132,133,145–147]. Devices constructed from materials such as thiol-ene polymers or ceramics ensure stability,

with hydrophilic surfaces preventing aggregation in styrene-aqueous systems [148–153]. Optimized flow rate ratios, for example, a continuous phase flow rate of 1–2 $\mu\text{L}\cdot\text{min}^{-1}$, can reduce the CV from 3.2% to 2.1%, yielding ultra-monodisperse PS particles superior to those produced by mechanical stirring. This is exemplified by 3D-printed parallel microchannels achieving high-throughput, with droplet frequencies up to 2.8×10^4 Hz, for uniform PS [70,149–151,154–158]. T-shaped microchannels further enable the creation of functional PS beads between 30 and 120 μm with a CV below 2%, adaptable for styrene polymerization.

Production using microchannel technology remains predominantly at lab-scale, with typical yields below $1 \text{ g}\cdot\text{h}^{-1}$ per device. While scale-up through parallel chips can reach pilot levels ($10\text{--}100 \text{ g}\cdot\text{h}^{-1}$), full industrialization is hindered by high device costs, typically hundreds to thousands of dollars, and the risk of channel blockage from styrene polymerization residues [159]. The market potential resides in pharmaceuticals and cosmetics within the 37 billion microfluidics sector, projected to grow to 74 billion by 2030, but is limited by significant waste, for instance, 7–1000 kg of product waste per kg of product from solvents. Disadvantages include inherently low throughput, channel fouling, which can increase CV in prolonged runs, and solvent-intensive processes that raise environmental impact. Future frontiers of research include recycling continuous phases, utilizing additive manufacturing for more cost-effective devices, and integrating with 3D structures for creating multifunctional PS particles, such as magnetic composites.

4.3. Acoustic field-assisted technology

Acoustic field-assisted technology leverages cavitation, micro-jets and streaming induced by ultrasound (20–100+ kHz) to enhance droplet breakup and mixing during the dispersion and polymerization stages for PS microspheres [160–171]. This approach significantly reduces reaction times, typically by 30% to 50%, for example, from hours to 7.5 min in PS-based molecularly imprinted polymers (MIPs), and achieves narrower particle size distributions with a CV below 3%. Low frequencies, specifically 20–40 kHz, are effective in enhancing mixing for uniform styrene droplet distribution. Medium frequencies, ranging from 40 to 100

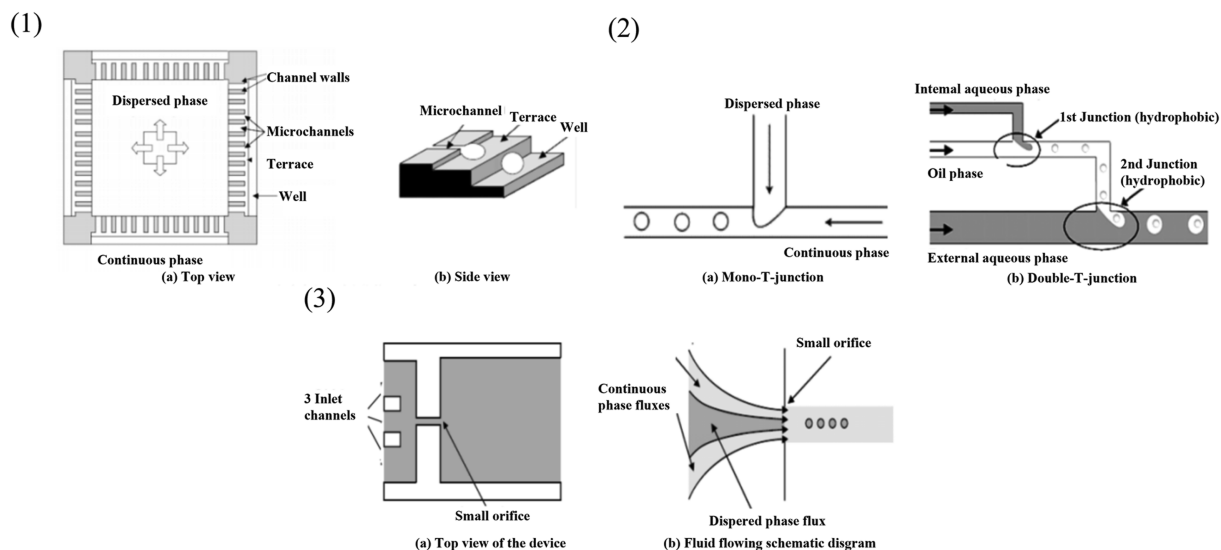


Fig. 8. Three commonly used emulsification devices for preparing microspheres or droplets using microfluidic technology. (1) Stepped microchannel emulsification device. (2) T-shaped vertical staggered microchannel emulsification device. (3) Fluid focused microchannel emulsification [145–147].

kHz, provide a balance for controlled cavitation-induced breakup. High frequencies, exceeding 100 kHz, enable finer breakup for producing smaller PS particles, as demonstrated in ultrasound probe-assisted synthesis yielding nanostructured magnetic PS-MIPs with high selectivity [168–171]. This technology accelerates styrene conversions, achieving up to 95% in optimized systems, and improves reproducibility compared to traditional methods, particularly for functionalized PS, such as molecularly imprinted polymers [119,170].

Achieving uniform acoustic distribution in large reactors presents challenges due to rapid acoustic attenuation and the presence of dead zones. Optimal designs, such as multi-transducer flow cells, can achieve variations in cavitation between 10% to 30% but require precise geometry for consistent PS particle formation [172,173]. Production scales to pilot levels, for example, 10 L reactors, for applications like MIPs, but full industrialization for PS polymerization remains elusive. This technology aligns with sonoprocessing niches within the broader ultrasound technology sector, valued at 1–2 billion [172]. Quantitative data indicate efficiencies ranging from 2×10^{-6} to $20 \times 10^{-10} \text{ mol} \cdot \text{J}^{-1}$, however, significant energy losses to heat, up to 50%, reduce scalability. For PS-MIPs, adsorption capacities can reach 10–20 $\text{mg} \cdot \text{g}^{-1}$ with a 1-h equilibration time [173]. Disadvantages include non-uniform fields in volumes exceeding 10 L, which can lead to a CV greater than 5% in large batches, transducer erosion, high energy costs, typically 0.1–1 $\text{kW} \cdot \text{h} \cdot \text{kg}^{-1}$ of product, and temperature rises of up to 20 °C, which can inhibit styrene reactions. Future studies should focus on optimizing multi-frequency reactors, modeling cavitation for uniformity, and exploring synergies with membrane or micro-channel methods for sustainable, large-scale PS microsphere production [174].

5. Summary and Prospects

5.1. Summary

Suspension polymerization is a well-established industrial technique for producing micron-sized PS microspheres through dispersing styrene monomer droplets in aqueous phases, where polymerization occurs to yield spherical particles. The process offers advantages including simplified post-processing, and mitigation of viscosity challenges. However, the final microsphere particle size and distribution are critically determined by initial droplet generation, stabilization and droplet evolution during polymerization, with droplet stage uniformity serving as a fundamental prerequisite for achieving narrow-distribution microspheres.

Traditional particle size control methods—including stirring parameter optimization, dispersant system design, oil–water ratio adjustment and temperature regulation—effectively modulate droplet dynamics to achieve target PS microsphere sizes (50–500 μm) suitable for economic, large-scale production. Stirring speed increases from 480 to 1800 $\text{r} \cdot \text{min}^{-1}$ can reduce mean diameter by up to 50%, while dispersants like PVA (0.5% to 2% (mass)) achieve size reductions of 67% with narrower distributions (span from 1.5 to 1.1). However, these conventional approaches are fundamentally limited by turbulent mixing principles, typically yielding broad particle size distributions with span indices greater than 1.5 and CV values of 20% to 50%, requiring extensive empirical optimization.

Emerging technologies offer transformative advances in monodispersity through deterministic control over droplet formation. Membrane emulsification (CV < 5%) utilizes porous membranes like SPG to achieve precise size control with droplet-to-pore diameter ratios of 3–10, producing uniform PS microspheres

from 700 nm to 25 μm with low energy consumption. Micro-channel technology (CV < 5%) leverages microscale fluid dynamics in 10–300 μm channels to generate ultra-monodisperse particles (10–300 μm) through controlled flow rate ratios, achieving CVs as low as 2.1%. Acoustic field-assisted technology (CV < 3%) employs ultrasound-induced cavitation and streaming to enhance droplet breakup and mixing, reducing reaction times by 30% to 50% while achieving exceptional uniformity, particularly for functionalized PS systems like molecularly imprinted polymers.

While these advanced techniques remain predominantly at laboratory or pilot scales due to challenges including membrane fouling, channel blockage, limited throughput (typically below 1 $\text{g} \cdot \text{h}^{-1}$ for microfluidics), high costs (hundreds to thousands of dollars per device) and scalability constraints, they demonstrate significant promise for high-value applications in biomedical separations, drug delivery and chromatography. Future developments focusing on cost-effective regeneration techniques, anti-fouling modifications, parallel systems for scale-up, multi-frequency reactor optimization and integration of hybrid approaches will be crucial for transitioning these technologies toward industrial-scale production of ultra-uniform PS microspheres with unprecedented precision for demanding applications.

5.2. Prospects

The increasing demand for highly monodisperse polymeric microspheres in precision applications spanning biomedicine, diagnostics and advanced materials underscores the imperative for continued innovation beyond current suspension polymerization capabilities. While traditional methods provide economic viability and scalability for microspheres with broader size distributions, their fundamental reliance on stochastic turbulent mixing inherently limits achievable monodispersity to CV values exceeding 20% to 50%. The emerging deterministic technologies reviewed herein—membrane emulsification, microchannel systems and acoustic field-assisted methods—demonstrate the feasibility of bridging this performance gap through controlled droplet formation mechanisms. However, realizing their full industrial potential requires addressing critical challenges in scalability, cost-effectiveness, and process robustness. Future research and development should strategically focus on several interconnected areas that advance both fundamental understanding and practical implementation.

Researchers are dedicated to addressing complex droplet dynamics and process instability issues through a deeper understanding of multiphase systems, and by developing physics-informed models and advanced *in-situ* characterization techniques. Future research will focus on the rational design and engineering of novel stabilizer systems, including leveraging AI for predictive design and exploring dynamic interfacial control strategies. To achieve industrial-scale production, it is necessary to integrate high-precision deterministic methods with traditional high-throughput processes and to optimize the entire production process through AI. Concurrently, precise regulation of polymerization kinetics, particularly by controlling intra-droplet viscosity changes, is essential to stabilize the final microsphere size distribution.

By systematically addressing these interconnected scientific and engineering challenges through coordinated fundamental research and applied development efforts, the field of suspension polymerization can transcend current performance limitations and scalability barriers. This multifaceted approach will enable the robust, economically viable, and environmentally sustainable production of PS microspheres with unprecedented uniformity

and functional sophistication, ultimately unlocking their full transformative potential in demanding high-value applications across biomedical diagnostics, advanced separations, precision drug delivery, and emerging materials technologies.

CRedit Authorship Contribution Statement

Yafeng Xiao: Writing – original draft, Resources, Data curation. Yiqing Zhang: Investigation, Data curation. Zhongtian Dong: Data curation. Jun Zhou: Visualization, Validation. Shaoping Ma: Investigation, Data curation. Shuang Wu: Data curation. Zhihui Wang: Writing – review & editing, Validation, Supervision. Qinghua Zhang: Writing – review & editing, Validation, Supervision, Funding acquisition, Conceptualization. Chao Yang: Writing – review & editing, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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