Aqueous Radical Polymerization of Poly (Methyl Methacrylate): A Comparative Study of Surfactant-Free Suspension and Copper-Mediated Emulsified Systems

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ABSTRACT

Poly(methyl methacrylate) (PMMA) is technologically important due to its wide range of applications, good chemical resistance and its high transparency. In this research, PMMA was prepared by two different radical polymerization methods in an aqueous medium. the first approach include surfactant free suspension initiated by potassium persulfate and second approach involved copper-mediated radical polymerisation take out in an emulsion system. these methods were employed to inspect essential way for PMMA synthesis under aqueous condtions. The impact of the reaction environment and initiator concentration on polymer formation, particle morphology, and monomer conversion was rigorously investigated. Suspension polymerization resulted in PMMA particles, which were formed via monomer droplet polymerization without surfactants; conversely, the copper-mediated system generated smaller particles that were stabilized by an emulsifier under aqueous conditions. FTIR and ^{1}H NMR spectroscopy confirmed the structure of PMMA, and SEM and TEM were employed to examine particle morphology and size distribution. The findings reveal distinct disparities in particle properties arising from the two aqueous polymerization methodologies, thereby illustrating the influence of the polymerization medium and catalytic system on PMMA synthesis. This comparative analysis offers valuable perspectives on aqueous radical polymerization techniques for PMMA, without suggesting controlled or living polymerization characteristics.

Keywords: Poly(methyl methacrylate) nanoparticles; aqueous dispersed polymerization; Cu-mediated radical polymerization; suspension polymerization

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is a widely used artificial polymer. Its mechanical strength, chemical resistance, optical transparency and compatibility with biological systems make it worthy for numerous applications, built in coatings, optics, biomedical devices, and advanced materials [1-4]. PMMA nanoparticles have recently gained attention. Synthesizing the polymer on the nanoscale enables to control over surface properties, increasing its performance in composite and functional materials [5-7]. Emulsion and suspension polymerization are frequently used to prepare the polymer particles with controlled size and shapes [8–10]. These approaches have benefits, which include good heat transfer, lower viscosity, and the capacity to use water as the main phase [11,12]. Consequently, the preparation of PMMA particles via aqueous methods has been the area of significant investigation, especially with respect to particle nucleation, growth dynamics, and stabilization strategies [13-15]. Conventional free-radical polymerization, performed under suspension conditions, continues to be a widely used and industrially significant method for PMMA synthesis, owing to its inherent simplicity and its capacity to accommodate impurities [16,17]. In suspension systems devoid of surfactants, polymer particles are generated via polymerization within dispersed monomer droplets, without the employment of stabilizing surfactants. Even though these systems are relatively easy to apply, they regularly result in wider particle size allotment and confined control over particle morphology [18]. Copper-mediated radical polymerization techniques, sketch from the idea of atom transfer radical polymerization

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(ATRP), have been used in aqueous and heterogeneous settings where exact molecular weight control is not the key concern [19-21]. Copper-based catalysts are frequently employed in controlled radical polymerization techniques such as ATRP. However, under heterogeneous aqueous conditions, copper complexes may also influence radical generation, propagation, and particle nucleation without necessarily providing controlled/living characteristics. In the present work, no molecular-weight evolution, dispersity measurements, chain-extension studies, or kinetic analyses were performed. Therefore, the CuCl/EDA/CCl4 system is treated as a copper-assisted radical polymerization system rather than a true ATRP or SET-LRP process. Inside these frameworks, copper species can adjust radical concentration, nucleation dynamics, and particle stabilization, thus determining the morphology of polymer particles formed under emulsified conditions [22-24]. Particularly, numerous examinations highlight the application of copper-mediated radical pathways as pragmatic synthetic approaches, instead of strictly controlled or living polymerization systems [25-27]. Although radical polymerization methods are extensively documented, direct experimental comparisons between surfactant-free suspension polymerization and copper-mediated emulsified radical polymerization under similar aqueous conditions are still scarce, especially concerning PMMA nanoparticle synthesis [28-30]. Furthermore, numerous applied investigations emphasize particle morphology and practical processing results, often at the expense of in-depth kinetic or mechanistic examinations [31-33]. Within this framework, the current research presents a comparative analysis of PMMA particle synthesis, employing two aqueous radical polymerization methodologies: surfactant-free suspension polymerization and copper-mediated emulsified polymerization. This study concentrates on particle formation and morphological attributes, assessed through spectroscopic and microscopic techniques, rather than on controlled or living polymerization dynamics. Through this applied and comparative approach, the research seeks to furnish reproducible perspectives on PMMA particle synthesis strategies pertinent to materials-focused applications [34-40].

Experimental Section

Materials

Methyl methacrylate (MMA), potassium persulfate (KPS), ethylenediamine, carbon tetrachloride, benzophenone, and Tween-80 were purchased from CDH (New Delhi, India), unless stated otherwise. Copper(I) chloride was received from Loba Chemie (New Delhi, India) and all other reagents were of analytical grade.

Methods

Surfactant-Free Suspension Polymerization of PMMA

Poly(methyl methacrylate) (PMMA) was synthesized via surfactant-free suspension polymerization in a three-neck round-bottom flask of 100 ml with a mechanical stirrer, a reflux condenser, a nitrogen inlet, and a thermometer to ensure proper mixing, an inert atmosphere, and temperature control throughout the process. Initially, methyl methacrylate (MMA, 2.0 g, 20 mmol) was dispersed in deionized (DI) water (20 mL) and stirred under a nitrogen atmosphere at room temperature for 1 hour, which promoted the formation of monomer droplets (Figure 2.2.1 (a)). The polymerization was then started by adding an aqueous potassium persulfate (KPS) solution (2 wt% relative to MMA; 0.04 g, 0.15 mmol) with continuous stirring at 70 °C for 5 hours under a nitrogen atmosphere. After completion of the reaction, the mixture was allowed to cool to room temperature. The resulting PMMA dispersion was then centrifuged at 8000 rpm for 15 minutes, followed by several washes with deionized water to remove any residual initiator and soluble impurities. The purified polymer was subsequently dried under vacuum at 40 °C until a stable weight was attained. To study the effect of initiator concentration on monomer conversion, the amount of KPS was systematically varied from 2 wt% to 20 wt% with respect to MMA, while keeping all other reaction conditions remained constant.

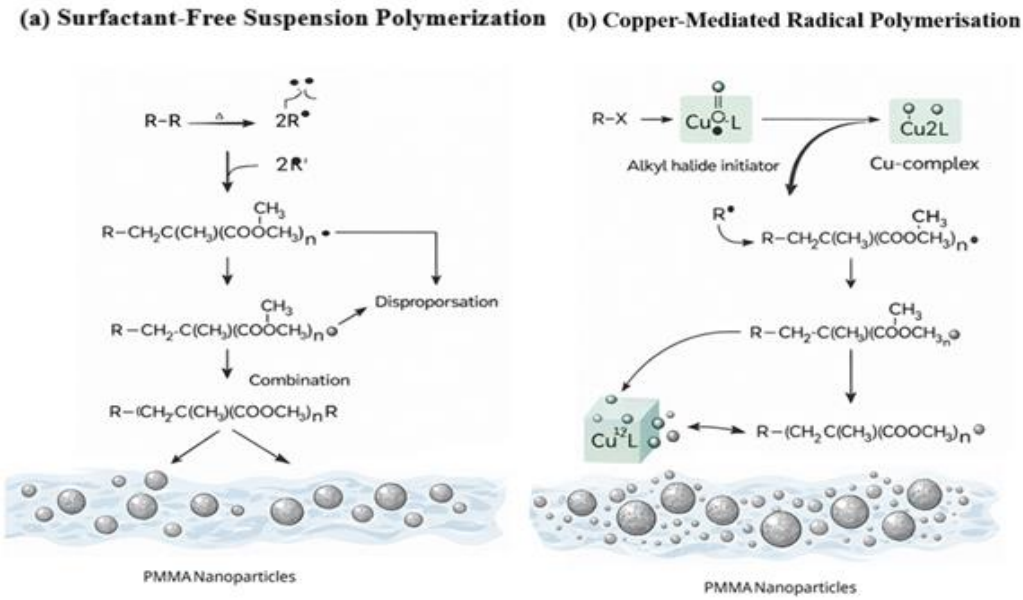

Figure: 2.2.1 A schematic depiction of radical polymerization results in how PMMA nanoparticles are established. This includes (a) the typical free-radical polymerization process, and (b) Copper-Mediated radical Polymerization.

Aqueous Copper-Mediated Radical Polymerization of PMMA Nanoparticles

Aqueous copper-mediated radical polymerization of PMMA nanoparticles was conducted under a nitrogen atmosphere, employing a similar experimental setup. MMA (2.0 g, 20 mmol) was mixed with copper(I) chloride (CuCl, 0.02 g, 0.2 mmol) and ethylenediamine (EDA, 0.012 g, 0.2 mmol) to form a catalytic complex, thus ensuring a Cu:EDA molar ratio of 1:1. Ethylenediamine was selected as a small, water-soluble bidentate ligand to improve catalyst solubility and regulate the concentration of active radical species within the aqueous biphasic system. The monomer–catalyst mixture was then dispersed in DI water (20 mL), which contained 1 wt% Tween-80 as an emulsifier and 5 vol% n-hexane as a co-solvent. In addition, carbon tetrachloride (2 mol% relative to MMA) was added as a halogen source.

The reaction mixture was purged with nitrogen and heated to 70 °C, followed by continuous stirring at 600 rpm for 8 hours, as depicted in Figure 2.2.1 (b). After completion, the reaction mixture was allowed to cool to room temperature and exposed to air to stop the radical reaction. After that, the mixture was centrifuged and thoroughly washed with DI water to eliminate any residual components. The PMMA nanoparticles were then dried under vacuum at 40 °C until a constant weight was achieved. Analogous to suspension polymerization, the initiator concentration was varied from 2 wt% to 20 wt% relative to MMA to assess its influence on monomer conversion under copper-mediated conditions.

Determination of Monomer Conversion

The degree of monomer conversion was assessed gravimetrically, employing the formula:

$$\frac{(\boldsymbol{mass\ of\ polymer})}{(\boldsymbol{mass\ of\ monomer})} \times \mathbf{100}$$

It is important to note the study's limitations: kinetic monitoring, molecular weight distribution analysis, and chain-extension experiments were not incorporated. Consequently, the copper-mediated process is presented solely as a comparative synthetic method for PMMA particle synthesis, rather than as a controlled or living polymerization system.

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Characterization Techniques

FTIR spectra were acquired to confirm PMMA synthesis by identifying characteristic ester carbonyl and C–O stretching vibrations. ^{1}H NMR spectroscopy was employed to validate the polymer's backbone and side-chain resonances, thus confirming PMMA's chemical structure. Particle morphology and size were evaluated using SEM and TEM analyses. Particle size distributions were confirmed by SEM/TEM micrographs, using image analysis software.

RESULTS AND DISCUSSION

Monomer Conversion

The impact of initiator concentration on the polymerization of MMA was assessed using a gravimetric technique, applicable to both surfactant-free suspension polymerization and copper-mediated emulsified radical polymerization. Monomer conversion exhibited a positive correlation with initiator concentration in both systems. Specifically, at an initiator loading of 20 wt% relative to MMA, conversions of roughly 85% and 95% were attained in the surfactant-free suspension and copper-mediated emulsified systems, respectively (Table 4.1.1). The comparatively elevated conversion observed in the copper-mediated emulsified system could be ascribed to variations in the reaction environment, encompassing the presence of copper species, emulsifier-assisted dispersion, and extended reaction duration. It should be noted that the conversion results are used only for comparison of polymer formation efficiency, and do not suggest controlled or living polymerization behavior.

Table 4.1.1 Shows how the concentration of the initiator affects how much the monomer converts when making PMMA. This was done using surfactant-free suspension polymerization and copper-mediated emulsified radical polymerization.

Polymer	Initiator (%)	Suspension Polymerization (%Conversion)	Copper Mediated Emulsified System (%Conversion)
MMA- 1	2.0	25	22.9
PMMA- 2	5.0	40	34.3
PMMA- 3	10	50	45
PMMA- 4	15	70	75
PMMA- 5	20	85	95

Structural Confirmation

FTIR characterisation of the synthesized polymers, derived from both surfactant-free suspension polymerization and copper-mediated emulsified systems, confirmed the successful formation of PMMA. Distinct absorption bands were detected, specifically at approximately 2959 cm^{-1}, which corresponded to $–CH_3$ stretching vibrations; a pronounced ester carbonyl (C=O) stretching band observed between 1722–1730 cm^{-1}; and C–O stretching vibrations within the 1140–1250 cm^{-1} range. Furthermore, the lack of the vinyl C=C stretching band, typically found around 1640 cm^{-1}, provided evidence for the effective polymerization of the MMA monomer (Figure 4.2.1-4.2.2). ^{1}H NMR spectroscopy provided additional confirmation of PMMA's chemical structure, revealing resonances corresponding to the α-methyl protons at 0.8–1.2 ppm, backbone methylene and methine protons within 1.8–2.1 ppm, and methoxy protons at 3.5–3.6 ppm. These spectral characteristics align with those previously documented for PMMA synthesized through radical polymerization methods. In accordance with these observations, the polymers displayed a predominantly atactic microstructure across both polymerization systems (Figure 4.2.3).

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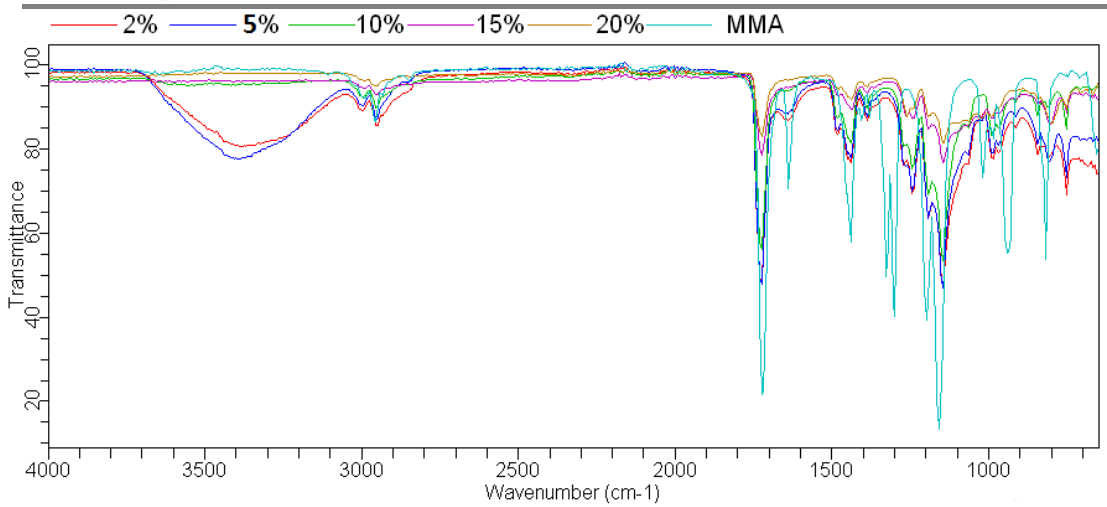

Figure 4.2.1 FTIR spectra of PMMA synthesized by copper-mediated emulsified radical polymerization at different initiator concentrations.

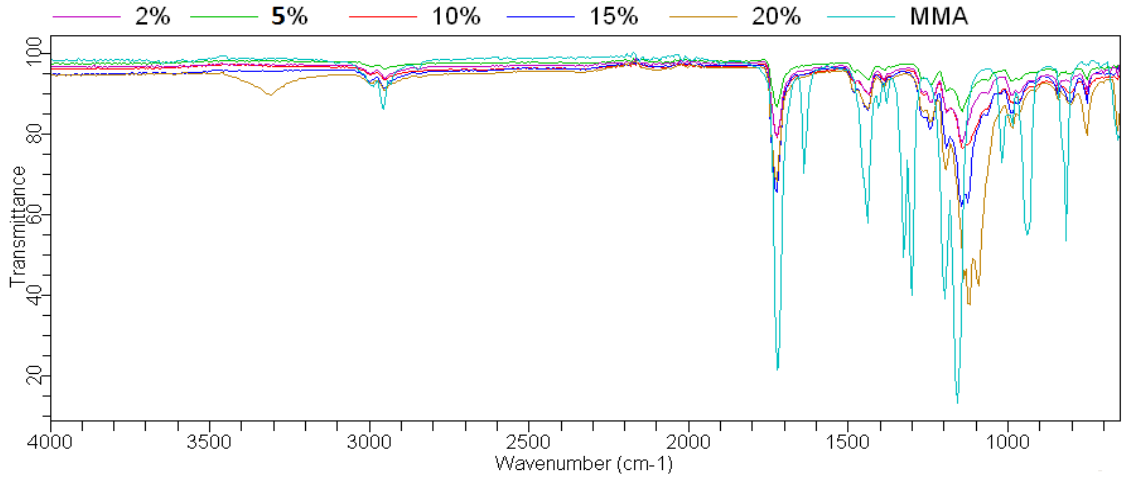

Figure 4.2.2 FTIR spectra of PMMA synthesized by surfactant-free suspension polymerization at different initiator concentrations.

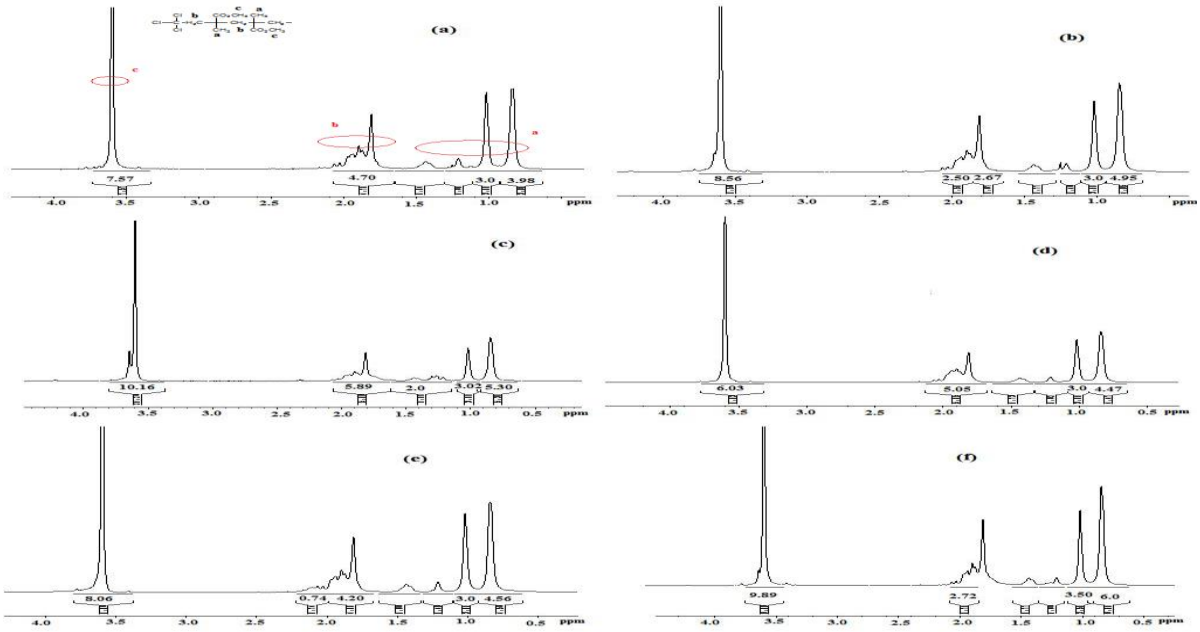

Figure 4.2.3 ^{1}H NMR spectra of PMMA prepared by aqueous radical polymerization at different initiator concentrations.

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Morphological Characterization

SEM and TEM clearly show differences in particle shape between the surfactant-free suspension polymerization and the copper-mediated emulsified system. The surfactant-free suspension polymerization produced particles with a wider range of sizes and less consistent shapes. But the copper-mediated emulsified system makes particles that were more spherical and had a more constant size distribution under the conditions studied. It's important to note that "uniformity" in this context refers only to the particle shape and size distribution seen in the microscopy images, not to the molecular weight distribution (Figure 4.3.1 & Figure 4.3.2).

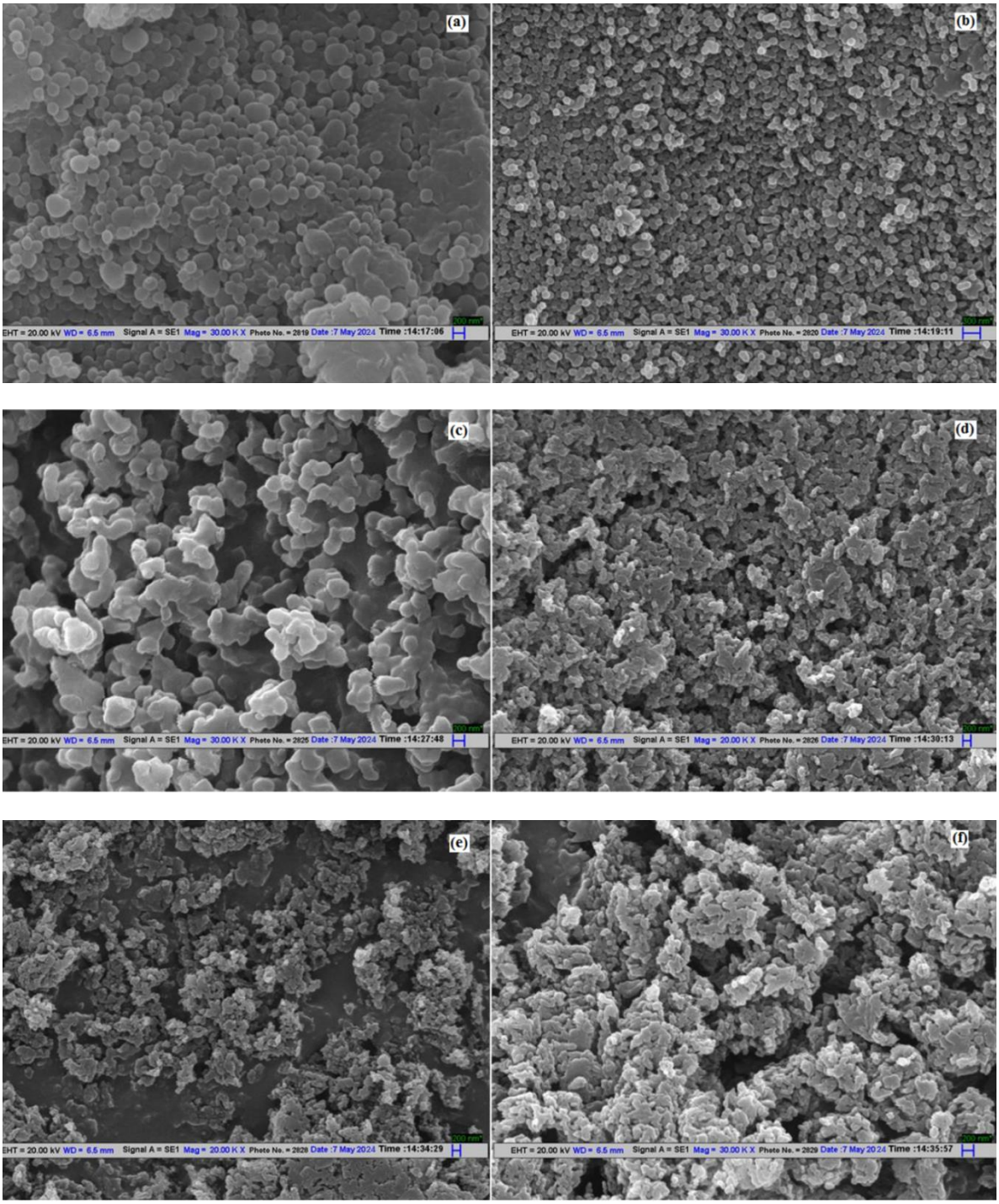

Figure 4.3.1 SEM images of PMMA particles synthesized by surfactant-free suspension polymerization (a–c) and copper-mediated emulsified radical polymerization (d–f) in aqueous media. Images correspond to initiator concentrations of 2%, 10%, and 20%, respectively, highlighting differences in particle size distribution and surface morphology.

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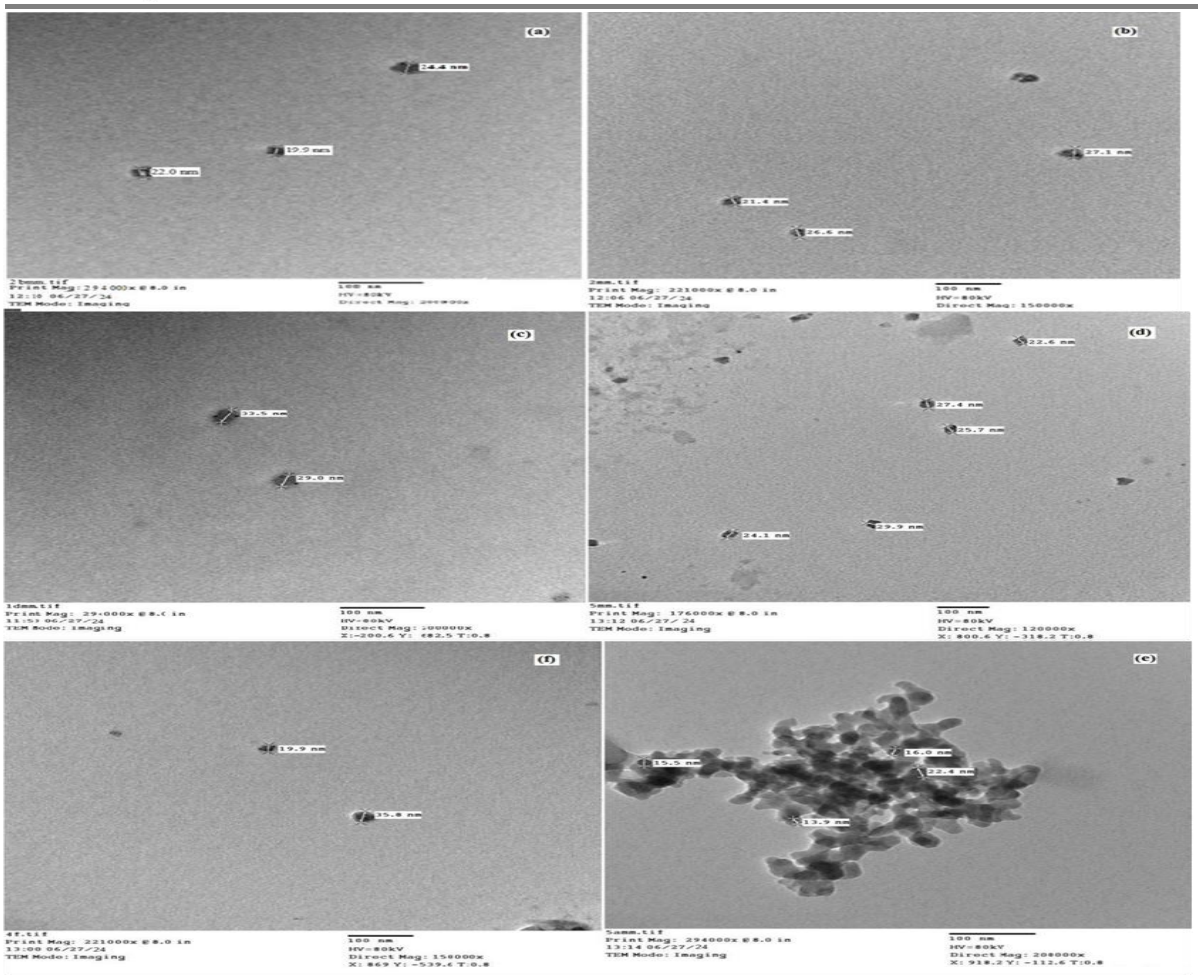

Figure 4.3.2 TEM images of PMMA particles obtained using surfactant-free suspension polymerization (a–c) and copper-mediated emulsified radical polymerization (d–f) at initiator loadings of 2%, 10%, and 20% in water. Differences in particle shape, internal contrast, and size uniformity are evident across the two synthetic routes.

Comparative Discussion and Practical Implications

The observed morphological disparities probably stem from differences in radical generation and subsequent polymerization dynamics within the two experimental setups. The inclusion of copper-based species could potentially modulate radical concentrations and polymer growth kinetics, thereby exerting an indirect influence on particle formation and stabilization within the aqueous medium. Nevertheless, this investigation is limited to the examination of visual and structural characteristics. As a result, since no information is available on molecular weight, reaction kinetics, or chain-extension studies, it is not possible to draw any conclusions about whether the polymerization follows a controlled or living mechanism. In this study, the term “uniformity” refers only to the particle size and morphology observed in electron microscopy images, and not to the molecular weight distribution of the polymer. In practice, the Cu-mediated approach demonstrated advantages in producing PMMA particles with a more uniform morphology given the experimental parameters; this attribute could be beneficial in applications where particle uniformity is critical. Conversely, the conventional free-radical method maintains its straightforwardness and circumvents the requirement for metal catalysts, which could be advantageous in applications demanding minimal post-polymerization purification.

CONCLUSIONS

This investigation offers a comparative analysis of two aqueous dispersed polymerization methodologies employed in the fabrication of PMMA nanoparticles. Spectroscopic assessments confirmed the successful production of PMMA particles via both conventional free-radical and Cu-mediated radical processes. Under the experimental parameters, the Cu-mediated approach resulted in particles exhibiting enhanced

morphological uniformity. Prioritizing particle morphology and practical synthesis results, rather than claims of controlled polymerization, this study furnishes pragmatic and reproducible perspectives that could inform subsequent refinements in PMMA particle synthesis.

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Competing Interests

The authors declare no competing interests.

Author Contributions

Dr. Sarvjeet designed the study. All authors contributed to experimentation, data analysis, and manuscript preparation.

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