

Maryam Mohammadpour Nazarabady and Gholam Ali Farzi*

Morphology control of silica/poly(methyl methacrylate-*co*-styrene) hybrid nanoparticles via multiple-mini-emulsion approach

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Abstract: An appropriate approach has been used for the preparation of silica/P(MMA-*co*-St) hybrid nanoparticles through converting previously prepared inverse mini-emulsions into a direct mini-emulsion and consequently, using the droplet nucleation polymerization technique. In the early stage of the procedure, silica particles were synthesized from TEOS in the presence of NH_4OH or HCl as a catalyst through a base or acid-catalyzed sol-gel process. TEOS, ethanol and trimethoxyvinylsilane were mixed in MMA:St (50:50) to create the inverse mini-emulsion I, similarly CTAB, NH_4OH /HCl and distilled water were dispersed into MMA:St (50:50) and called inverse mini-emulsion II. Then, the two mentioned inverse mini-emulsions were emulsified in water to achieve direct mini-emulsion. The nature of the catalyst and TEOS concentration varied, for the aims of investigation, their effect on the morphology and size of hybrid nanoparticles. This route provided a unique process for silica/polymer hybrid nanoparticles production, avoiding organic solvents. Transmission electron microscopy micrographs revealed that, the morphology of the hybrid nanoparticles can be controlled by the nature of the catalyst.

Keywords: hybrid nanoparticle; morphology; multiple-mini-emulsion; silica/P(MMA-*co*-St); sol-gel.

1 Introduction

The synthesis of silica/polymer hybrid nanoparticles has received much attention due to their important role

in the development of high-performance materials (1, 2). In most organic hybrids, as one of the main factors, interactions between the inorganic and organic phases among size and shape of the inorganic particles form the physical properties of materials (3, 4). This interaction becomes dominant as the physical interconnection between the polymer and the inorganic phase in many composite systems leads to large-scale phase separation and lack of physical properties (5, 6). As a solution, one can force polymer and inorganic phases to interact at a molecular level and upscale the physical properties of the ultimate composite material (7, 8). A standard technique for hybrid organic-inorganic material formation uses either hollow particles (9–11) or capsules (12, 13). Due to their ability to encapsulate versatile functional cargos; these methods gained wide applications in catalysis (14), drug-delivery systems (15, 16), biology (17), coatings (18, 19), and so on. Furthermore, in recent years, abundant novel techniques have been worked out in great detail to elaborate hollow particles or capsules. Such techniques, worthy of notice are hard and soft templating techniques, *in situ* and hetero phase polymerization (20–24). Most of these techniques are based on the sol-gel process, and includes preparation of a silica layer on the polymeric or hybrid particles via hydrolysis and condensation of the silica precursor (4, 25, 26), e.g. tetraethoxysilane (TEOS). This research line has been attractive to academic and technical applications in transformation of conventional alkoxides into silica with well-defined size, shape and narrow size distribution (2). In most cases, the process of silica nanohybrid fabrication is adapted with the Stöber method. However, controlling the monodispersity and the particle size in a few tens of nanometer using micro/mini-emulsion plays a significant role (27). An overview of critical issues concerning synthesis of hybrid materials was performed by Kickelbick (28) in which a variety of material preparation techniques such as mini-emulsion polymerization are introduced in detail.

By incorporating lipophilic compounds in acrylic latexes, in contrast to mini-emulsion polymerization, physical blending deals with hazy or non-uniform films,

*Corresponding author: Gholam Ali Farzi, Faculty of Engineering, Department of Materials and Polymer Engineering, Hakim Sabzevari University, Sabzevar, 9617976487, Iran, e-mail: alifarzi@yahoo.com

Maryam Mohammadpour Nazarabady: Faculty of Engineering, Department of Materials and Polymer Engineering, Hakim Sabzevari University, Sabzevar, 9617976487, Iran

which can be in large part attributed to the incompatibility of the two different ingredients as these highly hydrophobic compounds can be incorporated into monomer droplets during the miniemulsification process (29).

Regarding the miniemulsion polymerization as a way of preparation of organic/inorganic materials (30, 31), Landfester and Weiss (32), reviewed examples of a large variety of nanocomposite fabrication with an emphasis on the versatility of the miniemulsion process.

In a recent study, Nabih et al. (19) concluded that a multiple-mini-emulsion process is a new approach for synthesis of water-based inorganic-polymer hybrid particles. Using water-soluble or hydrophilic materials as starting materials, the inspired study can be extended in order to involve various inorganic and other materials (18, 19). However, no requirement for organic solvent and the use of polymerizable phase over a broad range composition has been discussed as the most prominent features of this method. Despite several benefits of the multiple-mini-emulsion technique for the production of water-based silica/polymer hybrids, to the best of our knowledge, no similar study has been reported regarding the morphology control of hybrid nanoparticles using this method.

In this study, an efficacious optimizing route comprising multiple-mini-emulsion technique is utilized for the production of silica/P(MMA-co-St) nanohybrids without a need to apply pre or post modification treatments and also with no organic solvent. The morphology of hybrid nanoparticles was controlled by the nature of catalyst.

2 Experimental section

2.1 Materials

Methylmethacrylate, styrene, trimethoxyvinylsilane (TEOS, 99%), ammonia solution (37%), hydrochloric acid (HCl, 37%), cetyltrimethylammonium bromide (CTAB, 99.0%), SPAN 60, trimethoxyvinylsilane (97%), ammonium persulfate (APS), sodium dodecylsulfate (SDS, 90%) were all purchased from Merck (Frankfurt, Germany) and used as received.

2.2 Miniemulsion preparation

Synthesis of $\text{SiO}_2/\text{P(MMA-co-St)}$ hybrid nanoparticles consists of four main steps, which are adapted with the

method reported by Nabih et al. (18, 19). In the first step, two inverse miniemulsions were prepared containing TEOS, trimethoxyvinylsilane, HCl/ NH_4OH and CTAB used as a silica source, coupling agent, catalyst and templating agent, respectively, in the dispersed phase while the continuous phase was composed of a mixture of polymerizable monomers and a suitable surfactant. In the second step, the two inverse miniemulsions were homogenized. In the third step, the resultant inverse miniemulsion was added to a surfactant-water solution followed by a homogenization to create a direct miniemulsion, whose dispersed phase consists of the monomers, and previously formed silica. Finally in the fourth step, the monomers of continuous phase were polymerized via the miniemulsion polymerization technique at a certain temperature. This four-step procedure is illustrated in Figure 1. Briefly, the dispersed phase of “inverse miniemulsion I” was prepared by dissolving a certain amount of TEOS (1 and 2 mol%) and 0.1 g trimethoxyvinylsilane in 10 g of 50:50 (w:w) deionized water and ethanol solution. The continuous phase was prepared by combining 25 g methyl methacrylate with 25 g styrene to which 7.5 wt% of the dispersed phase SPAN60 was added. Subsequently, the dispersed phase was added to the continuous phase and pre-emulsified after 5 min under strong magnetic stirring. The resultant crude emulsion, directly afterwards, was ultrasonicated in an ice bath for 4 min (amplitude of 90%, ultrasonication time of 4 min, pulse time of 10 s with a 5 s delay between each pulse). Likewise, in the preparation step, “inverse miniemulsion II” was formed as described above except for the dispersed phase which was provided by dissolving 0.135 g CTAB in 10 g of deionized water containing pH adjuster $\text{NH}_3\cdot\text{H}_2\text{O}$ (pH=12.3) or HCl (pH=1.3).

The next step comprises “co-homogenization of the inverse miniemulsions”. They (the two miniemulsions) were mixed together followed by ultrasonication at an amplitude of 90% for 6 min. During this stage, the sample was kept in an ice bath. Finally, they were “transferred to direct miniemulsion” through emulsification of some 37.91 g co-homogenized inverse miniemulsion in 110 g of deionized water containing, 1.01 g of SDS. The process was followed by pre-homogenization for 8 min and ultrasonication for 4 min while being kept in ice bath as mentioned. A polymerization process was carried out in a 250 ml three-neck round bottom flask. It was also purged for 30 min with nitrogen gas and was then inserted into a water bath and heated up to 85°C. The water solution of APS was introduced to reactor and miniemulsion polymerization was carried out for 3 h while the reactor content was mixed mechanically.

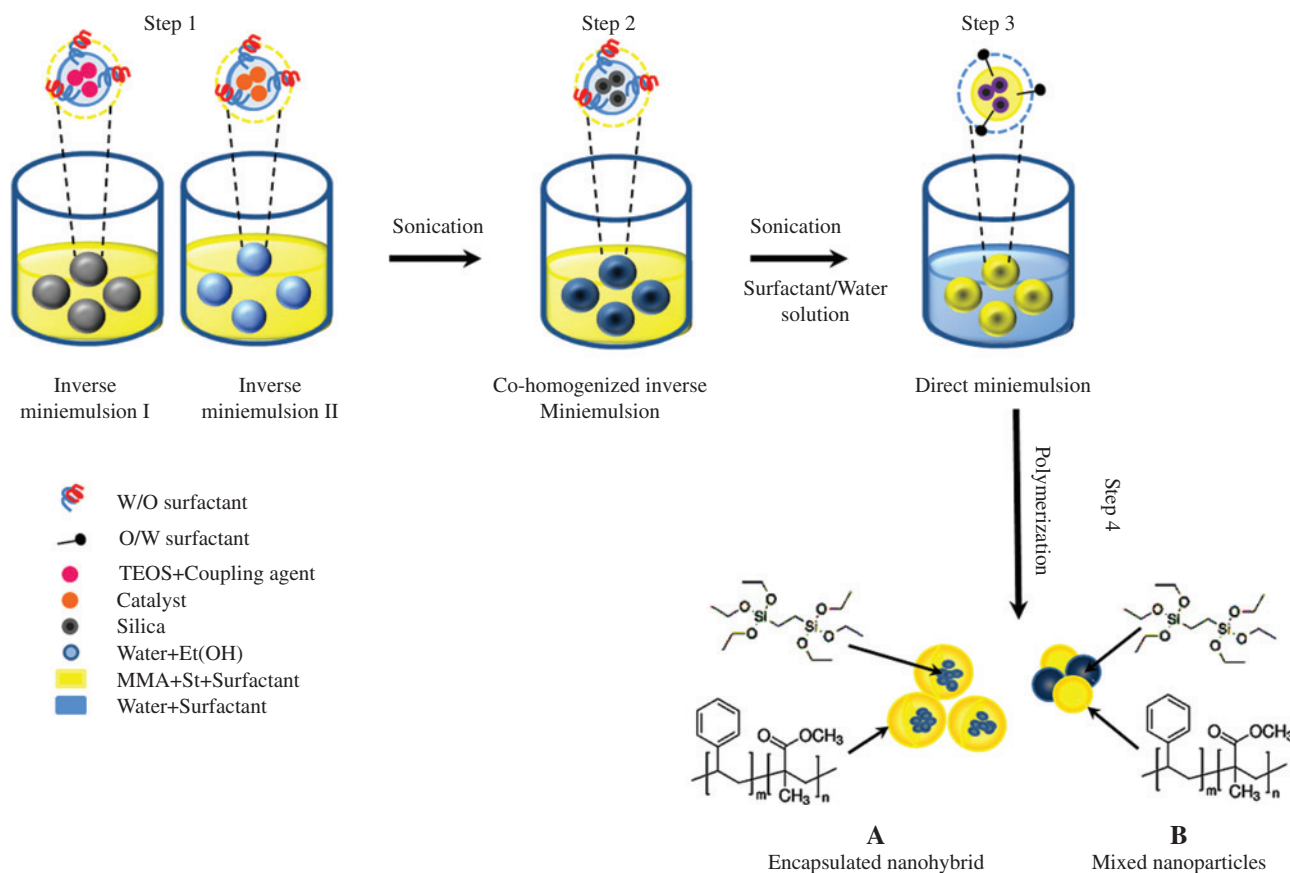


Figure 1: Synthesis of $\text{SiO}_2/\text{P}(\text{MMA-co-St})$ nano hybrids via multiple-mini-emulsion for morphology control: (A) encapsulated nano hybrids, (B) mixed nanoparticles.

3 Results and discussion

3.1 Chemical characterization of silica/P(MMA-co-St) hybrid nanoparticles

FT-IR spectra were recorded by a Shimadzu FT-IR 8400S spectrophotometer (Tokyo, Japan) using KBr discs. To avoid the effect of moisture, all samples (with 3–6 wt% silica relative to organic content and monomer conversion close to 100%) were dried overnight in a desiccator. As it seen in Figure 2, a distinct peak at 1108 cm^{-1} together with two less manifest peaks at 806 and 467 cm^{-1} appeared corresponding to the vibration absorption of Si-O-Si. However, a perceivable peak C-H stretch band at $3000\text{--}3100\text{ cm}^{-1}$, which is corresponds to aromatic C-H stretching vibration at 3027 cm^{-1} , as well as the characteristic peaks at 2921 , 2854 , 1733 , 760 , and 700 cm^{-1} are associated with the characteristic vibration of methyl (CH_3), methylene (CH_2), carbonyl ($\text{C}=\text{O}$), plane C-H bending, and benzyl groups, respectively (33, 34). Therefore, the

evidence confirms that the silica and P(MMA-co-St) are definitely formed. Besides, in these hybrids, the presence of the O-H absorption bands at 3400 cm^{-1} concomitant of the Si-O absorption at 1035 cm^{-1} can be owing to the formation of the effective O-H interaction between the copolymer chain and silanol groups of silica moieties. Meanwhile, the O-H bands were slightly broadened by changing from basic to acidic catalyst and gradually shifted from 3384 cm^{-1} to 3402 cm^{-1} , respectively (Figure 2). These observations may be the consequence of the strong hetero-associated hydrogen bonds between the organic and inorganic species. Also, the peaks reach a new level by changing the catalyst from acidic to basic type (t-test confirmed the significant difference between the two samples, $p\text{-value}=0.01$). The meaningful increase in peak level is likely to be caused by the fact that the mechanism of silica/P(MMA-co-St) nanoparticles formation is different under acidic and basic conditions. The mechanism of nano hybrid formation will be discussed in the following section in detail.

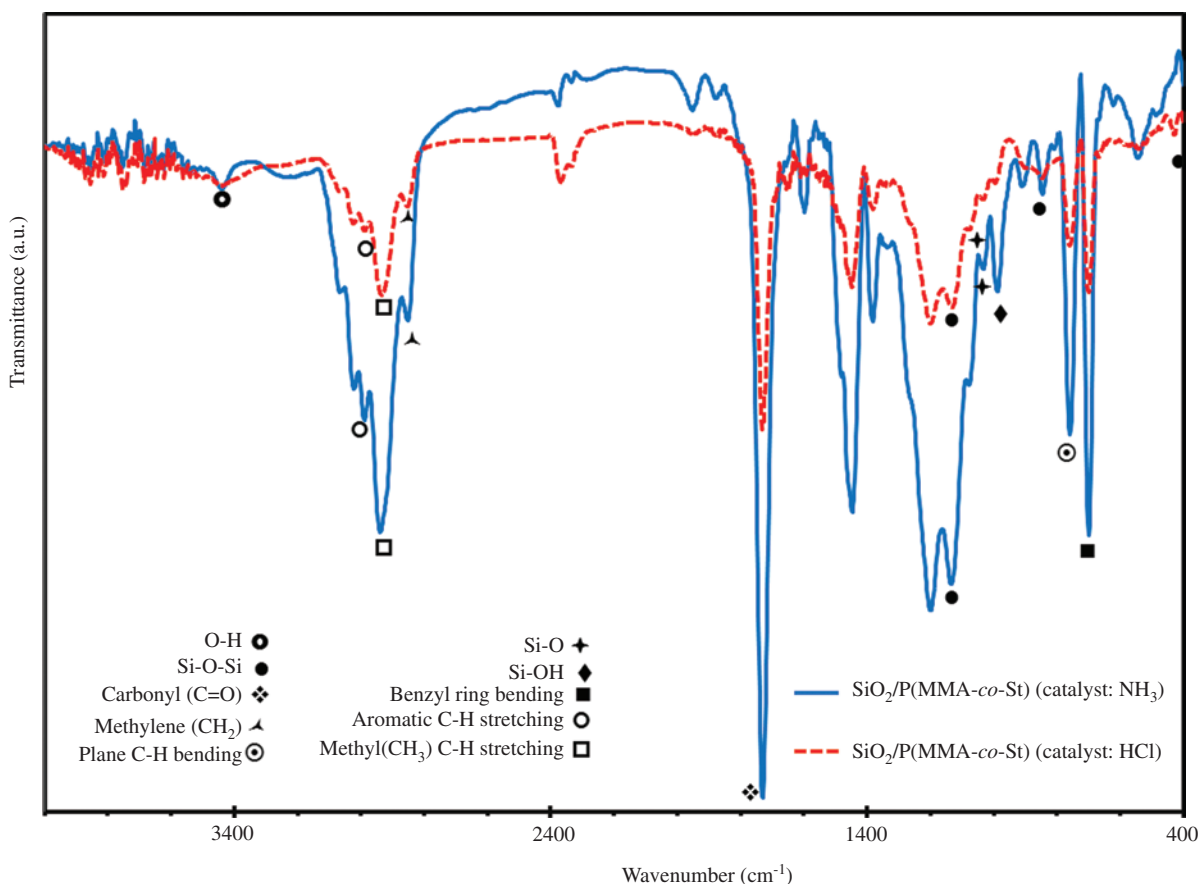


Figure 2: FT-IR spectra of $\text{SiO}_2/\text{P}(\text{MMA-co-St})$ nanohybrid particles with different catalysts.

3.2 Morphology of silica/P(MMA-co-St) hybrid nanoparticles

Transmission electron microscopy (TEM) studies were performed using an LEO 912AB Energy Filtering TEM microscope (Zeiss, Oberkochen, Germany) operated at 120 kV. One droplet of the origin suspension was diluted in alcohol and placed on a 300-mesh carbon-coated copper grid, then allowed to dry at room temperature, as illustrated in Figure 3. The samples were prepared with 1 mol% (0.1 g) TEOS loading in basic are presented in Figure 3(A–C) and acidic conditions in Figure 3(D–F), respectively. In these cases, the micrographs indicate that the spherical polymeric particles in the former are composed of inorganic material, while in the latter nanometer conglomerate of the moieties identified through the contrast, inorganic material would appear darker because of the higher atomic number. Another observation which was made using TEM regards different amounts of inorganic particles that were differently placed within or beside the polymeric particles. This observation also shows that there are different and

complex interactions between the inorganic and the polymeric particles depending on pH of the solution.

3.3 Formation mechanism of silica/P(MMA-co-St) particles in w/o/w miniemulsion under acidic or basic conditions

Before polymerization and during the process of being transferred to a direct miniemulsion, SPAN 60 would interact with other droplet constituents. In addition, it would mainly situate itself inside the droplets while it was expected to be situated at the interface, as hypothesized by Nabih et al. (19).

Based on this hypothesis, diffusion of tetraethoxysilane (TEOS) in the interface is possible from droplets formed in inverse miniemulsion I (w/o) to the ones formed in inverse miniemulsion II. Afterwards, in contact with water and catalyst (ammonia or hydrochloric acid) in the hydrophilic droplets, the silica source underwent

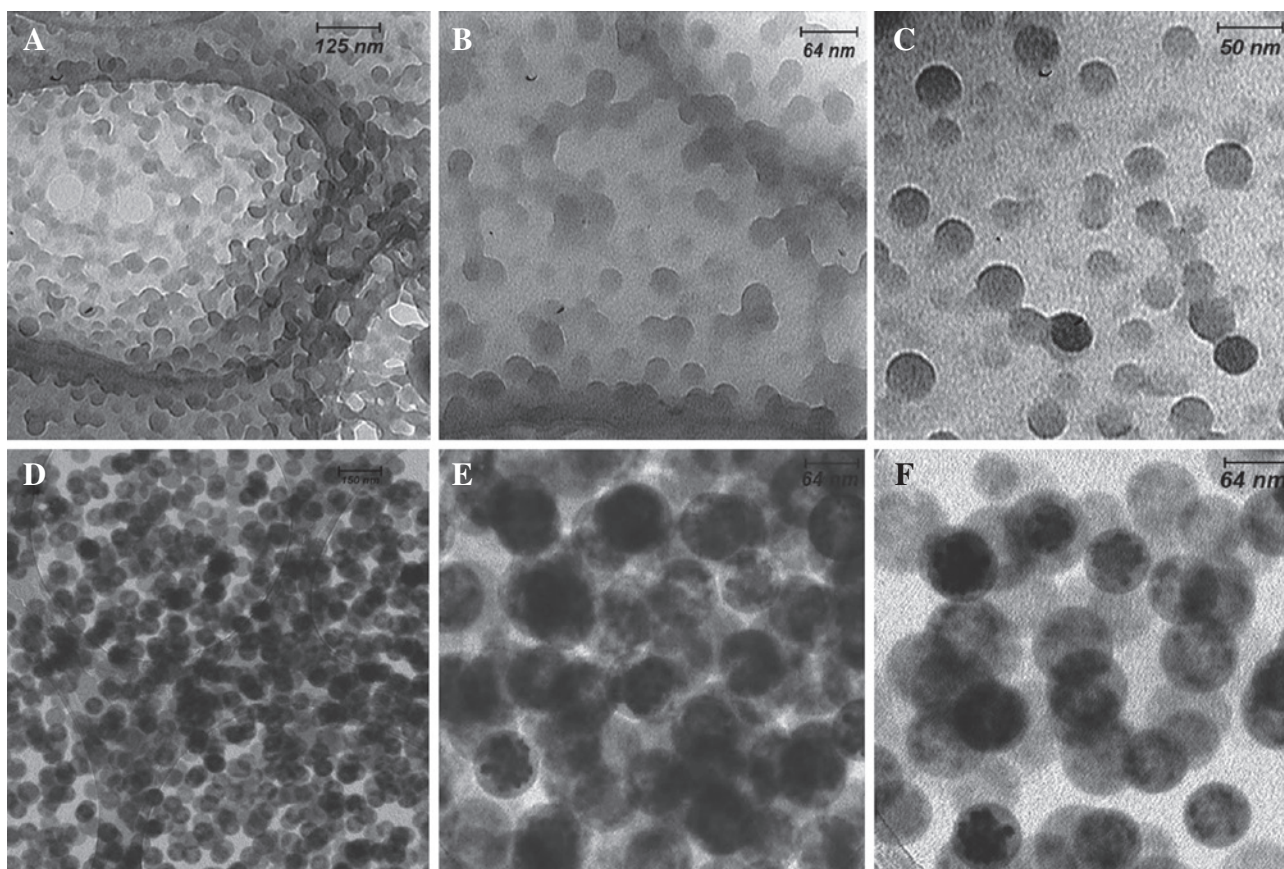


Figure 3: TEM observations of $\text{SiO}_2/\text{P(MMA-co-St)}$ nanohybrid particles synthesized under (A), (B) 2% mol TEOS and (C) 1% mol TEOS basic and (D), (E) 2% mol TEOS and (F) 1% mol TEOS acidic conditions.

hydrolysis and condensation. Nevertheless, both the thermodynamic (interaction between CTAB and silica species) and kinetic (e.g. viscosity) factors may significantly influence the particle morphology. As it is reported, the degree of hydrolysis of tetramethylorthosilicate may reach 70% at pH 1.05 after 2 min (35), meanwhile hydrolysis of silica precursors under highly acidic conditions is faster than that under the base conditions. The accelerated hydrolysis probably makes the abundant silanols easily dissolved in the aqueous droplets. According to the earlier hypothesis, the preferred locations of the as-formed silica species are the w/o droplet interfaces while the dissolution of the silanols provides trapping of the silica components which can be efficiently suppressed Ostwald ripening via the diffusion-preventing (30, 31). Hence, the observation of spherical polymeric particles comprising silica species could be explained. On the contrary, TEOS tends to form completely condensed silica species, which are easily separated from the aqueous solution under basic condition. This feeble conformation could be reflected in the same nearest-neighbor selection of same species by inorganic and organic components. Additionally, silica species

located at the droplet interfaces (as mentioned in the hypothesis) during the earlier stages (inverse miniemulsions) could affect stabilization of the droplets through the Pickering effect (36). As a consequence, spherical particles with nanometer corporation comprising two components might be expected (37, 38).

3.4 Particle size of silica/P(MMA-co-St) hybrid nanoparticles

Figure 4 depicts the particle size distribution of the resultant hybrids obtained by DLS (Zetasizer Nano-ZS, Malvern Instruments Ltd., Malvern, UK). The average particle size is approximately 35 and 73 nm under the basic (Figure 4A), and acidic conditions (Figure 4B), respectively. The larger size of the nanoparticles can be assigned to the relatively lower pH which may lead to accelerate hydrolysis reactions of TEOS, and providing silica encapsulation conditions. These results are in line with the previous researchers' findings (5, 37, 38). Meanwhile, there are a few points worth noting; in the presence of CTAB, the tendency of

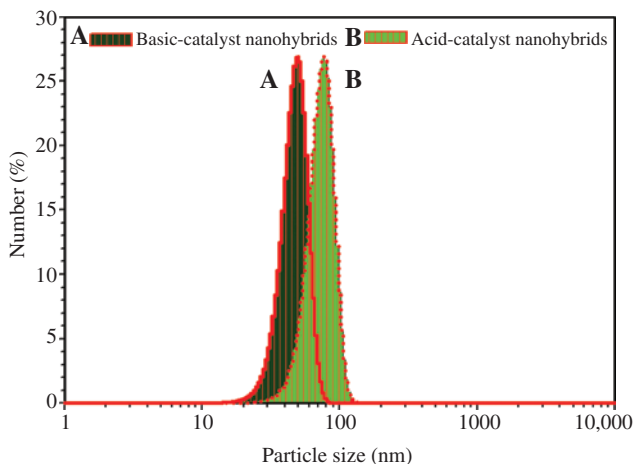


Figure 4: Particle size distribution histograms of the (A) basic-catalyst and (B) acid-catalyst nanohybrids.

SiO₂ moieties (in acidic condition) into the largish spherical coagulation would be increased (38, 39). Thus, it can be a cause for larger particle size in acidic environment in comparison with a basic one. Whereas the insolubility of silica derivatives can lead to the aggregation of the large particles (Laplace pressure increase) and the acceleration of Ostwald ripening (31), these derivatives may act as a hydrophobic agent that counteracts the droplet's pressure to make the miniemulsion system stable.

3.5 Thermal stability of silica/P(MMA-co-St) hybrid nanoparticles

To investigate the thermal properties of SiO₂/P(MMA-co-St) hybrid nanoparticles TGA analysis (Dupont 931, TA Instruments, New Castle, DE, USA) was carried out at 25°/min and temperature range of 100–600°C. TGA plots of the same silica-content nanohybrids obtained at different pH values and the pristine copolymer are shown in Figure 5. As it is revealed by the diagrams, the onset decomposition temperature of the nanohybrids is increased in comparison with pristine P(MMA-co-St), which can be attributed to the presence of the silica in the nanohybrids. The shifted onset decomposition temperature from 381.1°C [P(MMA-co-St)] was raised to 391.5 and 402.7°C for basic- and acid catalyst nanohybrids, respectively. The findings are in accordance with the previous studies (40–43). The weight loss value of SiO₂/P(MMA-co-St) hybrid prepared in acid condition is lower than that of SiO₂/P(MMA-co-St) hybrid synthesized in basic and pure P(MMA-co-St) which are ~88.7, 89.75 and 94.7% in air, respectively. These results can be explained by the fact that the interaction force between the copolymer and silica species is changed

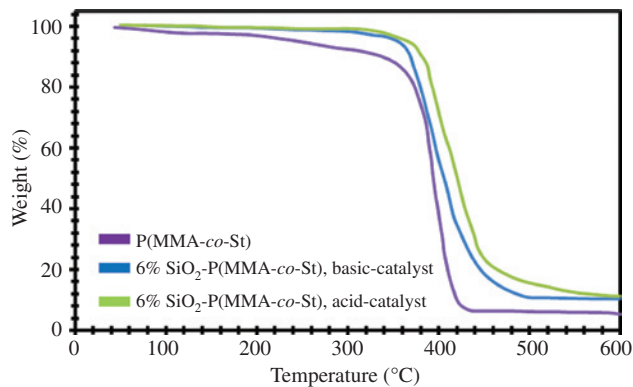


Figure 5: TGA analysis of SiO₂/P(MMA-co-St) nanohybrid particles with different catalysts.

from the weak hydrogen bonds to the strong hetero-associated hydrogen bonds (see Section 3.1), when the different catalyst used to prepare hybrid nanocomposites.

Thus, it seems that the results obtained from the observation of TGA are also because of the morphology diversity of nanohybrids, so that, the attachment between copolymer chains and the silica particles in the silica-entrapped is stronger than the close proximity between the components in the nanometer conglomerate morphology. These findings are obtained from the FT-IR data and TEM micrographs.

4 Conclusions

It has been shown that a hybrid silica/MMA co-St miniemulsion with a complex and adjustable polymer composition can be successfully prepared via a highly versatile synthetic route avoiding organic solvents. Using TEM, FT-IR and TGA analyses, the formation of the silica particles in both the direct vicinity of the co-polymer particle and their incorporation into the organic polymers has been revealed. This indicates an interesting fact in the mechanism of silica/P(MMA-co-St) nanoparticles formation under acidic and basic conditions. It was shown also that it is possible to control the morphology of hybrid nanoparticles by the nature of catalyst. The up-scaled multiple-miniemulsion that does not need organic solvent anymore makes it possible to provide the full potential of hybrid materials for the creation of more competitive and cleaner-source nanohybrids. According to the TGA results obtained, hybrid nanoparticles have a good thermal stability. Furthermore, this study opens the door to the application of wide range of inorganic materials as long as their precursors have the appropriate relative miscibility in one another.

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