RSC Advances

PAPER

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Cite this: *RSC Adv.*, 2015, **5**, 35325

Preparation of "hard-soft" Janus polymeric particles *via* seeded dispersion polymerization in the presence of *n*-paraffin droplets

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Received 21st March 2015
Accepted 13th April 2015

DOI: 10.1039/c5ra05026j

www.rsc.org/advances

A newly emerged class of Janus polymer particles, so-called "hard-soft" ones, were produced using seeded dispersion polymerization (SDP) of 2-ethylhexyl methacrylate (EHMA) with polystyrene (PS) particles in the presence of *n*-paraffin droplets. It was found that the presence of *n*-paraffin in the medium does not have any effect on the shape of the seed particles, but it changes the distribution of poly(ethylhexyl methacrylate) (PEHMA) domains on the surface of them from symmetric to asymmetric, resulting in the production of Janus composite particles. The effect of various polymerization conditions (*e.g.* type of the hydrocarbon, monomer concentration, *n*-paraffin content, amount of initiator, methanol–water weight ratio, stabilizer content, type of second monomer, and size of seed beads) on the shape of the final particles was investigated. From all of the obtained results, it was concluded that the size and concentration of precipitated PEHMA oligoradicals coupled with the presence of *n*-paraffin are the main parameters responsible for the production of Janus polymer particles.

Introduction

Polymer particles are one of the interesting functional materials which have been widely used in various applications (*e.g.* light scattering, drug delivery systems, chromatography, and so forth) for many years. Their functionality is mainly controlled by some parameters like composition, polarity, size, size distribution, shape, and so forth. It has always been a great goal for researchers to introduce particles with new functionalities by controlling these characteristics. Shape and morphology of the particles is one of these characteristics which have been used widely for such a reason. Therefore, particles with different shapes and morphologies including "spherical",[1–4] "hemispherical",[5] "egg-like",[6] "confetti-like",[7] "raspberry-like",[8–11] "snowman-like",[7,12] "rugby-ball-like",[13] golf-ball-like,[14] disk-like,[15–18] red blood corpuscle-like,[19] almond-shell-like,[20,21] bowl-like,[22,23] multi-layered,[24] cage-like,[25,26] and so forth have been developed.

As it is obvious, there is an immense variety of such functional materials, but among such variation, anisotropic "Janus" particles has attracted increasing interest because they can possess compartments which are opposing in nature, as a case in point, one part can be hydrophilic while the other side is hydrophobic.[27] Such opposing anisotropy paves a way for Janus particles to be applicable in the advanced applications. For instance, they can be used as emulsifier for Pickering emulsion polymerization.[28] Or they can fabricate intricate supracolloidal structures by their self-assembly.[29,30] Recently, new generation of Janus particles has been introduced. Such particles, which so-called "hard-soft" Janus particles, possess distinctive high and low glass transition temperature lobes which make them to be applicable for a variety of applications thanks to their different behaviour under ambient conditions. It means that one lobe can deform in such conditions while the other one remains robust and solid. Skelhon *et al.* reported their application as Pickering stabilizers thanks to their hierarchical assembly into colloidal molecule-type clusters.[31,32]

Such interesting properties of "hard-soft" composite particles have attracted the attention of scientific communities all around the world to develop new approaches for their production. Seeded emulsion polymerization is one of these techniques. Several groups have employed this approach and produced various kinds of such particles, however, swelling of employed seed particles with monomer following with the polymerization results in phase separation of two polymer phases which makes the situations very complex to adjust the final morphology on Janus one even though some techniques (*e.g.* cross-linking of seed beads) are employed in order to take the situations under control.[32–35] Hence, an alternative method would be required which does not have same restriction. SDP is the best candidate for such reason since in this reaction system, monomer remains in continues phase and generally does not swell the seed beads. This eliminates problems arising from the phase separation within seed particles. In addition, there is not

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any concern regarding the effect of charged residues from surfactants, initiators, or charged comonomers on final particle morphology in SDP system thanks to lowering the difference in interfacial tension between the continuous phase and the particle by the nonaqueous medium. Skelhon *et al.* used this approach and produced PS/poly(*n*-butyl acrylate) "hard-soft" Janus particles in a simple way. They found that surface nucleation by capture of the oligoradicals onto the surface of the seed particles thereby forming a distinct new polymer phase is the formation mechanism of such particles.[32]

As it is obvious, it is possible to produce this kind of Janus particles by adjusting SDP conditions in a way that second polymer forms on the surface of seed beads asymmetrically. This idea made us to try using SDP in the presence of solvent droplets for fabrication of such exceptional morphology since we already reported the production of asymmetric shapes using this technique.[36] However, changing the shape of seed particles because of the solvent diffusion into them following with reduction of their inside viscosity was the restriction that we had. Therefore, *n*-paraffin as the solvent which cannot be absorbed by PS seed particles was employed, resulting in the production of "hard-soft" Janus particles. In addition, it was tried to control the shape of the obtained particles by varying the reaction conditions and the results will be presented in the following paragraphs.

Experimental

Materials

Styrene (Merck Chemical, Germany) was purified by distillation under vaccum and was stored in the refrigerator before use. Reagent grade of 2,2′-azobis(isobutyronitrile) (AIBN) (Merck Chemical) was purified by recrystallization. All other materials were used as received, including 2-ethylhexyl methacrylate (EHMA), lauryl methacrylate (LMA), poly(vinyl pyrrolidone) (PVP) (weight-average molecular weight 36 000 g mol^{-1}, Merck Chemical), and guaranteed reagent grade of methanol, ethanol, 1-butanol, hexane, decane, dodecane, hexadecane, and *n*-paraffin (kinematic viscosity of 11 centistokes, density of 0.85 g cm^3 at 40 °C, and boiling point of 220 °C).

Typical dispersion polymerization of styrene

Dispersion polymerization of styrene was carried out in 40 ml glass bottles as follows: PVP (0.8 g) and AIBN (0.08 g) were mixed with a mixture of ethanol (20.8 g) and water (5.2 g). Then, styrene (4 g) was added to the previous solution. The bottles were purged with nitrogen, capped and sealed. The reaction bottles were then tumbled with tumbling device end-over-end at 24 rpm in a constant-temperature water bath at 60 °C for 24 h. The morphology of produced particles was observed directly by Zeiss optical microscope and scanning electron microscope (SEM) (Seron Technology, AIS2100). The average diameter (D_n) and polydispersity index (PSD) of PS particles were calculated using the following equations for the group of at least 100 individual particles observed in the microscopic images. Here, n_i is the number of particles with a diameter of d_i. D_n and D_w are the number and weight average of diameters of the particles, respectively.

$$D_w = \frac{\sum n_i d_i^4}{\sum n_i d_i^3} \quad (1)$$

$$D_n = \frac{\sum n_i d_i}{\sum n_i} \quad (2)$$

$$PSD = \frac{D_w}{D_n} \quad (3)$$

PS seed particles were used as seeds in the next step after centrifugal washing three times with methanol.

Table 1 Polymerization conditions for SDP

Ingredients	
PS seed particles (g)	0.25
EHMA (g)	0.125
AIBN (g)	0.003
PVP (g)	0.025
n-Paraffin (g)	1
Methanol (g)	8
Water (g)	2

Typical SDP

The SDP of EHMA was carried out in sealed glass bottles under the conditions listed in Table 1. The polymerization was performed for 24 hours under nitrogen atmosphere by shaking at 80 cycles per min (3 cm strokes) in a constant-temperature water bath at 65 °C. The obtained composite particles were observed with Zeiss optical microscope.

Results and discussion

The SEM micrograph of PS microspheres produced by dispersion polymerization according to the procedure explained in the Experimental section is shown in Fig. 1a. Analysis of the SEM images and calculations show that these particles have D_n and PSD values of 2 μm and 1.01, respectively. The PS seed beads were used as seed particles in SDP of EHMA in the presence of *n*-paraffin under the conditions listed in Table 1. Optical image of the obtained PS/PEHMA/*n*-paraffin composite particles having Janus morphology is shown in Fig. 1b. It is noteworthy to point out that because of the particle adhesion during drying due to the low glass transition temperature (T_g) of PEHMA phase, optical microscopic pictures instead of electronic ones were used for investigation of the morphology of the composite particles. As it can be seen, these particles own a dark part which is PS phase and a bright one that represents PEHMA/*n*-paraffin domain. This observation imply that PEHMA phase grow on the surface of the seed beads asymmetrically, resulting in the production of "hard-soft" Janus particles. The reason why

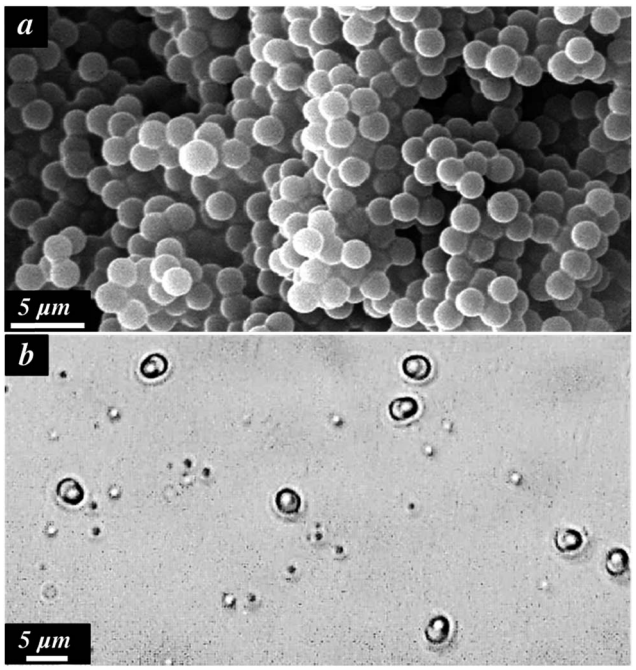

Fig. 1 (a) SEM micrographs PS particles produced by dispersion polymerization according to the procedure described in the Experimental section (b) optical image of PS/PEHMA/*n*-paraffin composite particles produced by SDP of EHMA with PS seed particles in the presence of *n*-paraffin droplets under the conditions listed in Table 1.

this type of growth happens could be explained with implementing further tests on this polymerization system.

First, the type of hydrocarbon, which is the key parameter, was changed in order to explain the reason. SDPs of EHMA were carried out in four separate experiments using hexane, decane, dodecane, and hexadecane as the solvent instead of *n*-paraffin. This change was implemented due to the fact that different hydrocarbons have different effects on the inside viscosity of PS particles because of their different diffusion ability into PS particles. The obtained results are shown as optical images in Fig. 2. It can be seen that Janus morphology is obtained only in the case of *n*-paraffin and the other hydrocarbons participate in the formation of other morphologies from hamburger-like in the case of hexane and decane to polyhedral one in the case of dodecane and hexadecane. In previous studies, it was shown that the affinity of PS phase and hydrocarbon decreases with an increase in length of the alkyl chain of hydrocarbons, resulting in less diffusion of hydrocarbon into PS particles, less decrease of their inside viscosity, and therefore production of less nonspherical morphologies.[15–18] In addition, time course monitoring of this reaction system showed that PS particles with hemispherical shape are produced in the beginning of the reaction[15] which means that PEHMA domains form on one side of seed particles in the beginning of the reaction but with increment of EHMA conversion and precipitation of PEHMA chains on the surface of them coupled with further reduction of viscosity inside the seed beads because of the hydrocarbon diffusion, these domains grow in other regions, resulting in the production of symmetric morphologies such as hamburger-like.

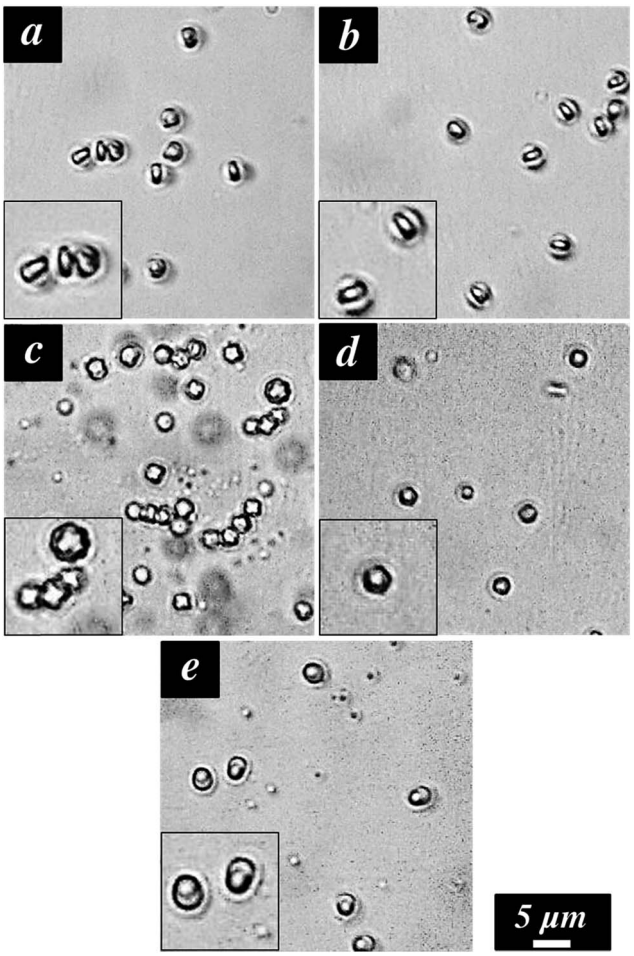

Fig. 2 Optical micrographs of PS/PEHMA/hydrocarbon composite particles produced by SDP of EHMA with PS seed particles in the presence of various hydrocarbon droplets under the conditions listed in Table 1: (a) hexane (b) decane (c) dodecane (d) hexadecane (e) *n*-paraffin. The scale belongs to bigger micrographs.

From all of these observations, it can be inferred that *n*-paraffin which has less diffusion ability rather than the other hydrocarbons does not affect the shape of PS beads and only

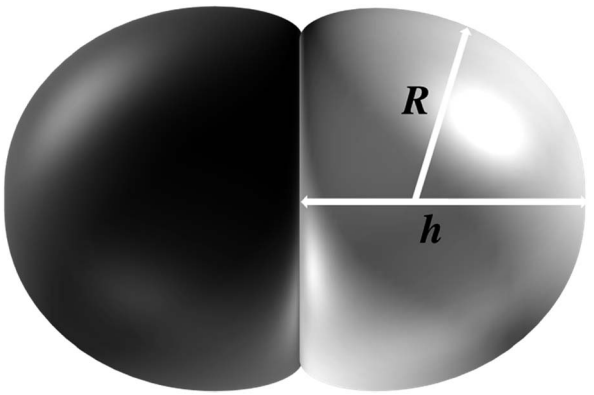

Fig. 3 Schematic of the measurements used for calculation of the volume of the PEHMA/*n*-paraffin lobe (bright) growing off a PS seed bead (dark).

participate in the growing of PEHMA domains which are formed in the beginning of the reaction. These domains absorb PEHMA chains as well as EHMA quickly from methanol–water medium over the bare PS particles' surface, and as a result, grow asymmetrically, resulting in the production of PEHMA/*n*-paraffin lobe as the soft compartment of PS/PEHMA/*n*-paraffin "hard-soft" Janus particles. As it is obvious, this method is so simple for the production of such unique particles owing to it is ability for controlling the growth manner of second polymer on the surface of the seeds.

One of the important issues about Janus particles is the volume of each one of the compartments. In the case of PS/PEHMA/*n*-paraffin composite particles, the volume of PS phase is constant and can be calculated easily, but it is required to generate an equation for calculation of the volume of PEHMA/*n*-paraffin since this value can be an excellent measure for determining the effect of various polymerization conditions on the shape of Janus morphology. To do so, we used the scheme presented in Fig. 3 that is as same as the one suggested by Skelhon *et al.* According to this scheme, the volume of the growing PEHMA/*n*-paraffin lobe can be modeled as a spherical cap, whereby the lobe is treated as a hemisphere of a sphere. It should be noted that the area of contact between the PS and PEHMA/*n*-paraffin lobe is treated as planar rather than a 3D curved surface.[32] The following equation can be generated for calculation of the volume by using this scheme:

$$V = \frac{\pi h^2}{3}(3R - h) \quad (4)$$

where R is the radius and h is the height of the lobe. As it was also mentioned, this equation will be used in the following paragraphs for investigation of the effect of each reaction parameter on the morphology of obtained particles.

The presence of *n*-paraffin in this medium is one of the key parameters responsible for preparation of Janus morphology. Therefore, in order to investigate the effect of this parameter, three separate SDPs were carried out in the presence of various amounts of this material in addition to the one without using any *n*-paraffin. Fig. 4 shows the obtained results as optical micrographs in addition to a curve. As it is obvious, spherical particles are obtained in the absence of this component. It means that PEHMA domains grow on the surface of PS beads symmetrically. With addition of 0.25 g of *n*-paraffin, the lobes growing off PS particles are seen. The interesting point is shown with white arrows which is the presence of composite particles having double lobes. The population of these particles is presented in Fig. 4e which has been obtained by counting at least 200 individual particles. With further increment of *n*-paraffin content, number of particles owning double lobes diminish sharply from around 45% to 2.5%. This observation implies that the presence of higher amounts of the hydrocarbon provides a situation in which PEHMA domains which form in the beginning of the reaction grow faster by absorbing the hydrocarbon, resulting in the capturing most of the PEHMA chains and EHMA from the medium, and therefore, formation of one lobe. However, in the case of lower amounts of *n*-paraffin, these domains get a lower surface area, so provide an opportunity for other bare regions to acquire PEHMA and *n*-paraffin which results in the formation of double lobes. Another important parameter is the average volume of each lobe that increases with an increase in *n*-paraffin content. Nevertheless, this functionality diminishes in higher contents of the hydrocarbon which means that PEHMA phase absorbs a restricted amount of *n*-paraffin. This observation also shows that each lobe is made mostly from PEHMA phase.

All of the observations showed that asymmetric distribution of PEHMA domains on the surface of PS seed beads is the main phenomenon responsible for the formation of Janus morphology. It suggested that implementing any change on the concentration of PEHMA might have a great effect on the morphology of final particles. Therefore, three separate SDPs were designed to investigate the effect EHMA concentration on the shape of final particles using 0.075, 0.125, and 0.5 g of this material. The optical micrographs of the composite particles produced from these experiments as well as the related curves are shown in Fig. 5. It can be seen that number of the particles having double lobes is high in the case of high and low concentrations of EHMA. In addition, the average volume of each lobe is low for both of the concentrations. These phenomena can be explained as follows: the solvency of the medium reduces with a decrease in EHMA concentration, resulting in precipitation of higher number of oligoradicals which have short lengths. These numbers of oligoradicals are enough for almost symmetric distribution of PEHMA domains on the surface of PS seed microspheres which growing them results in the formation of double lobes. The presence of particles having two lobes with different sizes (see white arrow in Fig. 5a) also approves this idea. Furthermore, the volume of each lobe decreases with a decrease in monomer content which is because of lower available feed in the medium for growing each lobe as well as availability of the feed as smaller precipitated oligoradicals. Symmetric distribution of PEHMA/*n*-paraffin domains on the surface of seed particles also intensifies the decrease of the volume because for each particle, there are two sites for consumption of oligoradicals and monomers. On the other hand and in the case of higher concentrations of EHMA, because of increasing the available feed in the medium, the chance of capturing the oligoradicals by bare regions increases, resulting in the almost symmetric distribution of PEHMA domains on the surface of seed microspheres, and therefore, formation of double lobes. Moreover, as it can be seen, size of the lobes decreases in higher EHMA concentration which is because of the consumption of PEHMA feed by two sites thanks to the development of second lobe on the seed particles. These results show that for getting Janus morphology, monomer concentration should be adjusted on an optimum value.

In a dispersion polymerization medium, the solubility of continues phase is a key parameter for controlling the size of final particles.[1–4] We already show the importance of this parameter in the above paragraphs by changing the monomer concentration and as it was observed, the volume of a PEHMA/*n*-paraffin lobe as well as the population of composite particles having double lobes were controlled *via* implementing any

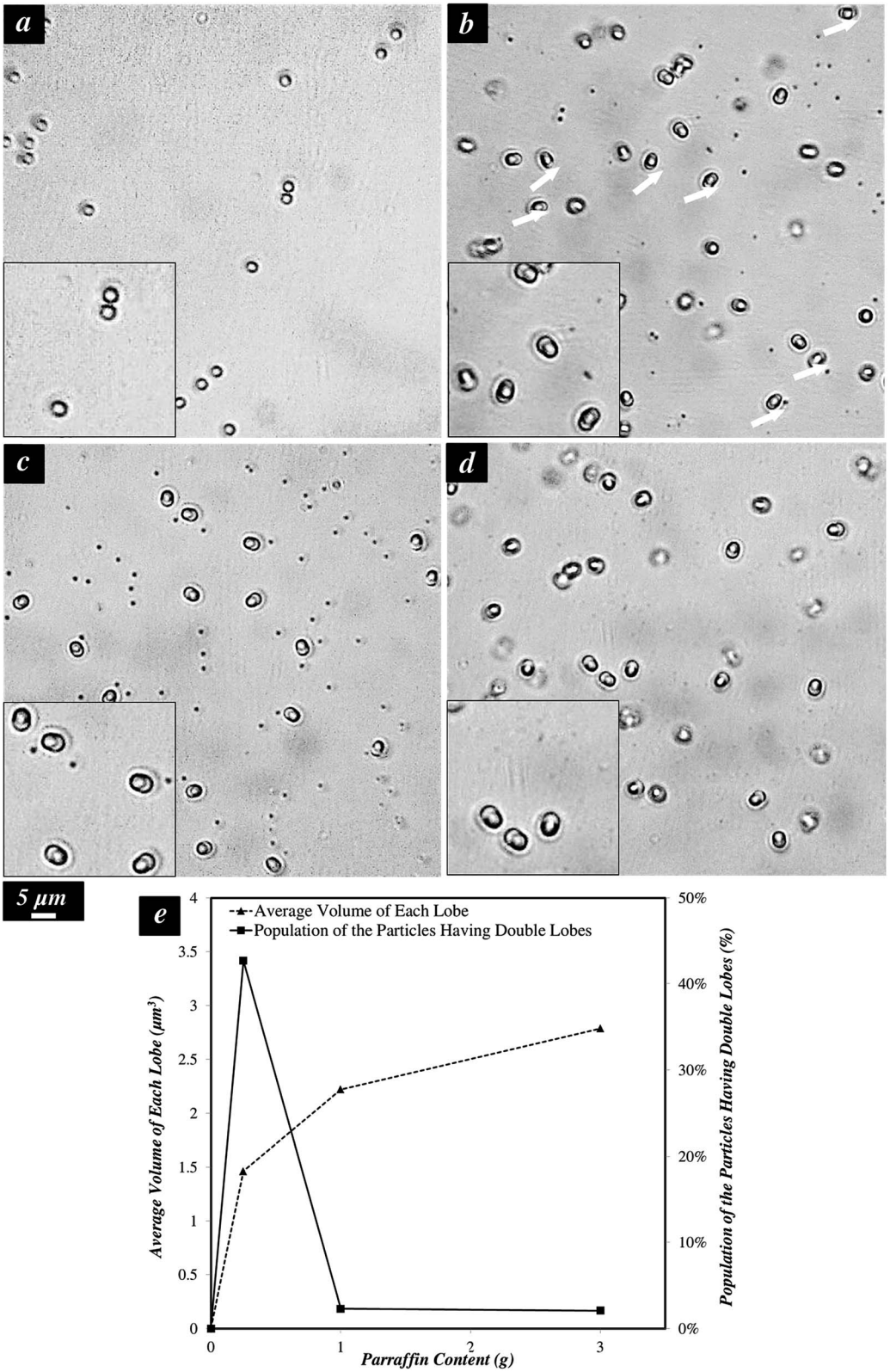

Fig. 4 Optical micrographs of PS/PEHMA/*n*-paraffin composite particles produced by SDP of EHMA using PS seed particles in the presence of various amounts of *n*-paraffin droplets under the conditions listed to in Table 1: (a) 0 (b) 0.25 (c) 1 (d) 3 g and (e) the average volume of each lobe and the population of the particles having double lobes *versus* *n*-paraffin content curves. The scale belongs to bigger micrographs.

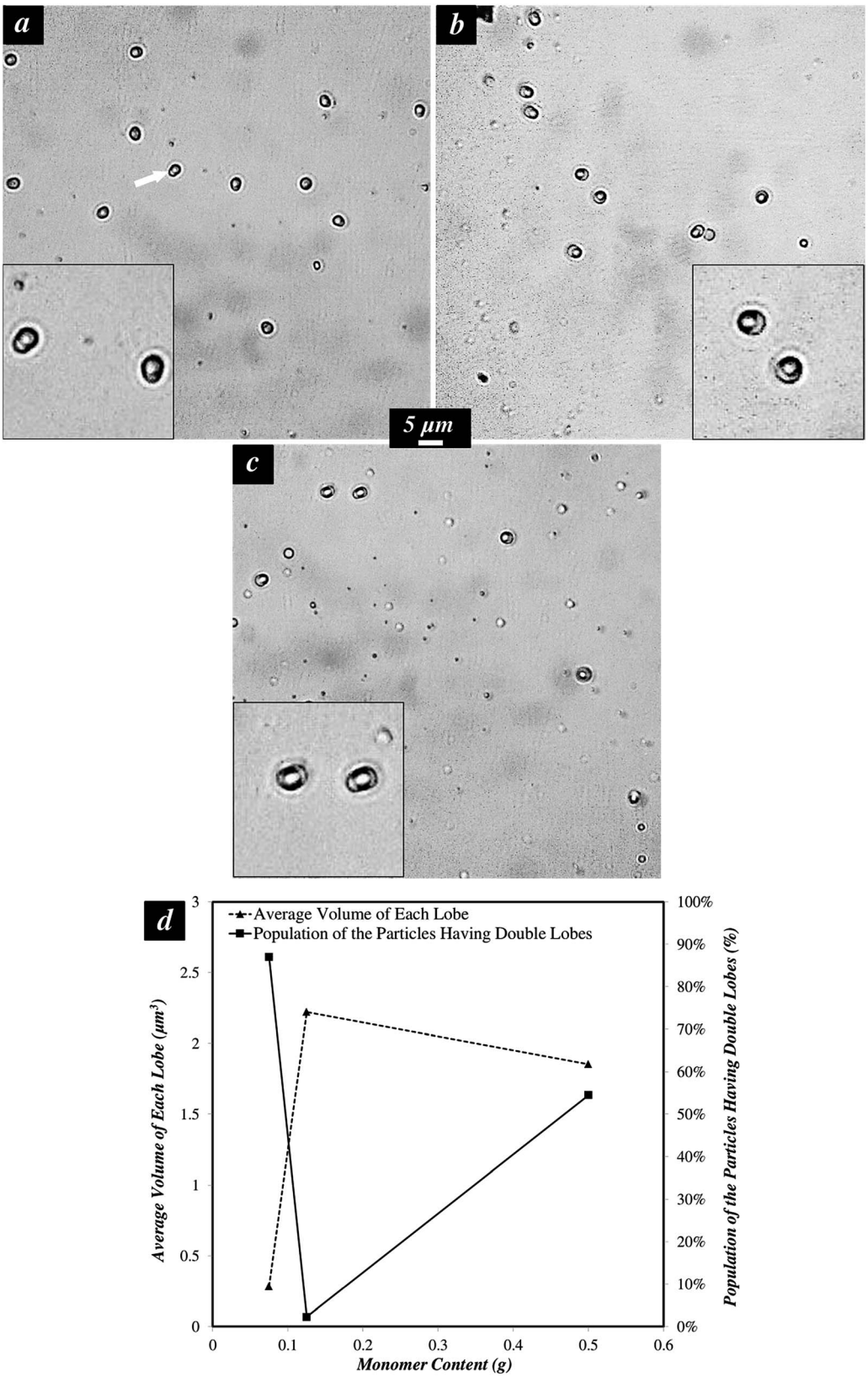

Fig. 5 Optical micrographs of PS/PEHMA/*n*-paraffin composite particles produced by SDP of EHMA using PS seed particles in the presence of *n*-paraffin droplets under the conditions listed in Table 1 using various amounts of EHMA: (a) 0.075 (b) 0.125 (c) 0.5 g and (d) the average volume of each lobe and the population of the particles having double lobes *versus* monomer content curves. The scale belongs to bigger micrographs.

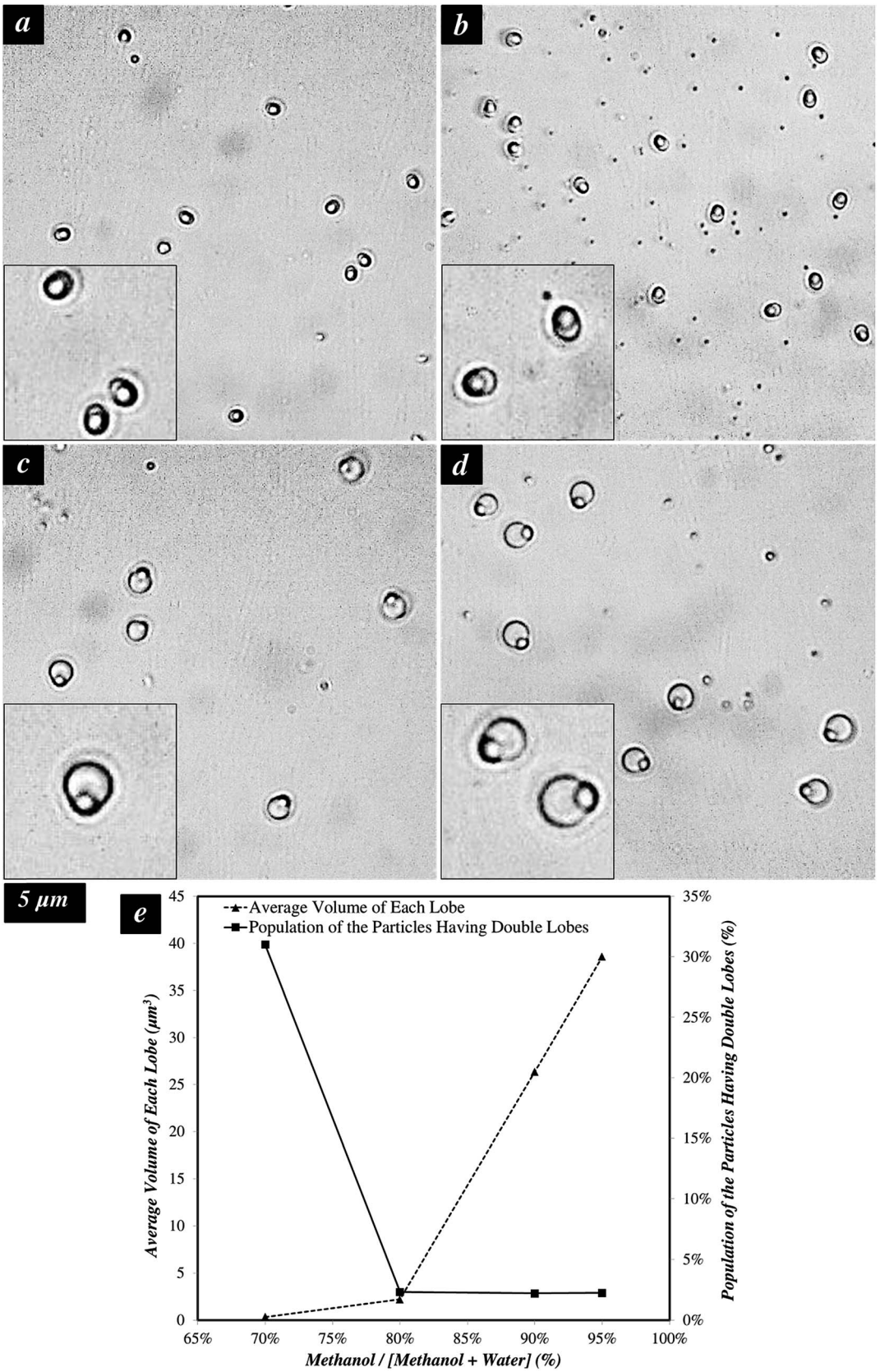

Fig. 6 Optical micrographs of PS/PEHMA/*n*-paraffin composite particles produced by SDP of EHMA using PS seed particles in the presence of *n*-paraffin droplets under the conditions listed in Table 1 using various methanol–water weight ratios: (a) 70/30 (b) 80/20 (c) 90/10 (d) 95/05 w/w and (e) the average volume of each lobe and the population of the particles having double lobes *versus* methanol/[methanol + water] (%) curves. The scale belongs to bigger micrographs.

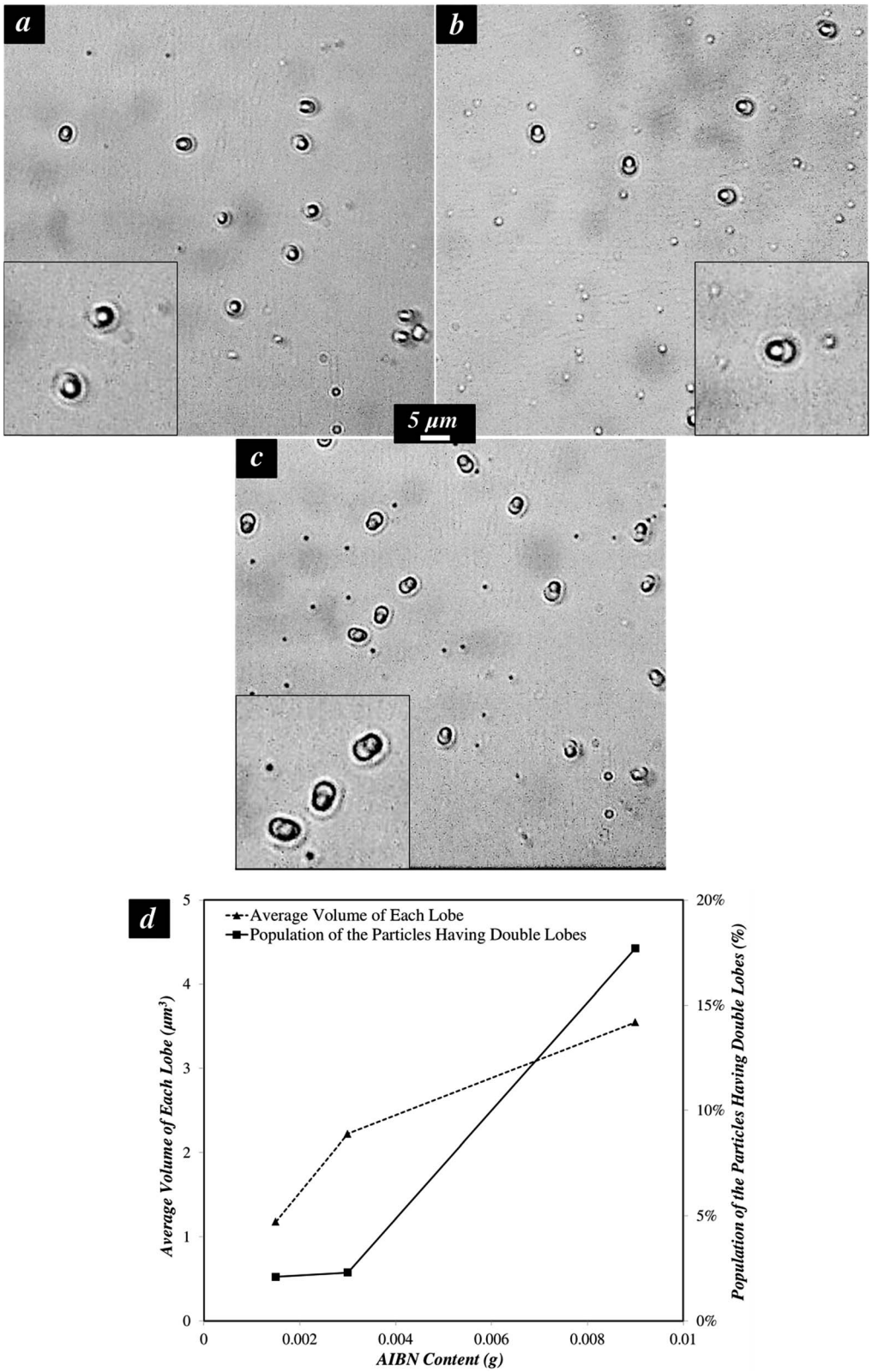

Fig. 7 Optical micrographs of PS/PEHMA/*n*-paraffin composite particles produced by SDP of EHMA using PS seed particles in the presence of *n*-paraffin droplets under the conditions listed in Table 1 initiated by various amounts of AIBN: (a) 0.0015 (b) 0.003 (c) 0.009 g and (d) the average volume of each lobe and the population of the particles having double lobes *versus* AIBN content curves. The scale belongs to bigger micrographs.

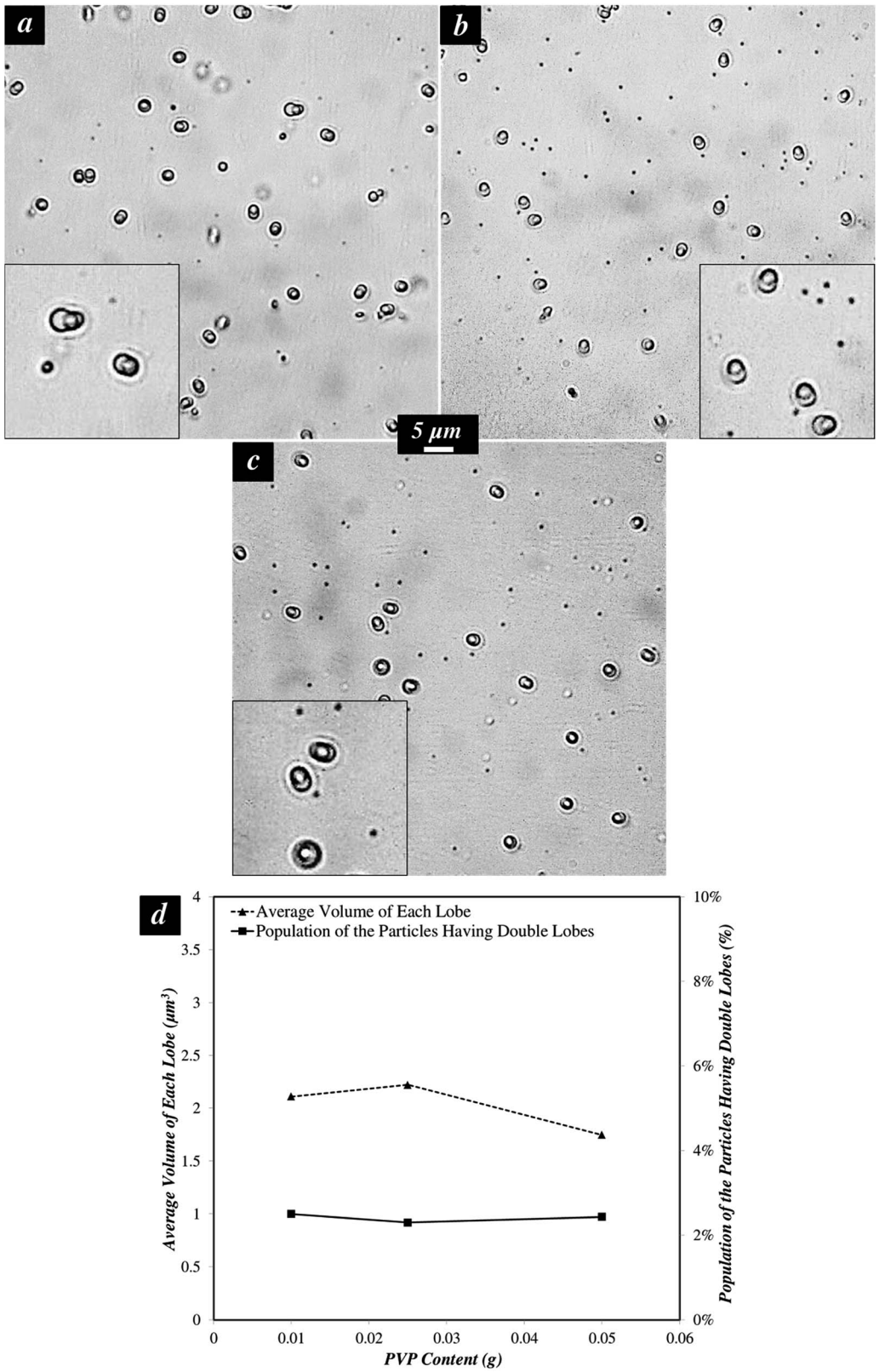

Fig. 8 Optical micrographs of PS/PEHMA/*n*-paraffin composite particles produced by SDP of EHMA using PS seed particles in the presence of *n*-paraffin droplets under the conditions listed in Table 1 stabilized by various amounts of PVP: (a) 0.01 (b) 0.025 (c) 0.05 g and (d) the average volume of each lobe and the population of the particles having double lobes *versus* PVP content curves. The scale belongs to bigger micrographs.

changes on this parameter. Even though monomer content can affect the solvency of the medium, in such polymerization system, solvency depends mostly on methanol–water weight ratio. Therefore, in order to understand the effect of this parameter deeply, four separate SDPs were designed using different methanol–water weight ratios including 70/30, 80/20, 90/10, and 95/05 w/w. The obtained results from these experiments are shown in Fig. 6. It can be seen that in the ratio of 70/30, particles containing double lobes have higher population rather than other ratios. In addition, the volume of each lobe is very low when lower amount of methanol is employed. These observations are due to the decrease in the size and increment of the number of precipitated oligoradicals because of reduction of solvency of the medium. These results approve the idea which was mentioned in the above paragraphs regarding the effect of lower amounts of monomer concentration. With further increment of methanol–water ratio, the volume of each lobe increases and snowman-like particles are produced instead of Janus ones. Moreover, the population of particles having double lobes decreases sharply with such change. It seems that with in augment of methanol content which contributes in increasing the solvency of the medium, bigger oligoradicals having less population form. These chains precipitate on the surface of PS microspheres asymmetrically in the beginning of the reaction and start to absorb *n*-paraffin as well as EHMA and oligoradicals, and as a result, very big PEHMA/*n*-paraffin domains form. Due to the absorption of such big chains the volume of each lobe increases while the chance for bare surfaces to capture the chains decreases. All of these phenomena result in the production of a dispersion containing composite particles having a big lobe with a population of around 98%. The results clearly show the importance of the solvency of the medium for controlling the morphology of the final particles.

All of the investigations suggested that oligoradicals' concentration is one of the important parameters for fabrication of "hard-soft" Janus particles. Ergo, in order to realize the effect of this parameter deeply, different concentrations of AIBN were employed for initiation of the same polymerization reaction. Fig. 7 represents the obtained results. As it can be seen, the volume of each lobe increases with an increase in the concentration of the initiator. Furthermore, the population of the particles having double lobes becomes high with the same change. It seems that increasing the oligoradicals' concentration, which is the main parameter responsible for such observations, provides enough feed for the domains growing off the PS seed particles as well as increasing the chance of symmetric growth of PEHMA/*n*-paraffin domains on the surface of them, resulting in the formation of bigger lobes in addition to the production of composite particles owning double lobes. These observations are in an excellent agreement with the ones referred to above.

Stabilizer content is another important parameter in a SDP system because it determines the stability of the produced dispersion and excessive amounts of this component can participate in secondary nucleation. In order to study the effect of this parameter, a set of SDPs stabilized by various concentrations of PVP was carried out and the obtained results are presented in Fig. 8. The results reveal that varying the content of PVP does not affect the morphology of final particles. However, a little decrease in the volume of PEHMA/*n*-paraffin lobe is observed with an increase in the concentration of this material

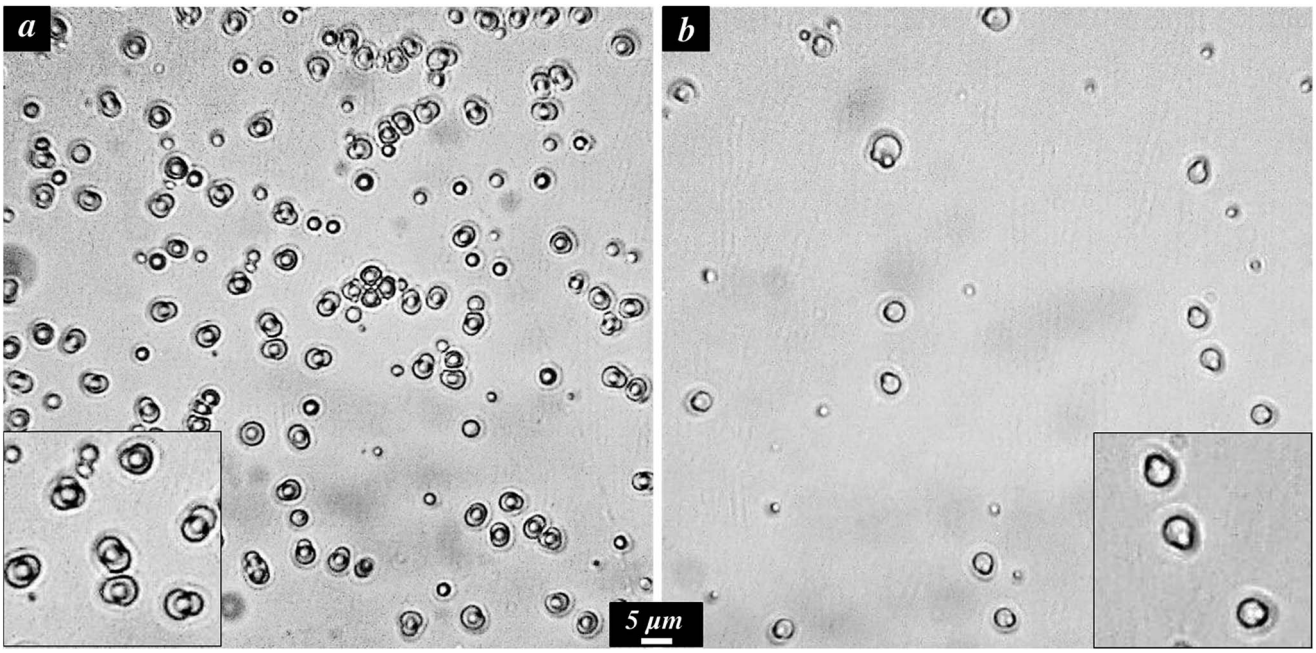

Fig. 9 Optical micrographs of PS/PLMA/*n*-paraffin composite particles produced by SDP of LMA using PS seed particles in the presence of *n*-paraffin droplets under the conditions listed in Table 1 using various methanol–water weight ratios: (a) 80/20 (b) 95/05 w/w. The scale belongs to bigger micrographs.

which might be because of the secondary nucleation. This phenomenon participates in a little reduction of monomer and free oligoradicals' content available in the medium that can be absorbed by the lobes growing off PS microspheres, resulting in a little reduction of their sizes. In term of stability, the obtained dispersions remained fully stable (there were not any coagula in the dispersions) even in lower contents of the stabilizer.

PEHMA, as the soft compartment of the Janus particles which owns T_g of around −10 °C,[37] were used in all of the investigations. In order to realize whether it is possible to employ other polymers with even more softness in the same function using this technique or not, LMA was used as the monomer which can result in poly(lauryl methacrylate) (PLMA) having T_g of around −65 °C.[37] As it is obvious, this component owns much higher softness rather than PEHMA under ambient conditions. SDP of LMA with same PS seed particles was carried out in the presence of *n*-paraffin droplets under the conditions listed in Table 1. The obtained composite particles are shown in Fig. 9a. It can be seen that particles having multiple lobes were obtained. From all of previous experiments, the reason of such observation seemed to be lower solubility of PLMA in this medium in comparison to PEHMA[4] which could result in the production of huge amounts of small oligoradicals, and therefore, symmetric distribution of PLMA phase on the surface of PS seed beads. As it was also mentioned in the above paragraphs, such distribution participates in an augment of the population of particles with multiple lobes. In order to examine this idea and increase the solvency of the medium, the weight ratio of methanol–water was changed from 80/20 w/w to 95/05 w/w and the result is shown in Fig. 9b. Under these conditions, as it can be seen, Janus morphology which a little bit tends to be snowman one is fabricated. Such observation totally approves that size and population of oligoradicals are the main parameters for controlling the morphology of the final particles as well as confirming the fact that this approach is able to produce Janus morphology using soft components other than PEHMA.

At last, in order to examine the reliability of this method regarding its ability for production of "hard-soft" Janus morphology by employing smaller seed particles, SDP of EHMA with PS seed particles having D_n and PSD values of 1.1 μm and 1.012, respectively produced under the conditions listed in Table 2 was carried out in the presence of *n*-paraffin droplets. This test was implemented because in some of the applications referred to in the introduction section smaller particles have more convenient functionality rather than bigger ones. Fig. 10 presents the optical micrographs of the produced composite particles as well as the ones produced by SDP using the bigger PS microspheres. As it can be seen, Janus morphology is obtained even by using small seed particles. This observation

Table 2 Polymerization conditions for dispersion polymerization of styrene employed for the synthesis of PS particles with average particle size of 1.1 μm

Ingredients	
Styrene (g)	4
AIBN (g)	0.08
PVP (g)	0.8
Ethanol (g)	15.6
Water (g)	10.4

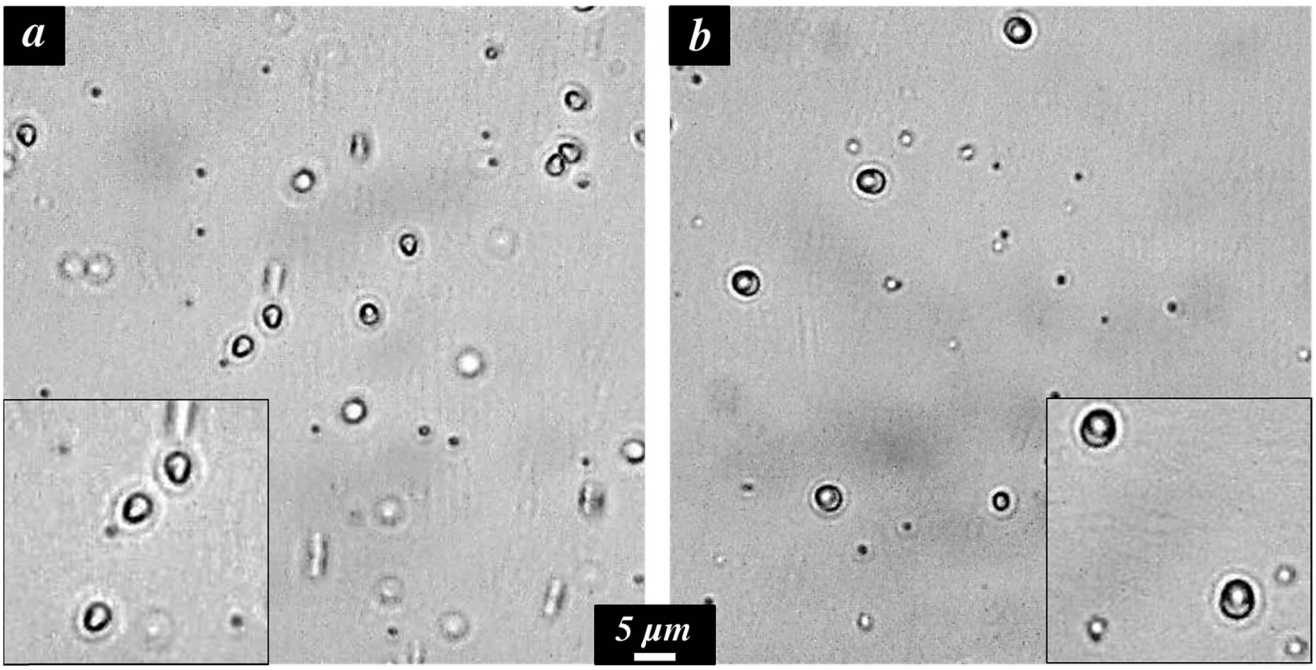

Fig. 10 Optical micrographs of PS/PEHMA/*n*-paraffin composite particles produced by SDP of EHMA using different PS seed particles in the presence of *n*-paraffin droplets under the conditions listed in Table 1: PS seed particle having (a) 1.1 (b) 2 μm average diameter. The scale belongs to bigger micrographs.

implies that this method is capable for preparation of such unique particles even by using smaller particles which have higher surface area.

Another point which deserves some words here is the stability of such Janus morphology in term of thermodynamic. In order to evaluate this issue, a dispersion containing these particles was kept under ambient conditions for 10 days while it was tumbled end-over-end at 24 rpm to make sure particles would not settle on the bottom of their container. After this time, an optical image was taken from the dispersion showing that the morphology has remained stable. This result was expected since the hemispherical morphology of PS particles was the most stable one for PS/PEHMA/hydrocarbon composite particles as it was reported in previous studies.[15,16]

The polymerization was performed for 24 hours under nitrogen atmosphere by tumbling at 24 rpm in a constant-temperature water bath at 60 °C.

The presence of some very small particles in all of the samples is another issue about the obtained results. As it has also been explained in previous studies,[17,18,32,36] secondary nucleation which occurs due to the presence of excessive amounts of stabilizer in the medium is responsible for production of such tiny particles and it is possible to decrease the abundance of them by only a simple decrease in stabilizer content.

Conclusions

In conclusion, the preparation of "hard-soft" Janus PS/PEHMA/*n*-paraffin composite particles *via* SDP of EHMA with PS seed beads in the presence of *n*-paraffin droplets was reported. This simple method was also used for preparation of same unique particles having a soft compartment with more softness rather than PEHMA. In addition, it was observed that this approach is reliable for fabrication of the same morphology even by employing smaller seed beads. The effect of various polymerization conditions (*e.g.* type of the hydrocarbon, monomer concentration, *n*-paraffin content, amount of initiator, methanol–water weight ratio, stabilizer content, type of second monomer, and size of seed beads) on the shape of the final particles was investigated. All of the result showed that the size and concentration of precipitated PEHMA oligoradicals coupled with *n*-paraffin content are the main parameters responsible for production of Janus polymer particles. It was found that the volume of the soft lobe increases with an increase mainly in the size of precipitated oligoradicals. In addition, increasing the concentration of oligoradicals resulted in the production of the composite particles having double lobes. The obtained results coupled with the time course analysis of similar SDP in the presence of hydrocarbons with shorter alkyl chain lengths rather than *n*-paraffin[15] paved a way for us to demonstrate the formation mechanism of such exceptional morphology as schematically depicted in Fig. 11. As it

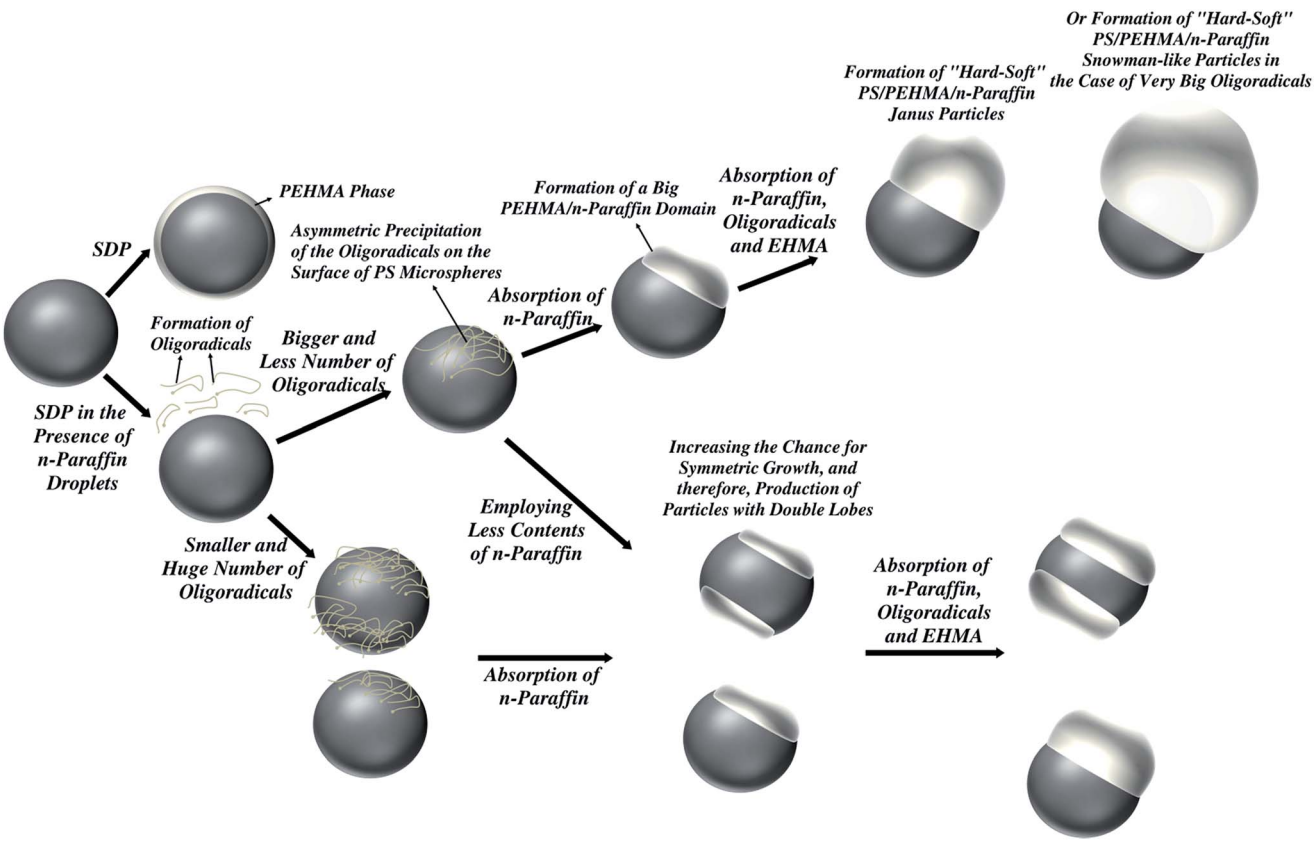

Fig. 11 Schematic formation mechanism of "hard-soft" Janus particles produced by SDP of EHMA with PS seed particles in the presence of *n*-paraffin droplets.

is obvious, spherical particles are produced in the absence of *n*-paraffin droplets while nonspherical morphologies are obtained in the presence of this component. With the initiation of the polymerization, oligoradicals start to precipitate. As it can be seen, the size and population of the oligoradicals, which depend on the solvency of the medium, are the key parameters for controlling the morphology of final particles. Smaller oligoradicals that precipitate symmetrically and asymmetrically on the surface of seed particles result in the production of Janus morphology in addition to the particles with double lobes having high population. Same thing happens in the case of bigger oligoradicals using fewer contents of *n*-paraffin since the rate of asymmetric growth decreases by a decrease in the amount of this material, resulting in an increase in the chance of symmetric precipitation and growth. However, if enough content of *n*-paraffin is employed, bigger oligoradicals form a big domain on one side of seed particles by the absorption of the hydrocarbon in the beginning of the reaction. With further development of the polymerization, this domain absorb PEHMA chains as well as EHMA and *n*-paraffin quickly from methanol–water medium over the bare PS particles' surface, and therefore, grows asymmetrically, resulting in the formation of "hard-soft" Janus or snowman-like (in the case of very big oligoradicals) morphology.

In addition to the points described above, it was revealed that *n*-paraffin content does not have so much effect on the volume of the soft lobe while this value highly depends on the size and concentration of PEHMA chains themselves. This observation implies that the soft lobe is mostly made of PEHMA. Hence, it is not needed to have a concern regarding removal of the hydrocarbon from the final composite particles.

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