

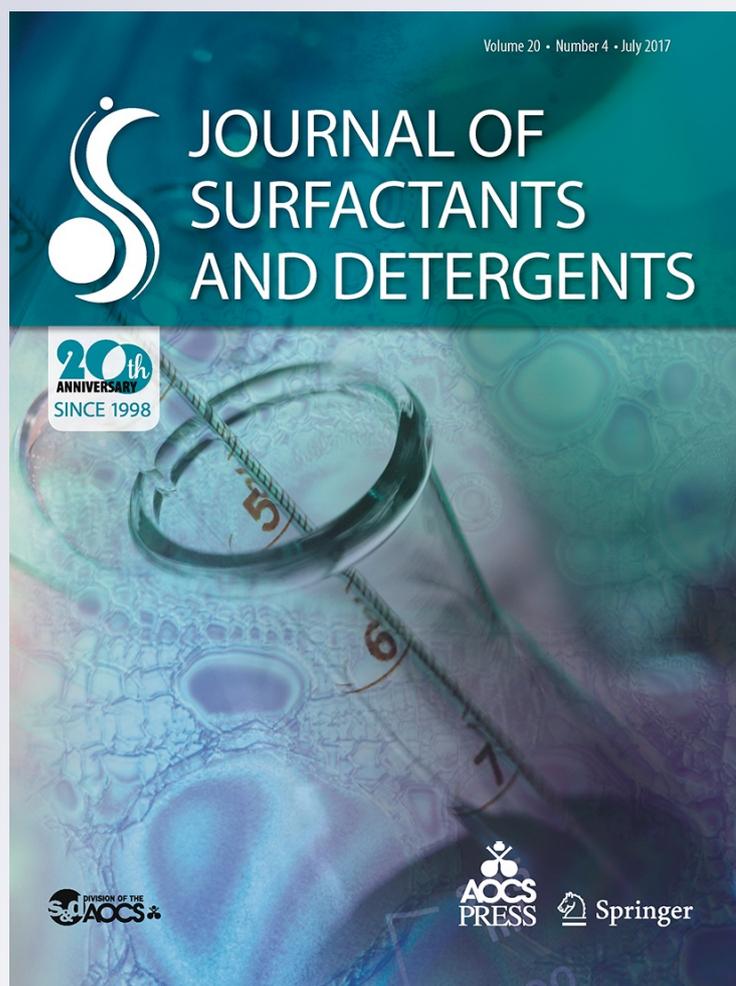
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Novel Synthesis Method and Characterization of Poly(vinyl acetate-butyl acrylate) Latex Particles: Effect of Silanol-Terminated Poly(dimethylsiloxane) Surfactant on the Seeded Emulsion Copolymerization

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Abstract In a conventional semi-batch seeded emulsion copolymerization of vinyl acetate/butyl acrylate (VA/BA) using hybrid surfactants namely, dioctyl sulfosuccinate (DOSS) as an anionic surfactant, nonylphenol ethoxylate (KENON 30) as a non-ionic type, and polydimethylsiloxane surfactant (having hydrophilic silanol-terminated, called PDMS). The effect of PDMS on the properties of the latex synthesized was investigated by measuring solid content, viscosity, colloidal stability, particle size distributions of the base latex, viscosity average molecular weight (\bar{M}_v) of the copolymer, latex particle morphology, glass transition temperature (T_g) of a copolymer and thermal gravimetric analysis (TGA). Particle size of the base latex decreases (Z-average from 246.48 to 143.69 nm) upon increasing the amount of PDMS surfactant in the recipe (up to 6 wt%). The presence of PDMS surfactant in the hybrid surfactants led to a significant increase in the solid content (from 48.71 to 51.31 wt%), viscosity (from 334 to 806 centipoise, cp) and \bar{M}_v (from 1.91×10^5 to 2.34×10^5 g mol⁻¹). Thermal stability and T_g of the copolymer were increased with addition of PDMS surfactant (thermal stability from 344.77 to 389.81 °C and T_g from -20.7 to 21.7 °C). The colloidal stability evaluated using the electrolyte addition method was improved with addition of PDMS surfactant. The uniform morphological structure of the final particle is the main effect of using PDMS in the hybrid surfactants.

Keywords Emulsion copolymerization · VA/BA copolymer · PDMS surfactant · Morphological structure · Thermal stability

Introduction

Emulsion polymers of vinyl acetate have widespread industrial application (i.e., exterior and interior architectural waterborne coatings, adhesives, and paints) which is due to their low risk of fire, toxicity and cost [1–5]. Vinyl acetate copolymerizes with butyl acrylate and produces useful latex for application in acrylic emulsion paints [6–9]. The performance properties of colloidal stability, thermal resistive coating, and control of particle morphology were also evaluated in emulsion polymerization [10–21]. Moreover, the quantity and nature of the surfactants were used for the polymerization are major factors in the final properties of the polymer latex [22–28].

Polymeric surfactants are most important materials that are used in a wide range of industries for emulsion polymer synthesis, paints, adhesives, agrochemicals, plastic and so on [29–32]. Silicone surfactants (e.g. poly(dimethylsiloxane) and its derivatives) are commonly used in various industrial applications. Some of their applications are in the formulations of household, personal care and cosmetic products, paints and coatings, drug delivery and surface active agents [33–35]. The most common application of silicone surfactants (without polar groups) is to improve the stability of water-in-oil (w/o) emulsions. Emulsion systems can be stabilized by silicon surfactants [36, 37]. Moreover, several papers have shown that siloxane surfactants consist of a permethylated siloxane hydrophobe coupled to one or more polar groups can be used in microemulsion polymerization. Polydimethylsiloxane-

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polyoxyalkylene copolymers and polyalkylmethylsiloxane–polyoxyalkylene copolymers have been studied as surfactants [38–40]. Kumar et al. [41] and Strey et al. [42] explained the role of siloxane polyoxyalkylene copolymer as an ideal material to increase the efficiency of microemulsions. The silicone-oil-in-water emulsions, which are sometimes described as microemulsions have been discussed by Hou [43]. Katayama et al. [44] used salt + amino-functionalized siloxane + *N,N*-dimethyl ethanolamine myristate + alcohol to prepare silicon-oil-in-water microemulsions. The relationship between hydrophilic-lipophilic difference (HLD) and microemulsion formulation for silicone oils and silicone alkyl polyether surfactants have been discussed by Castellino et al. [45]. The amphiphilic nature of siloxane compounds with few polar groups can be used for the preparation of emulsions [46–49]. In the other word, silicon-oil-in-water emulsions refers usually to nonionic dimethylsiloxane polyoxyalkylene copolymers [50, 51].

More importantly, the high polarity of the end groups supports a more surfactant-like structure, which can interfere with the progressions seen in the silanol-terminated poly(dimethylsiloxane) surface tension isotherm diagrams [35].

In the present work, the effect of PDMS surfactant (having hydrophilic silanol-terminated) in the hybrid surfactants systems on solid content, \bar{M}_v and viscosity of the latex, colloidal characteristics (colloidal stability, particles morphology, mean particle diameter and particle size distribution) and thermal stability of VA/BA copolymer latexes were investigated.

Experimental

Materials

Butyl acrylate [BA, BASF Chemical Company (Ludwigshafen, Germany)] and vinyl acetate [VAc, Shazand Petrochemical Co (Arak, Iran)] were distilled under reduced pressure before use. The other materials were used as received, including the acrylic acid monomer (AA, Aldrich, +99%, 3–5 ppm MEHQ), ammonium persulfate (APS, 99%, Aldrich, Lancaster, UK) and sodium acetate (CH_3COONa , Aldrich) were used as initiator and buffer respectively. The surfactants used were dioctyl sulfosuccinate (DOSS, Aldrich) as an anionic surfactant, nonylphenol ethoxylate [KENON 30, Kimyagaran Emrooz Chemical Industries Co (Arak, Iran)] as non-ionic surfactant and silanol-terminated poly(dimethylsiloxane) surfactant (poly(dimethylsiloxane) 1050/0, OKS, Germany, which was supported by FT-IR data (Fig. 3),

$\bar{M}_n = 5200 \text{ g mol}^{-1}$). Deionized water was used throughout the work.

Apparatus

The particle size was measured using a VASCO-3 particle size analyzer (Cordouan Instruments Co, (measurement range (nm): 0.5–6000). Gravimetric method was used for the determination of total solid content of an acrylic emulsion sample [52]. The viscosity of the final copolymer latexes were evaluated with using a Brookfield RVDV-II+ viscometer with a 3# rotor at 60 revs min^{-1} at 26 °C. The thermal stabilities of the copolymers were evaluated using thermogravimetric analysis (Perkin-Elmer 7 series Shimadzu-TGA 50 H thermal analysis system). The glass transition temperature, T_g , values of the acrylate copolymers were determined using differential scanning calorimetry (DSC). A DSC-60A (Shimadzu, Japan) was used. All samples were subjected to two heating/cooling cycles from –100 to 200 °C. The first cycle was used to eliminate any thermal history. The second heating cycle from –100 to 200 °C was used for determination of T_g . All heating/cooling cycles were performed at a rate of 10 °C min^{-1} and 4 mg of the sample was used for the analysis. The FT-IR spectrum of PDMS was measured by a FT-IR spectrometer (Thermo Scientific Avatar 370, USA) in the wave number of 450–4000 cm^{-1} .

The morphology of the latex was observed by transmission electron microscopy (TEM) using a Philips/CM120 instrument. The viscosity average molecular weight (\bar{M}_v) of the copolymer was determined using an Ubbelohde-type viscometer in acetone solvent at 25 °C.

Extraction of the copolymer was done using a solvent (acetone) antisolvent (deionized water) method. The molecular weight was determined using Mark-Houwink-Sakurada equation [53].

$$[\eta] = K\bar{M}_v^\alpha \quad (1)$$

($\alpha = 0.75$, $K = 6.85 \times 10^{-5} \text{ (dl g}^{-1}\text{)}$), copolymer concentration in acetone was 0.1 wt%).

Preparation of Poly(dimethylsiloxane)/Water Emulsion

The required amount of PDMS (Table 1) was dispersed into deionized water by ultrasonic irradiation at a frequency of 42 kHz (Sper Scientific, Model U 4800) for 30 min to obtain an o/w emulsion [54, 55]. This o/w emulsion was stable for at least 6 months at 25 °C and used instead of deionized water as the continuous phase in the emulsion copolymerization process.

Table 1 Recipe used for the semi-batch emulsion polymerization

Materials	Part A (g)	Part B (g)
BA	28	288
VA	7	73
AA	4	0
DOSS	2	6
KENON 30	4	12
Buffer (CH ₃ COONa)	0.3	0.5
Initiator (NH ₄) ₂ S ₂ O ₈	0.1	0.3
PDMS ^a	Variable	Variable
Deionized water	120	180

^a The concentrations of PDMS surfactant were 0 (sample A1), 2 (sample A2), 4 (sample A3) and 6 (sample A4) wt% based on total solid content of the latex (58.63 wt% total solid content)

Semi-Batch Emulsion Copolymerization of VA/BA

Polymerizations were carried out in a 1-L four-necked glass reactor equipped with a circulator, a mechanical stirrer, an addition funnel and a thermometer. The emulsion copolymerization was carried out with the formulas according to Table 1. The seed was prepared at 72 °C by means of batch emulsion copolymerization of VA and BA using the recipe given in part A in Table 1.

The recipe given in part B in Table 1 were pre-emulsified and continuously added to the seed latex over 6 h at 75 °C. The polymerization was continued in a batch at 79 °C for 1 h further to complete the reaction of residual monomers. FT-IR and ¹H NMR were used to determine the structure of the synthesized copolymer (Figs. 1, 2, respectively).

Characterization

The chemical structure of pure copolymer was examined by FT-IR (Bruker Alpha FT-IR) and ¹H NMR (Bruker AC 80 spectrometer, 80 MHz for ¹H). As shown in Fig. 1, the peaks at 2958, 2923 and 1738 cm⁻¹ were associated with the characteristic vibration of methyl (CH₃), methylene (CH₂) and carbonyl (C=O) groups respectively. The C–O stretching vibration of VA in 1222 cm⁻¹ and C–O stretching vibration of BA in 1167 cm⁻¹ are present in the copolymer. These results show that copolymerization has taken place between vinyl acetate and butyl acrylate [56].

Figure 2 represent the ¹H-NMR spectrum of the copolymer obtained. The pure copolymer sample was dissolved (5 wt%) in deuterated acetone. The spectra were recorded at 24 ± 1 °C. In the ¹H-NMR spectra of the copolymer the signals at around 4 ppm and 3.5 ppm are assigned to the protons of the VA and BA, respectively [57].

Determination of Colloidal Stability

As a guide to aggregation, the turbidity of aqueous colloids was measured using a Hach Analytical Nephelometer Model 2100 Qis at room temperature. Each sample (0.1 g latex) was diluted with distilled water (60 mL), the required amount of Al₂(SO₄)₃ (20 mL of the solution containing 0.025, 0.050, 0.075 and 0.100 mol L⁻¹) was added with stirring. The mixture was left to stand for 24 h at room temperature in a turbidimetric cell, turbidity was measured according to the literature [58].

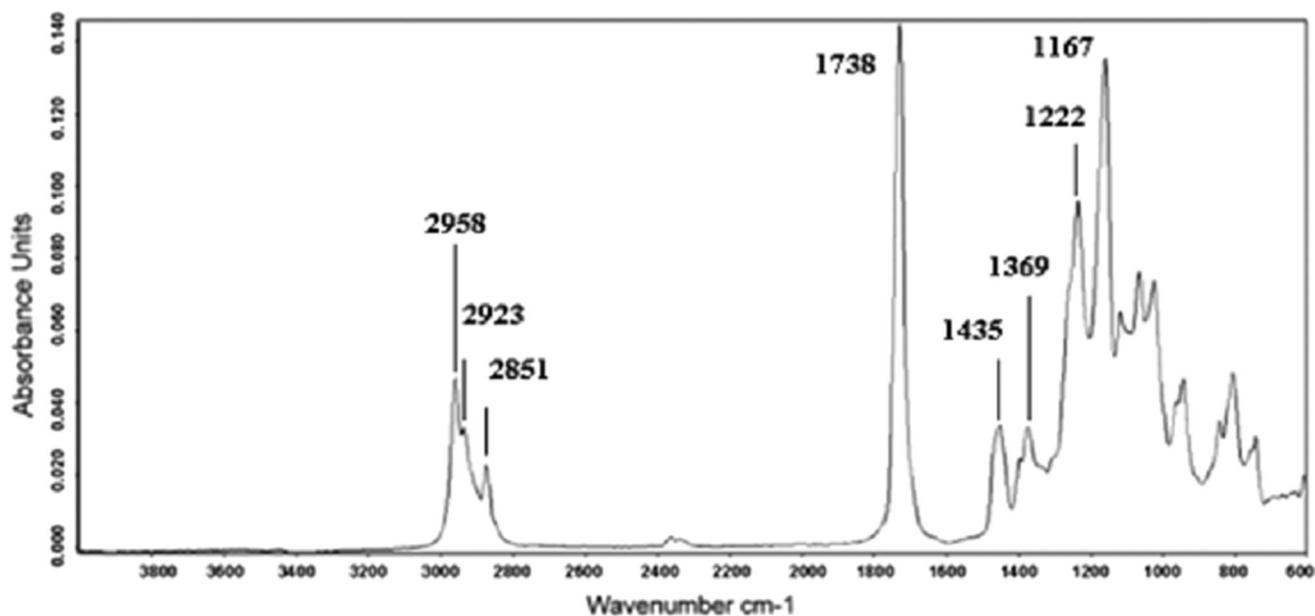


Fig. 1 The FT-IR spectra of VA/BA copolymer

Fig. 2 $^1\text{H-NMR}$ spectrum for VA/BA copolymer

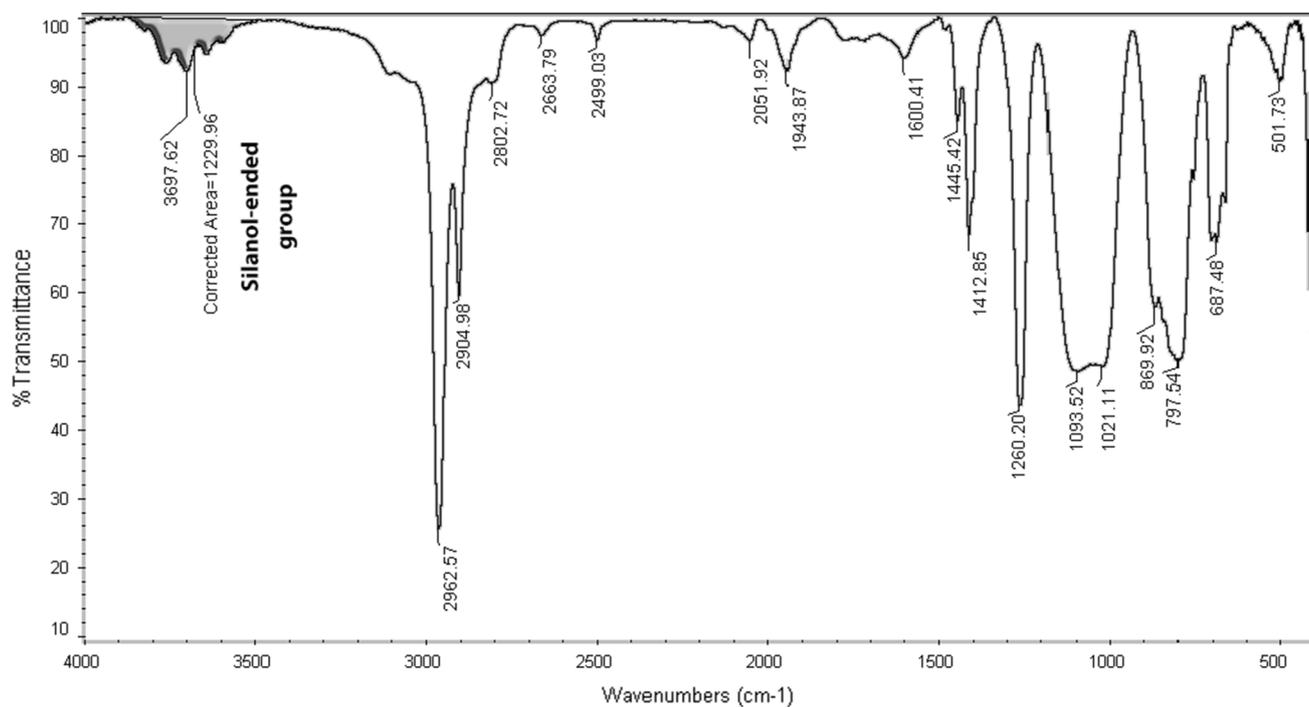
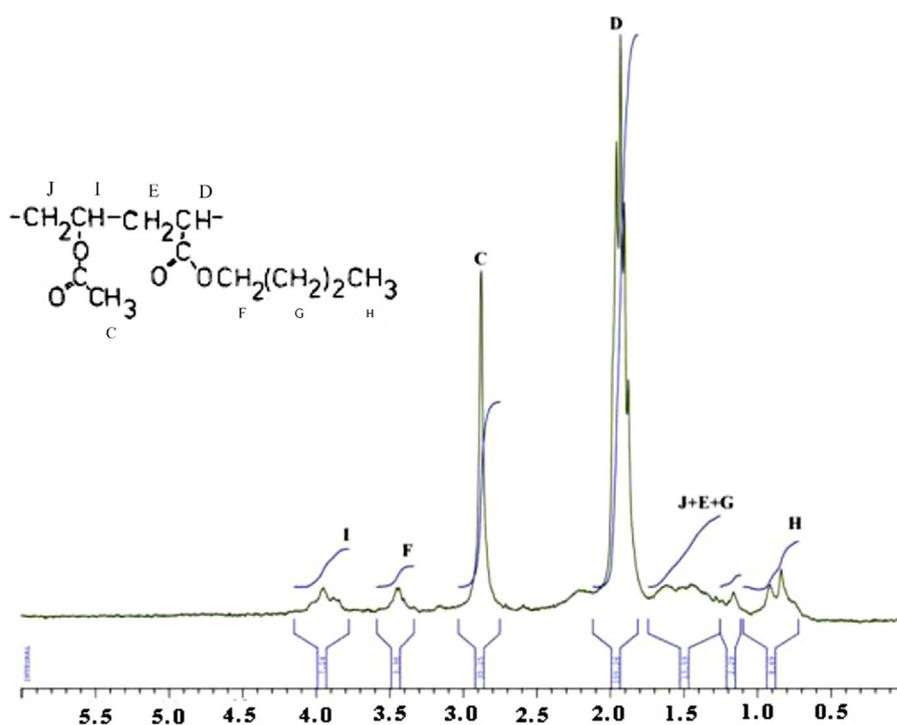


Fig. 3 The FT-IR spectrum of silanol-terminated poly(dimethylsiloxane)

The Chemical Structure of PDMS

As shown in Fig. 3, the typical absorption peak of PDMS at 3697 cm^{-1} [ν (O–H stretch of the SiOH group)], 1021 and

1093 cm^{-1} [ν (Si–O–Si stretching vibrations on the backbone)], 2962 and 2904 cm^{-1} [ν (C–H stretches of CH_3)], 869 and 797 cm^{-1} [ν (Si–C stretches of SiMe)] could be seen clearly in the FT-IR spectrum.

Results and Discussion

Influence of PDMS Surfactant on Particle Size

The mean particle size of the latex decreased with increasing concentration of the PDMS surfactant (Table 2 and Fig. 4I–IV). As reported previously, type and concentration of surfactant play a major role in the final particle size [59–61]. Previous investigations have shown that the hydrophilic-lipophilic balance (HLB_{mix}) value of the surfactant system is important in assessing the final particle size and its distribution [62–65]. The mixed HLB values were calculated according to Eq. 2 [66]:

$$[\text{HLB}_{\text{mix}} = xA + (1 - x)B] \quad (2)$$

where x is the proportion of a surfactant having an HLB value of A , and the other surfactant has an HLB value of B . Values of 8.5, 32 and 17.1 denote the HLB values of PDMS, DOSS and KENON 30, respectively (were obtained from the supplier company). When a lipophilic surfactant with low HLB value (silicon surfactant with lipophilic nature) was added to the surfactant system with high value of HLB_{mix}, the surface area per surfactant molecule increased, owing to a change in the HLB_{mix} balance and reduction in the entropy of the total system [62]. It can be seen from Table 3 that the HLB_{mix} and Z-average size (hydrodynamic diameter) decrease with an increasing percentage of PDMS surfactant in the mixed surfactant systems. Therefore, it may be concluded that with increasing PDMS content (from 0 to 6 wt%), the hydrodynamic diameter of the latex particles declines from 246.48 to 143.69 nm.

Effect of PDMS Surfactant Concentration on the Copolymerization Behavior

Increasing the PDMS amount in the recipe resulted an increasing, both the solid content of the latex and \bar{M}_v of the polymer obtained linearly (Fig. 5). After the nucleation period, three types of kinetic processes determine the kinetics of emulsion polymerization: radical entry, polymer chain formation (especially bimolecular termination) and radical desorption.

Radical entry is given by Eq. 3:

$$\varepsilon = \frac{\rho_e}{k_p[M]_p N_T} \quad (3)$$

where ρ_e is the rate of radical entry into polymer particles, including the re-entry of desorped radicals, N_T is the number of polymer particles, $[M]_p$ is the monomer concentration in the monomer-swollen polymer particles and k_p is the propagation rate constant [67].

Bimolecular termination is given by Eq. 4:

$$\xi = \frac{2k_{tp}}{k_p[M]_p v_p N_A} \quad (4)$$

where k_{tp} is the bimolecular termination rate constant, N_A is Avogadro's number and v_p is the volume of a swollen polymer particle.

Radical desorption is given by Eq. 5:

$$\delta = P_{\text{des}}(1 + C_f + (n - 1)\xi) + \frac{k_0}{k_p[M]_p} \quad (5)$$

where k_0 is the desorption rate coefficient for an oligomeric radical, n is the number of radicals in the polymer particle, C_f chain transfer frequency and P_{des} chain transfer reaction [67].

Increasing the amount of PDMS in the hybrid surfactants system causes the final number of latex particles per unit volume (N_T) to increase or reducing the volume of a swollen polymer particle (v_p) and the possibility of multiple radicals in the polymer particle (n), the polymerization system due to no desorption and fast termination (invariant amount of initiator) follows Smith-Ewart case II kinetics ($n = 0.5$) given by Eqs. 6 and 7. In the Smith-Ewart case II, high rates of polymerization and high molecular weights of the polymer are obtainable [67].

$$\frac{dN_i}{dt} = \frac{\rho_e}{N_T(N_{i-1} - N_i)} + \frac{k_0 a_p}{v_p [(i + 1)N_{i+1} - iN_i]} + \frac{k_{tp}}{v_p [(i + 2)(i + 1)N_{i+2} - (i - 1)N_i]} \quad (6)$$

(N_i , $i = 0, 1, 2, \dots$) where (N_i , $i = 0, 1, 2, \dots$) is number of latex particles containing i free radicals per unit volume of water and a_p is surface area of single particle [67].

Table 2 The effect of PDMS on particle size of the latex

Sample	Dmean volume (nm)	Dmean number (nm)	PDI ^a	Z-average size (nm)
A1	369.71	66.69	0.3990	246.48
A2	359.12	64.83	0.3950	241.19
A3	228.42	49.33	0.3300	178.07
A4	151.17	41.80	0.2950	143.69

^a Polydispersity index of particle size

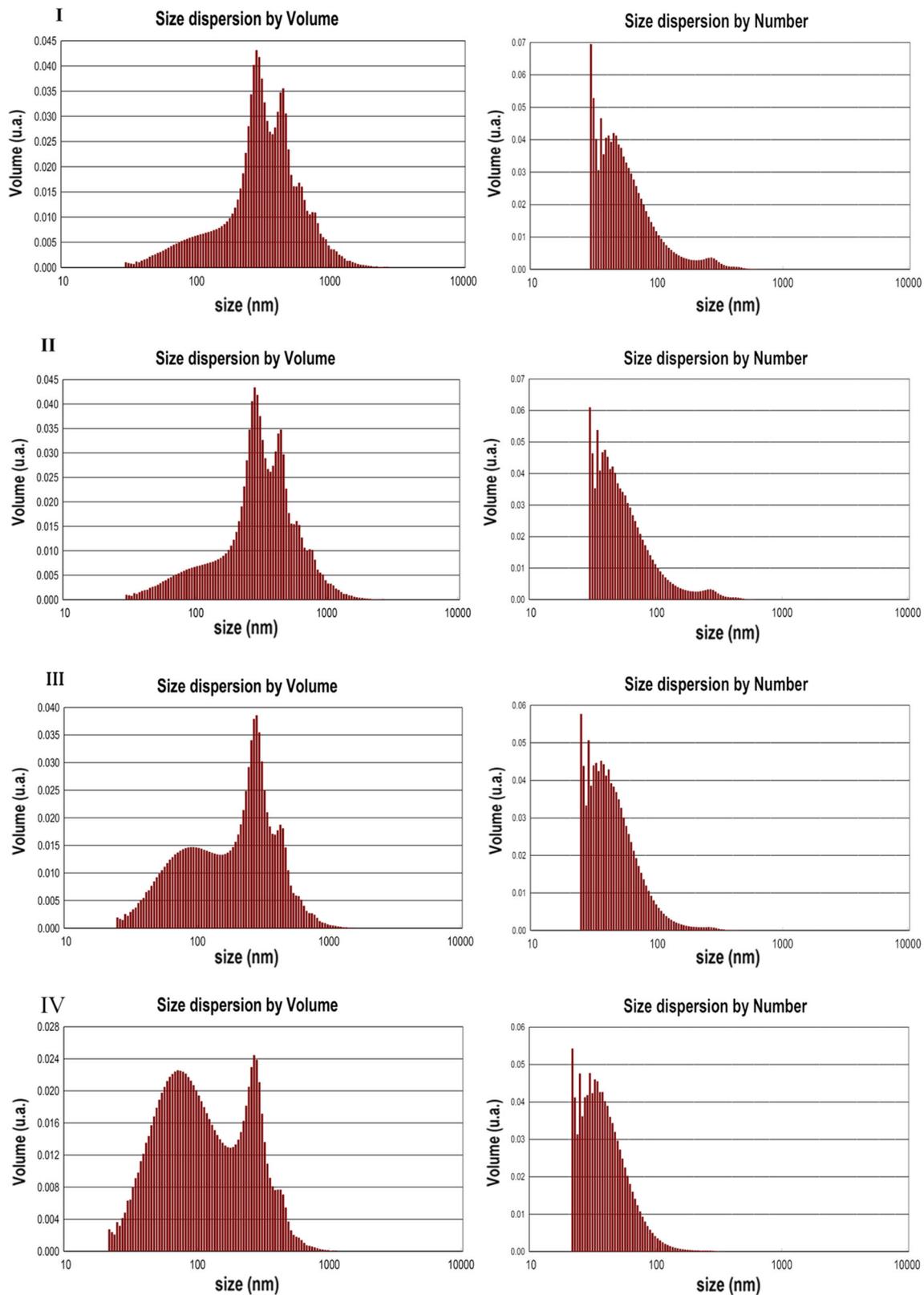


Fig. 4 Influence of PDMS surfactant on particle size and particle size distribution of the latex (*I*) sample A1; (*II*) sample A2; (*III*) sample A3; (*IV*) sample A4

Table 3 The relationship between the final particle size and the mixed HLB values for samples with different quantities of PDMS surfactant

Z-average(nm)	HLB _{mix}	HLB _{monomer}	Ratio of surfactant	Surfactant
PDMS ¹	0	8.5 ^b	246.48	22.02
DOSS	0.33	32 ^a		
KENON 30	0.67	17.1 ^a		
PDMS ²	0.26	8.5	241.19	18.59
DOSS	0.25	32		
KENON 30	0.49	17.1		
PDMS ³	0.42	8.5	178.07	16.81
DOSS	0.20	32		
KENON 30	0.40	17.1		
PDMS ⁴	0.52	8.5	143.69	15.01
DOSS	0.16	32		
KENON 30	0.32	17.1		

^a Were obtained from the supplier company

^b Valid website (http://www.Chemicaland21.com/info/HLB_VALUES.htm)

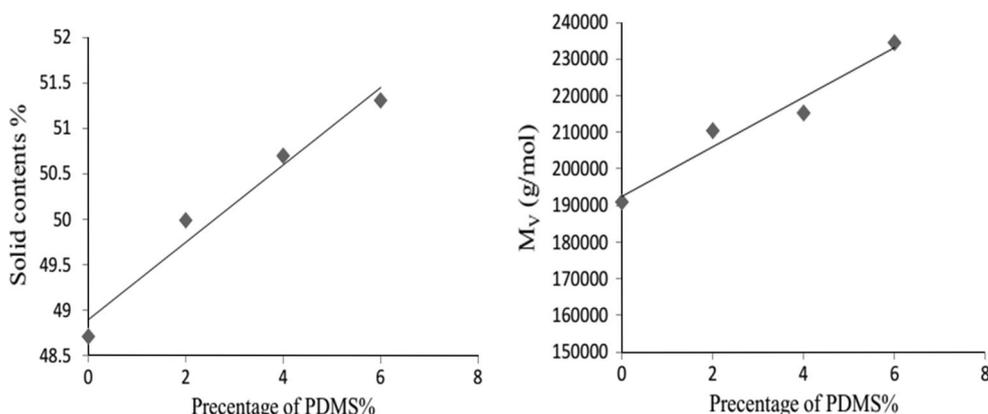
¹ Sample A1

² Sample A2

³ Sample A3

⁴ Sample A4

Fig. 5 Effect of PDMS surfactant on the solid contents and the viscosity average molecular weight (M_v)



case II: $\frac{k_0 a_p}{v_p} \ll \frac{\rho_e}{N_T} \ll \frac{k_{tp}}{v_p}$ (no desorption and fast termination) (7)

$n = N_1 / (N_0 + N_1) = 0.5$

A monotonic increase in viscosity with increasing PDMS surfactant concentration was observed (Fig. 6). Studies of high solids content lattices have shown that the latex viscosity at a fixed shear rate is directly dependent on the polymer concentration and molecular weight (as already emphasized in Fig. 5) [68, 69]. The viscosity also increases with decreasing particle size and increasing volume fraction (ϕ) of latex particles (Fig. 4) [68, 69]. These

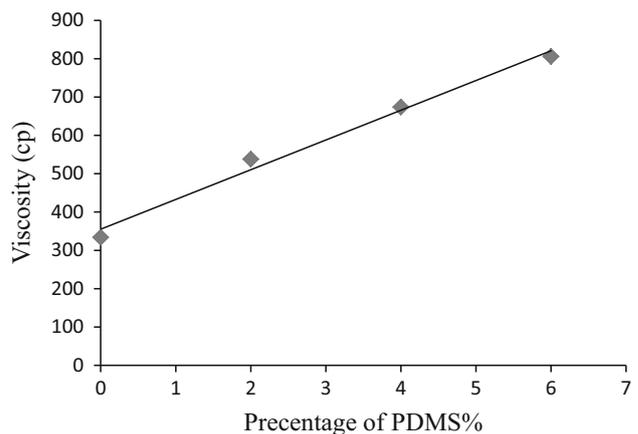


Fig. 6 Effect of PDMS surfactant on viscosity of the latex obtained

results are consistent with other findings which illustrate that reducing of particle size, increasing of solid contents and \bar{M}_v are more intensive in viscosity of the latex [68–70].

Effect of PDMS Surfactant on the Particle Morphology

Core-shell particles with BA (reactivity ratio = 5.5 and water solubility = 1–1.5 g L⁻¹) mainly located in the core (dark region) and the shell (light region) contains rich VA (reactivity ratio = 0.04 and water solubility = 25 g L⁻¹)

copolymer were produced for instance by seeded emulsion polymerization in the presence of various conventional surfactants such as sodium dodecyl sulfate and octylphenoxy polyethoxy ester (Fig. 7a) [71, 72]. Based on the minimum surface free energy change principle, by simply changing the type of surfactant used in the polymerization, the particle morphology can change from core-shell to other morphologies that agree with thermodynamic predictions [73, 74]. Addition of PDMS surfactant to the hybrid surfactants systems (DOSS + KENON 30), a transition from the core-shell to uniform morphological

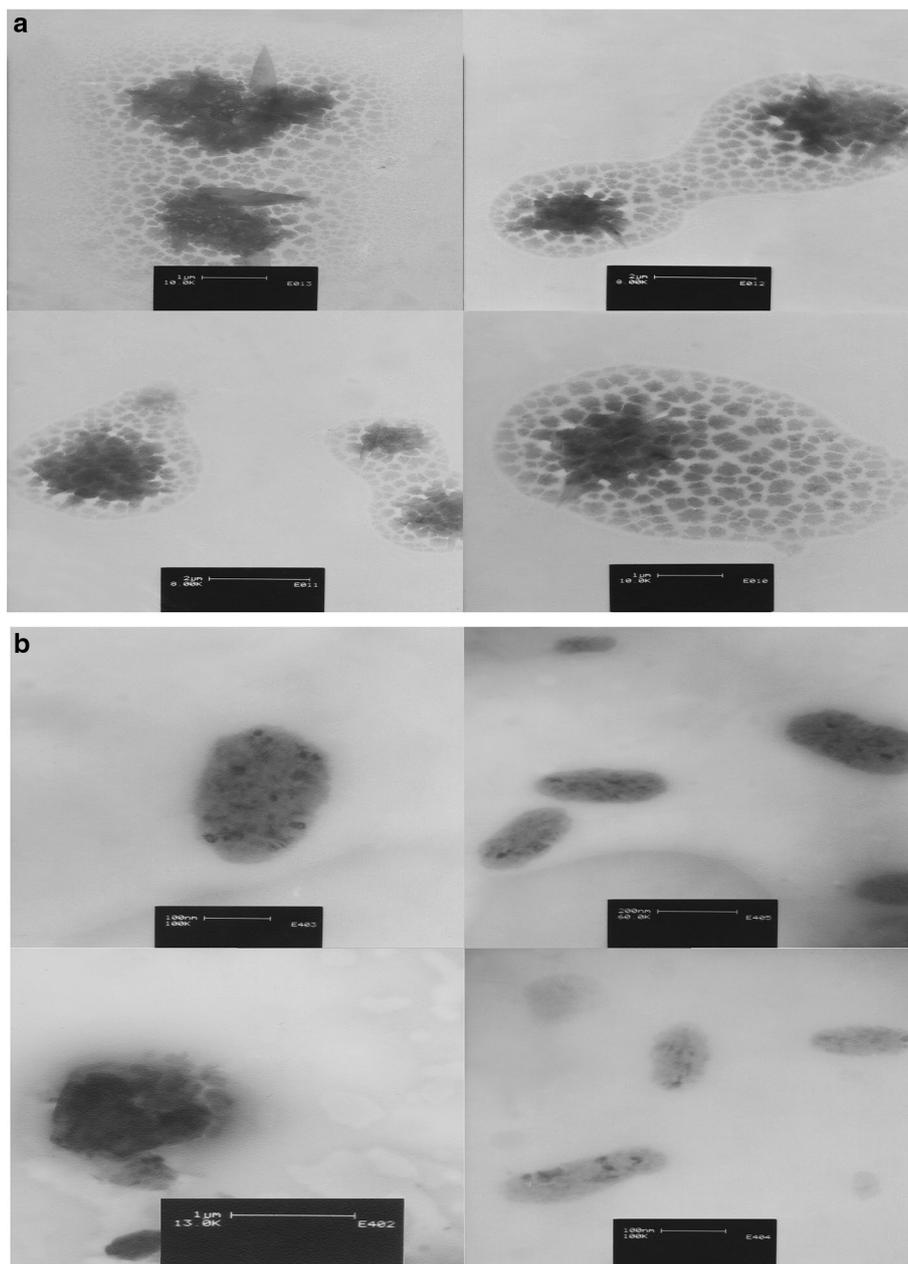


Fig. 7 TEM images of **a** core-shell particles with BA as core (*dark regions*) and VA as shell (*light regions*), using conventional surfactants (DOSS + KENON30); **b** throughout uniform morphological structure, using hybrid surfactant systems (DOSS + KENON30 + PDMS)

structure in final particle morphology takes place (Fig. 7b). This behavior could be the result of a reduction in the polymer (core)/polymer (shell) interfacial tension and overall free energy of the system by PDMS surfactant. Furthermore, PDMS as a lipophilic surfactant can solubilize many organic monomers into the interior of the micelles and can create a homogeneity environment for the polymerization [62, 75, 76]. This fact is attributed to the coiling of the long lipophilic chain in order to reduce the entropy loss (due to the molar mass distribution of PDMS used, it is well known that many properties of polymers strongly depend on their average molecular weight, particularly below 10^4 g mol⁻¹, because of the strong influence of oligomer chain ends. Therefore, short oligomeric PDMS chains with low molecular weight and strong polar end groups and long chains (red structures in Fig. 8) of PDMS shift to outer (hydrophile, surfactant layer) and inner (hydrophobe) part of micelles respectively) [35, 62]. This effect has been reported in the literature [76]. It can be

concluded that in the presence of PDMS bulk polymerization in micro-reactors may convert to more homogeneous system in the emulsion polymerization. A model of the particle as microreactors for synthesis of the polymer is shown that is consistent with the available and presented results (Fig. 8) [75].

Influence of PDMS Surfactant on Thermo-Oxidative Degradation of VA/BA Copolymer

TGA curves for VA/BA copolymers are shown in Fig. 9. There is a clear increase in thermal stability of copolymer with increasing PDMS surfactant. This behavior could be attributed to the greater participation of VA and BA for copolymerization and increasing molecular weight (Fig. 5). Similar behavior was reported for VA/BA copolymer prepared by free radical mechanism [56, 77].

Influence of VA/BA ratio on the copolymers VA/BA copolymers have higher thermal stability compared with a

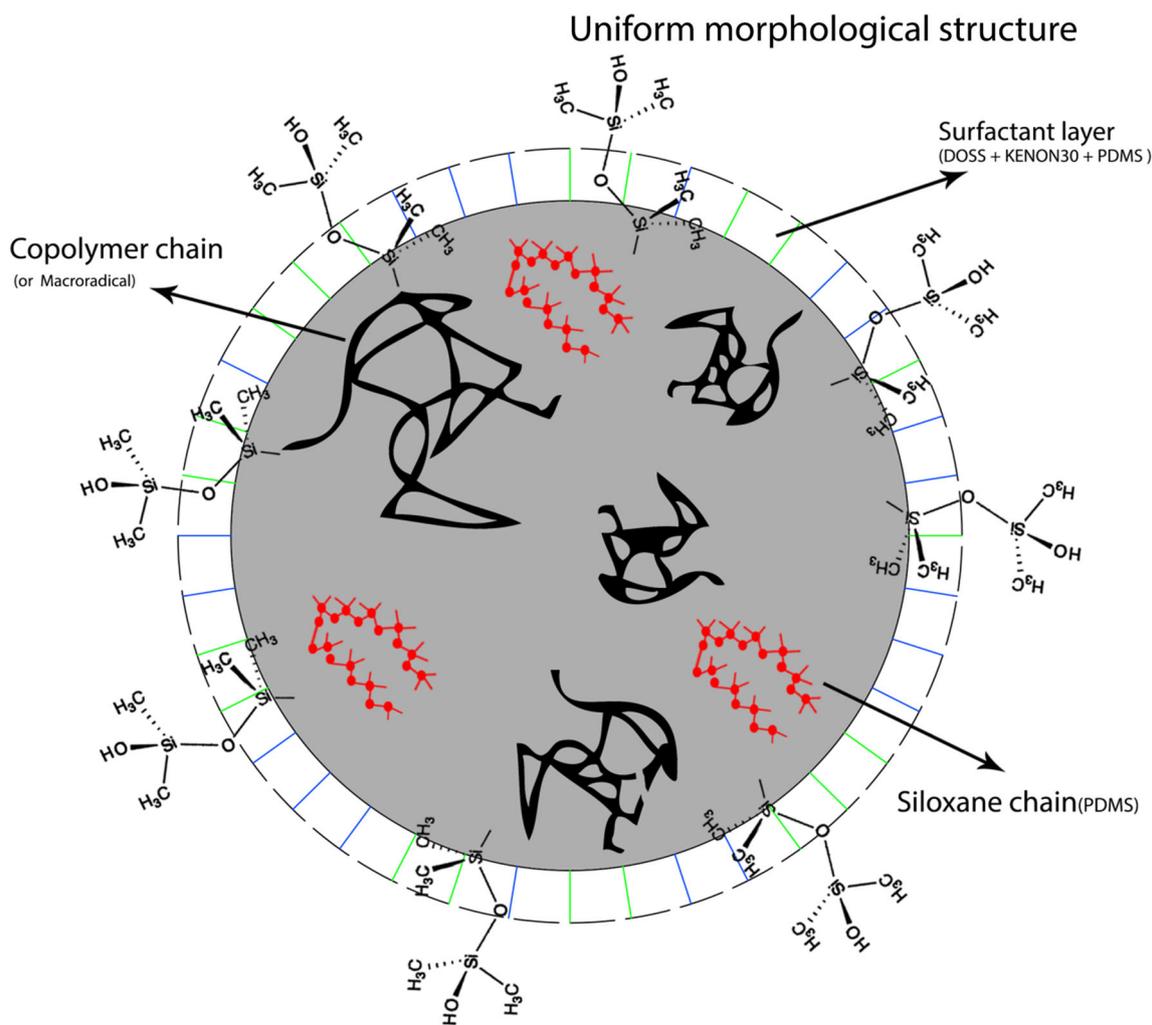


Fig. 8 A model of formation of microreactor and its emulsion polymerization acrylic monomer in presence of PDMS surfactant

Fig. 9 TGA thermogram of VA/BA copolymer with variable PDMS surfactant concentration under air, 10 °C min⁻¹

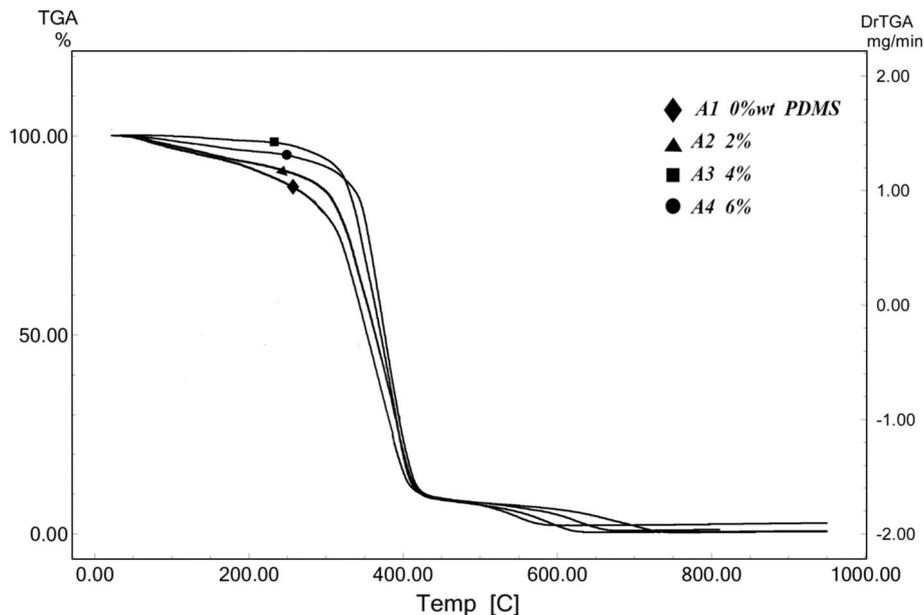
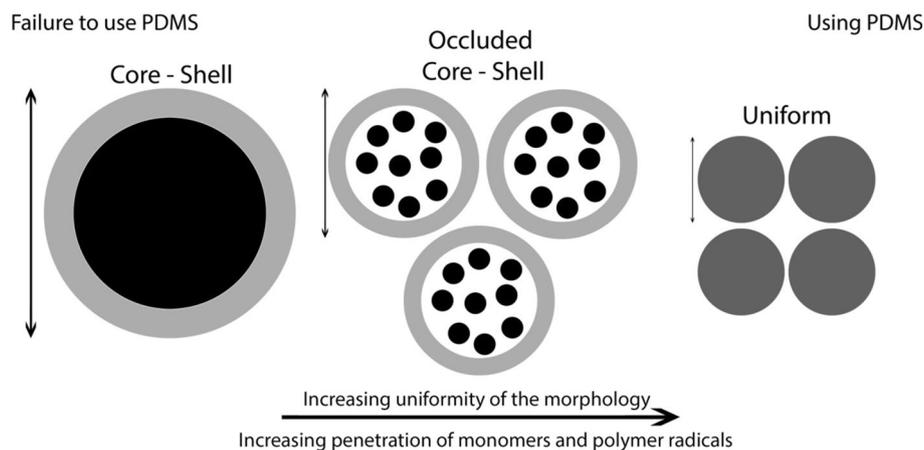


Fig. 10 Effect of PDMS on particle size and morphological development



polyvinyl acetate and poly(*n*-butyl acrylate) alloy [56]. The dual nature of PDMS surfactant molecule leads to the formation of particles having a more homogeneous distribution of both monomers (Fig. 7b). Furthermore, when penetration ratio of monomer and polymer radicals are rapid relative to the reaction rate, we would expect the monomer to be uniformly distributed throughout the particle, the behavior could lead to the greater participation of VA and BA for copolymerization together and uniform morphological structure of the latex particles (Figs. 7, 10). This result has been formulated via Eqs. 8 and 9 [74]:

$$PR_M = (D_M/x^2)/\{(k_p.n)/(v_p.N_A)\} \quad (8)$$

where PR_M is the penetration ratio for the monomers, D_M is the diffusion coefficient for the monomer assuming Fickian diffusion, x is the jump distance for a diffusive step, k_p is

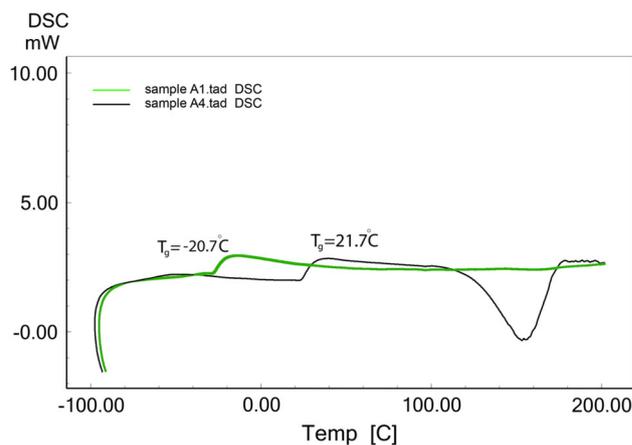


Fig. 11 Influence of PDMS surfactant on glass-transition of the copolymer

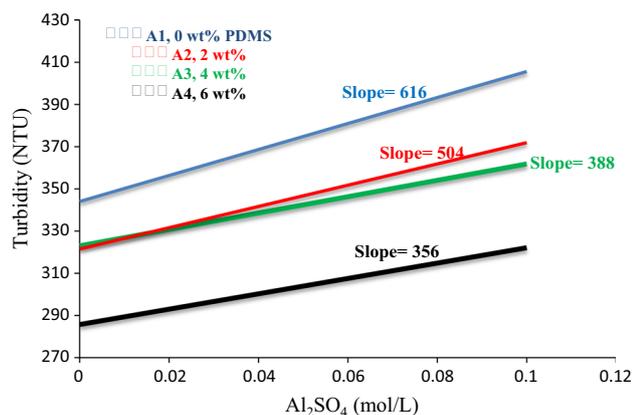


Fig. 12 Determination of colloidal stability by plotting turbidimetry versus concentration of $\text{Al}_2(\text{SO}_4)_3$ solution for VA/BA copolymer latices

the propagation rate coefficient, n is the number of radicals per particle, v_p is the particle volume and N_A is Avogadro's number.

$$\text{PR}_P = (D_P/x^2)/\{(k_t \cdot n)/(v_p \cdot N_A)\} \quad (9)$$

where PR_P is the penetration ratio for polymer radicals, D_P is the diffusion coefficient for polymer radical chain end and k_t is the termination rate coefficient.

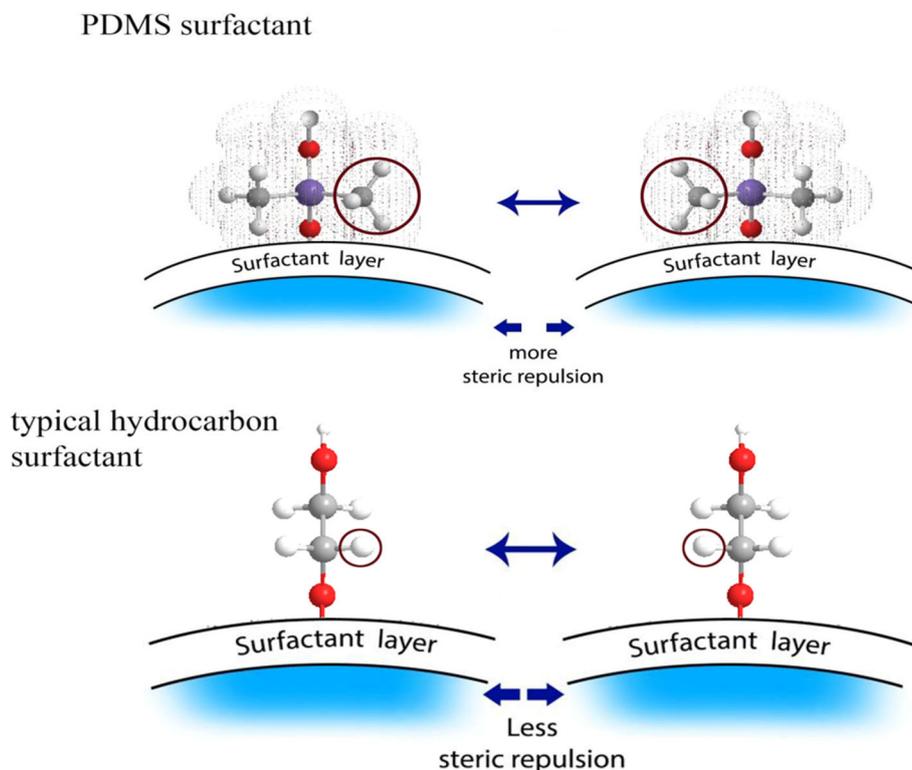
Note that the PR_P and PR_M depends on the particle size in emulsion polymerization, and are larger for smaller polymer particle and high volume fraction (ϕ) of latex

particles (Fig. 4). There is a good conformity between experiment data (Figs. 7, 11) and Eqs. 3 and 4. In this paper, the total mass and ratio of monomers were fixed, but two polymers with different T_g were obtained at different quantities of PDMS, as a result of greater participation of VA as hard monomer for the copolymerization that cause to increasing T_g of the copolymer (Fig. 11).

Colloidal Stability

The stability against electrolyte is very important for many applications in combination with pigments, e.g., paints and paper coatings [11]. The latex stability upon addition of electrolyte can be determined by the turbidity ratio method; the higher the slope of turbidity ratio of the latices, the less stable the system [78]. Figure 12 illustrates the change of slope of the turbidity ratio for the diluted latices with various PDMS surfactant contents in hybrid surfactant systems. The higher concentration of PDMS surfactant, the lower slope of the turbidity ratio obtained in the range studied. The higher colloidal stability of the latex in presence of PDMS surfactant could be due to the unique structure of the PDMS such as longer bond lengths of Si–O, larger bond angles of Si–O–Si and the presence of a methyl group, more steric repulsion, compare to typical hydrocarbon surfactants (Fig. 13) [33, 34]. In other words, with increasing steric repulsion between adjacent particles, aggregation is reduced.

Fig. 13 Schematic representation of colloidal stability of the particles due to more steric repulsion between the particles with using PDMS surfactant



Conclusion

A series of VA/BA latexes were synthesized using hybrid surfactant systems. The influence of PDMS surfactant (having hydrophilic silanol-terminated groups) on the copolymerization behavior was investigated. Increasing the PDMS surfactant decreases the particle size while \bar{M}_v , viscosity of the latex and its solid content were increased. Increasing of PDMS concentration showed a positive effect on thermal and colloidal stability, these improvements could be due to an increase in the molecular weight (\bar{M}_v), uniformity of the morphology and steric repulsion between the particles obtained respectively. T_g of the copolymer also increases (from -20.7 to 21.7 °C) with addition of PDMS.

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