

Ethoxysilyl- modified hyperbranched polyester as an effective hydrophob agent in miniemulsion polymerization

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Abstract : Hydrophobe agent, modified aromatic-aliphatic-hyperbranched polyesters (aaHBP) were synthesised by melt polycondensation reaction of Diphenolic acid as AB₂ type monomer with 4 drops of dibutyltin diacetate with mechanical stirrer, a gas inlet and an outlet. The polycondensation was done in two steps, first in a N₂ stream and second applying vacuum to drive the reaction to higher conversion and molar mass. Then modified with 3-isocyanatopropyl triethoxysilane (IPTES) in the presence of dibutyltin dilaurate as a catalyst to obtain ethoxysilyl-modified aliphatic-aromatic hyperbranched polyesters. The obtained polymer materials were characterized by NMR, FTIR, TGA and DSC. Then these modified ethoxysilyl-modified hyperbranched aromatic-aliphatic polyesters (aaHBPs) were effectively using as hydrophobing agent in the preparation of a spacer in miniemulsion polymerization of polystyrene.

Keywords: Miniemulsion, hyperbranched polyester, polystyrene, nano-polymer and hydrophob.

Introduction

Miniemulsion polymerization is one of unique eco-friendly polymerization techniques. In addition, control in the size of prepared polymer spheres are a novel challenge which developed through addition of hydrophobe agent. Hyperbranched polyesters (HBP) have concerned more interest and attained severe studying in the last four decades. They are members of a group of macromolecules called dendritic polymers, obtained from their three-dimensional structure, also large number of functional groups, having peculiar and distinctive properties. They have extremely branched backbone, which give contact to reactive groups; their structure give brilliant flow, handling properties and categorized as lower viscosity than linear polymers^{1,2,3,4,5}. These properties construct hyperbranched polymers interesting for different applications; coatings⁶, UV-curing applications⁷, Nanomedicine⁸ and Drug Delivery systems^{9,10} and also have attracted a huge contract of interest for other applications e.g. for high solid powder coatings¹¹, fire retardant coatings¹², barrier coatings for flexible packaging¹³, thermoplastic-toughened thermosets¹⁴, hydrophobic surface patterns from hyperbranched fluoropolymer¹⁵, waste water treatment¹⁶ and they have been recently suggested as a hydrophobing agent in preparation of polystyrene by miniemulsion polymerization.

Ibrahim *et al.*,¹⁷ prepared miniemulsion polymerization with three different types hydrophobic agents (hexadecane, Jaffamine M-600 and polycarbonate) in a controlled particle size. They synthesized polystyrene within a size 100 nm by miniemulsion polymerization, here the particle size related to the nature and amount of the added hydrophobes.

Sangermano *et al.*,¹⁸ modified hyperbranched polyesters by silicon nanoparticles and using as coupling agents with multifunctional for epoxy-silica hybrid coatings. They obtained highly clear hybrid coatings with better thermal and mechanical properties. The adding of ethoxysilyl-modified hyperbranched polyester serve as hydrophobic agent during the construction of the inorganic silicon sphere generated in-situ with sol-gel process starting from the 3-isocyanatopropyl triethoxysilane as inorganic precursors¹⁹. By following these criteria of research, we synthesized modified hyperbranched polyester for using as a hydrophobic agent in the preparation of polystyrene by miniemulsion polymerization. The obtained materials were characterised and the results compared.

2. Experimental Part

2.1 Materials

Styrene (98 %, Aldrich) was purified twice with sodium hydroxide treatment and distilled over CaH₂ freshly before used. 4,4-bis-(4'-hydroxyphenyl) valeric acid, dibutyltin dilaurate, tetrahydrofuran, (3-isocyanatopropyl) triethoxysilane, dimethylformamide, tetraethoxy-silane (TEOS), Dimethylacetamide (DMAc), 1,6-diisocyanatohexane, Dicyclohexylcarbodiimide (DCC), p-toluenesulfonic acid monohydrate (p-TSA), N, N-dimethylaminopyridine (DMAP), toluene, Methanol (p.A. 99.99%) were from Aldrich and they were used as received. Sodium dodecyl sulfate (SDS) (>99% Fluka), potassium persulphate KPS (>99% Fluka), NaHCO₃ (>99%), Hydroquinone (HQ, p.A.Fluka), Hexane (99% MERCK), Hexadecane (>98%, Fluka) were used as received. Millipore water was used as continuous phase. For the experiments with KPS the water was refluxed under a N₂ stream to remove the CO₂ for 60 min. The St was twice extracted with 0.1 N NaOH, followed by washing with water and brine in order to remove the stabilizer. Prior to use it was heated over CaH₂ to 80°C under vacuum until the evolution of H₂ disappeared and distilled under vacuum (Kp27-28 mbar 49-50°C). It was stored under nitrogen in a refrigerator not longer than one week.

Preparation of Aliphatic-Aromatic Hyperbranched Polyester (aaHPOH)

The polymerization of aaHBP-S has been performed as described in the reference¹⁸. 4-4'bis(4-hydroxyphenyl) valeric acid (10.0 g, 34.94 mmol) and 3 drops of dibutyltin diacetate were placed in a flask equipped with a mechanical stirrer, a gas inlet and an outlet. The polycondensation was done in two steps, first in a N₂ stream and second applying vacuum to drive the reaction to higher conversion and molar mass. The monomer was stirred in a nitrogen stream for 70 min at 210 °C, after that, a vacuum was applied at 230°C for 3 h with stirring and then without stirring for 1 h reaching a final vacuum of 0.010 mbar. The crude product was dissolved in THF and precipitated into water.

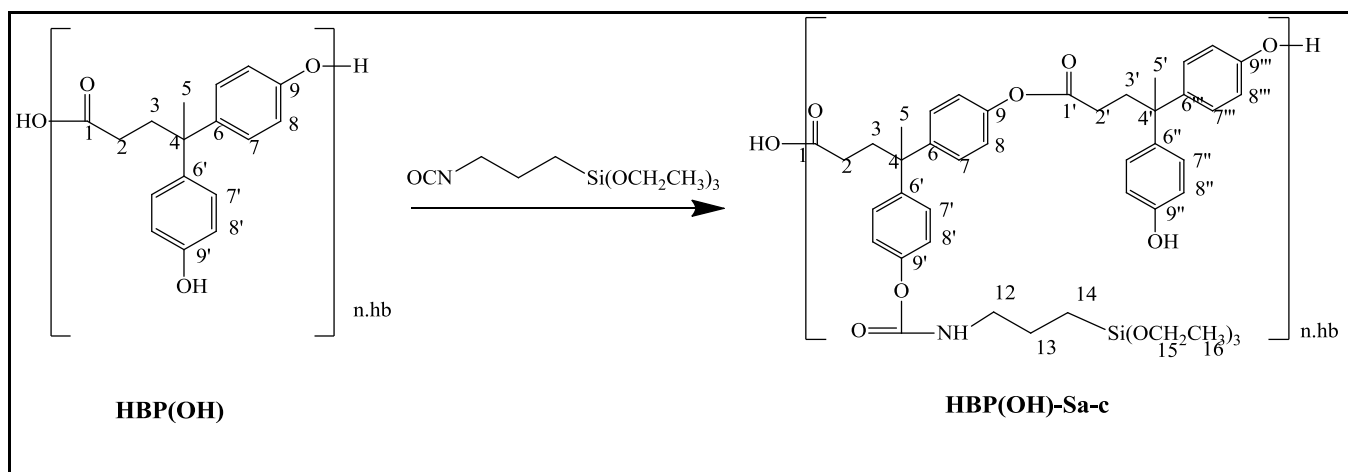
Yield: 16 g (80%)

¹H NMR (DMSO-d₆, δ in ppm) : 11.98 (br, COOH, 0.039 H); 9.25, 9.18 (Ar-OH, 1H); 7.19, 6.99, 6.68 (Ar-H, 8H); 2.49–2.30 (CH₂-CH₂, 4H_{2,3}); 1.59–1.50 (CH₃, 3H₅).

M_n by ¹H and ¹³C(quantitative) NMR analysis: 3900 g/mol = 14.4 repeating units.

FT-IR (KBr): 3065 m (C-H_{arom.}), 2966 s (C-H_{aliph.}), 1734 s (C=O_{phenyl ester}), 1508 s (C=C_{arom.}), 1206, 1170 s (C-O-C_{phenyl ester}), 831 cm⁻¹ m (m C-H_{1,4} disubst. arom. ring).

Modification of aaHBP with (3-isocyanatopropyl) triethoxysilane



Scheme 1: Modification reaction of HBP(OH) leading to the synthesis of aaHBP(OH)-Sa-c.

Aliphatic-aromatic hyperbranched polyester aaHP(OH) was subsequently modified with (3-isocyanatopropyl) triethoxysilane to different degree of modification. For that 1 g of the aaHBP-OH (0.86 mmol % of functional group) was added to a flask containing 20 mL of dry dimethylformamide (DMF) or THF under Ar atmosphere. Then different amounts of (3-isocyanatopropyl) triethoxysilane and one drop of catalyst dibutyltin dilaurate were added. The mixture was kept under stirring and heated at 40°C by means of an oil bath. After 2 h the bath was removed and the reaction was continued over night. The reaction mixture was poured into cold n-hexane in order to precipitate the polymer, which was then filtered and dried under vacuum.⁽¹⁸⁾

¹H NMR (DMSO-*d*₆, δ in ppm) : 9.23-9.16 (ArOH), 7.20 (Ar-H), 6.98 (Ar-H), 6.68-6.67 (Ar-H), 3.7-3.6 (Si(O*CH₂CH₃)₃), 2.90-2.83 (*CH₂-CH₂-CH₂-Si), 2.4-2.2 (CH₂CH₂O), 1.62-1.51 (CH₃), 1.3-1.2 (CH₂-*CH₂-CH₂-Si), 1.15-1.04 [Si-(OCH₂*CH₃)₃], 0.49-0.41 (CH₂-CH₂-*CH₂-Si).

Miniemulsion polymerization of St homopolymer

18.43 g of purified styrene, 600 mg hydrophobe, hexadecane or 680 mg melting HBP dissolved in 10 ml DMSO and 450 mg KPS were mixed and added to a solution of 172.8 mg sodium dodecyl sulfate (SDS) in 71.38 g of water as shown in table 1. The mixture was degassed (110 min⁻¹, 5x vac/N₂, min. 30 mbar), followed by stirring 1h under N₂ (800 min⁻¹) in order to prepare the pre-emulsion. Then the stirrer was removed from the vessel and the mixture was transferred to the sonifier. During this a moderate stream of N₂ was applied. The miniemulsion was prepared by sonication of the pre-emulsion for 660s with an ultrasonic disintegrator Branson 450W using a 1/2" minitip. The connection between vessel and tip was realized by a special Teflon adapter. Due to the adapter a tight connection between minitip and vessel could be realized. During all operations the vessel was purged with a slight stream of nitrogen.

The reaction vessel with the formed miniemulsion was transferred to the thermostat, and the temperature was raised to 70 °C. The reaction was performed at 400 min⁻¹ for 6.0 hrs. Then the mixture was cooled to 25 °C within 10 min using ice-water.

Table 1. Recipes of miniemulsion polymerization of styrene in presence of different hydrophobe agents.

Exp.	Initiator, mg	Hydrophob, mg	Temp.	M/I, Mole	Sonication %/time, Min.
MH0	450	600, Hexadecane	75	51.6	95/9
MH1	450	680, (aaHBP-S)	75	51.6	95/9
MH2	450	680, (aaHBP-Sa)	75	51.6	95/9
MH3	450	680, (aaHBP-Sb)	75	51.6	95/9
MH4	450	680, (aaHBP-Sc)	75	51.6	95/9

Analysis and characterization

The NMR measurements were performed with a JEOL DELTA 2 ECA 500 NMR spectrometer operating at 500.15 MHz for ^1H . DMSO- d_6 was used as a solvent for all NMR experiments. For internal calibration, the solvent peaks of DMSO were used: $\delta (^1\text{H}) = 2.50$ ppm.

GPC was used to investigate the molecular weight of the prepared polymers. The instrument was from Knauer, Berlin, with a RI detector in combination with a PL-GEL 5 mm mixed C column, 3007.5 mm (Polymer Laboratories, UK) using a flow rate of 1 ml/min and THF as eluent. Calibration was performed with linear polystyrene (PS) standards

Dynamic light scattering (DLS) analysis was done using a Zetasizer Nano ZS (Malvern) instrument. Average particles diameters (z-average) were determined from intensity-weighted size distributions.

DSC measurements were performed with a DSC Q1000 TA Instruments at the heating rate of 20°C per minute. Thermogravimetric analysis (TGA) measurements were performed in nitrogen at the heating rate of 10°C per minute by means of a TGA 7 Perkin Elmer instrument.

FT-IR The obtained sample was ground into small particles and dried in vacuum at 50 °C for 24 h. The dried samples were analyzed in KBr discs by FT-IR (JASCO FT/IR-4100, Japan). Samples were prepared for transmission electron microscopy (TEM) observation by Ar ion polishing system GATAN PIPS, working at 3.5 keV at an angle of 78. They were examined in a 300 keV transmission electron microscope Philips CM30. TEM micrographs were processed with a slow scan CCD camera and analyzed with the Digital Micrograph program. The TEM observations were always performed using a very low electron flux to avoid any structural modification of the sample induced by the electron beam

Results and discussion

The modification of aaHBP(OH) were synthesized for using as hydrophobing agent in the polystyrene preparation. The aaHBP (OH) was modified partially with 3-isocyanatopropyltriethoxysilane (IPTS). Three types of aaHBP with increasing percent of modification have already prepared, aaHBP-S1a (40%), HBP-S1b (60%) and HBP-S1c (80%) depending on the percent of ethoxysilyl modification. The chemical structures of the ethoxysilyl-modified HBP are shown in scheme 1.

The ^1H -NMR spectra of the aaHBP(OH) show that, it was so easy to differentiate the protons of $-\text{CH}_3$ groups at 1.48- 1.6 ppm. The signals at $\text{CH}_2\text{CH}_2\text{COOH}$ didn't split from water and appeared at 3.3 ppm. The terminal ($-\text{OH}$) and linear ($-\text{OH}$) groups resonated at 9.15 and 9.21 ppm, respectively. The modification degree was calculated to be correspondingly 40%, 60% and 80% and it was evaluated from the ^1H NMR signals at 3.7-3.6 and 1.62-1.51 owing to the methylene and methyl groups in the ethoxysilane, respectively.

IR spectrum showed characteristic peaks of the chemical groups of unmodified and modified aaHBP(OH)s samples in Figure 1. The absorbance bands are identified as follows: a strong and broad overlapping band in the range of 3600-3200 cm^{-1} was assigned to NH bond in the urethane group in modified HBP and for the OH of carboxylic group in the polymer, the bands at 2948, 2868 cm^{-1} are due to $-\text{CH}_3$ and $-\text{CH}_2$ stretching vibrations for hyperbranched polyesters, the strong bands at 1707 - 1753 cm^{-1} is due to $\text{C}=\text{O}$ of ester carbonyl, the bands at 1388 cm^{-1} and 1457 cm^{-1} are due to $-\text{CH}_3$ and $-\text{CH}_2$ bending vibration. The band at 1203 cm^{-1} was assigned to NH bending vibration of the urethane groups and the bands at 1220-1248 cm^{-1} is attributed to the strong $-\text{C}-\text{O}-\text{C}-$ of aaHBP. Finally, For the modified aliphatic-aromatic hyperbranched polyester, the bands near 1129 cm^{-1} , was because of the $\text{Si}-\text{O}-\text{C}$ stretching, and the band from 670-780 cm^{-1} for vibration of $\text{Si}-\text{O}-\text{C}$.

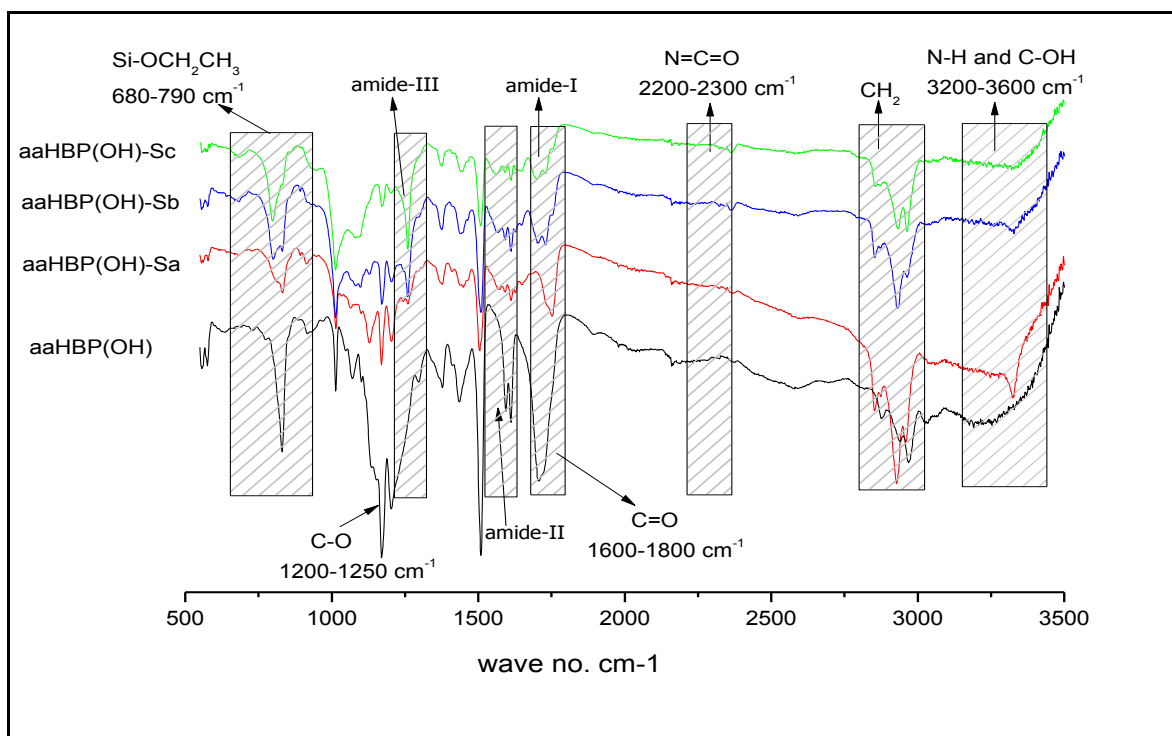


Figure 1: IR spectra of aaHBP(OH) and aaHBP(OH)-Sa-c with different degree of modification

Differential scanning calorimetry was useful to examine the thermal behaviour of polyesters. Table 1 shows the differential scanning calorimetry thermograms of the second heating scans of aaHBP(OH) before and after modification, from aaHBP(OH) to aaHBP(OH)-Sa-c. The results of the 1st heating show a broad peak at 90-100°C related to evaporations of water absorbed in the polymers. The second heating of aaHBP(OH) and aaHBP(OH)-Sa-c show a mediate in the heat flow of the glass transition.

The glass transition temperatures of unmodified polyester aaHBP(OH) and the modified aaHBP(OH)-Sa-c was estimated and can concluded that, modified aaHBP-Sa-c gave higher Tg values matched with unmodified aaHBP(OH). As the amount of the precursor (IPTES) increased, the Tg increased, reaching the higher value with aaHBP(OH)-Sc =120°C for 80wt% modification from unmodified polyester aaHBP(OH) =98°C. The high temperature related to the formation of inter- and particularly intra-molecular hydrogen bonds networks within aaHBP(OH) and aaHBP(OH)-Sa-c.

Table 2 : DSC and TGA off the aaHBP(OH) and aaHBP(OH)-Sa-c with different percent of modification

	aaHBP(OH)	aaHBP(OH)-Sa (40%)	aaHBP(OH)-Sb (60%)	aaHBP(OH)-Sc (80%)
DSC	98°C	108°C	110°C	120°C
TGA	330°C	384°C	393°C	405°C

Thermal Gravimetric analyses of unmodified and modified aaHBP were achieved in inert nitrogen gas in the temperature range from 25-850°C within a heating rate of 10 K/min. The degradation started after 300°C for all unmodified hyperbranched polyesters aaHBP(OH) showing quit good thermal stability. Table 2 shows the maximum of decomposition temperature of modified aaHBPs with a diverse percent of modification. The decomposition of unmodified aaHBP(OH) start early at temperature of about 330°C, However the main decomposition of modified aaHBP(OH)-Sc reach to the maximum temperature at 405°C.

Table 3 shows the mean diameter distributions of PS nanoparticles in presence of different hydrophobe agents (hexadecane and aaHBP). Prepared polymers are exhibited narrow distributions which verified uni-modal behavior of the particles. According to previous results, a vital role of hydrophobe is as stabilizer for

mini-emulsion droplets. In addition, narrow polydispersity of the prepared mini-emulsion was decreased by increasing the amount of hydrophobe.

Table 3. Molar ratios and particle size of polystyrene prepared in presence and absence of different HBP hydrophobe agents.

EXP	Hydrophobe agent, Mole%	Mn, g/mol	Mw, g/mol	PDI	diameter, nm by DLS
MH0	13.11	23000	52900	2.3	132
MH1	9.15	27000	56700	2.1	68
MH2	9.15	28500	54200	1.9	54
MH3	9.15	33000	52800	1.6	87
MH4	9.15	26700	37400	1.4	93

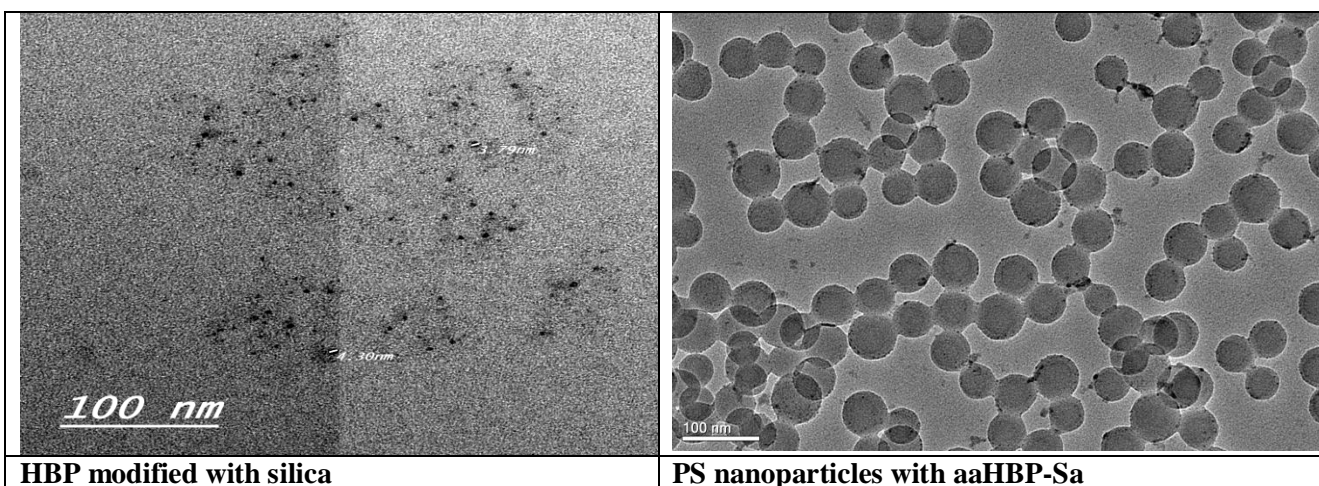
Number average molecular weight, Mn & weight average molecular weight, Mw & polydispersity index, PDI.

Furthermore, Table 3 stated the results of gel permeation chromatography, Mn, Mw and PDI results were determined for characterization of polystyrene in presence (hexadecane and aaHBP) as hydrophobes. These results reflected that increase in monomer / initiator ratio results in a decrease in Mn and increase in Mw and consequently PDI was increased.

Also, gel permeation chromatography results for all of the chosen hydrophobes, as the hydrophobe percentage increased the size of polystyrene particle decreased. It was a result of the poor water solubility of the two types of the hydrophobes which are able to prevent any monomer from diffusing through the aqueous phase. In addition, average diameter size of mini-emulsion prepared by HD was 132 nm and in range from 55-90 nm for that prepared by modified HBP. This revealed that the most stabilized polystyrene particles were performed in presence of modified aaHBP with silica nanoparticles.

TEM

Transmission electron microscopy was applied for morphological study of the prepared polystyrene (using HBP as a hydrophobe) mini-emulsion spheres. Figure 2 shows some shadowy low contrast groups representing silica domains of 3-5 nm in size for the modified HBP. The average diameter measurement of polystyrene particles is less than 60 nm as shown on the Figure 2. Moreover, the Figure illustrates that the nature of the prepared polystyrene particles is spherical, smooth and have low particle size distribution.



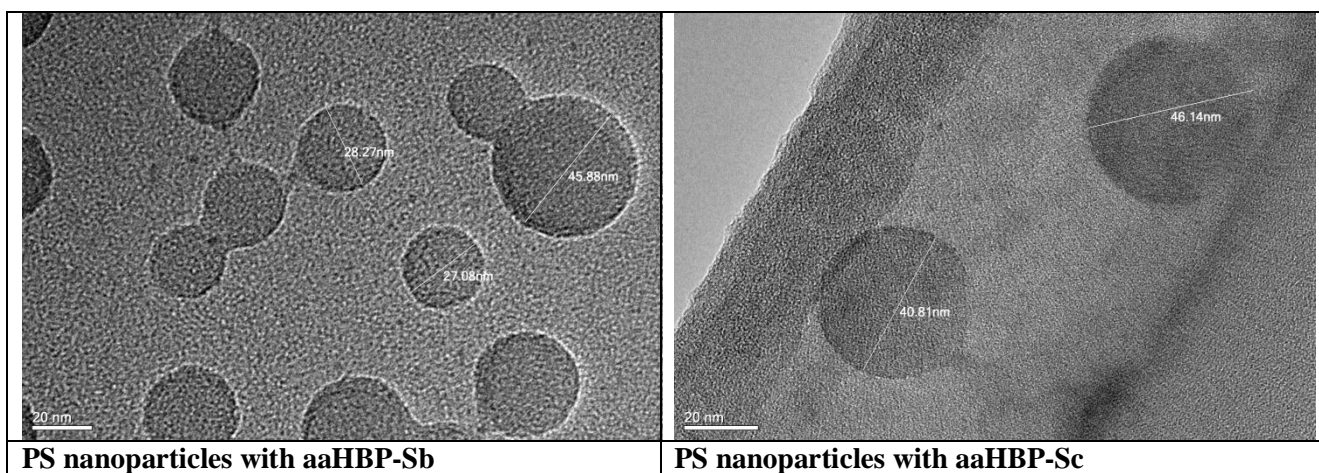


Figure 2. Transmission electron micrographs (TEM) of modified HBP and polystyrene using HBP/silica as a hydrophobe

Conclusion

Ethoxysilyl-modified aliphatic-aromatic hyperbranched polyesters with different degree of modification were successfully synthesized for using as hydrophobe agent in miniemulsion polymerization techniques. By increasing the ethoxysilyl groups in the modified hyperbranched polyesters, the silica cluster size decreased from 15-20 nm to a very small dimension with an average value of 3-5 nm which permit the formation of strong interconnected hybrid networks.

Very tight diameter size distributions of prepared polystyrene particles are detected with TEM and DLS. Smooth and sphere and uniform polystyrene nanoparticles are synthesized as one of most usable polymer in many industrial applications specially packaging materials and leather industry. To conclude, ethoxysilyl-modified aliphatic-aromatic hyperbranched polyester is a highly effecting hydrophobe agent for micelle formation and further polymerization process through miniemulsion.

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