# PEO-Based Star Copolymers as Stabilizers for Water-in-Oil or Oil-in-Water Emulsions

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ABSTRACT: A series of well-defined poly(ethylene oxide) (PEO)-based star copolymers with controlled number of arms, compactness, and compositions were prepared by atom transfer radical polymerization using a simple "arm-first" method. Tuning the composition of the arms allowed these star polymers to stabilize either oil-in-water or water-in-oil emulsions. Stable oil-in-water emulsions were obtained with star copolymers containing only hydrophilic PEO arms due to their better affinity to the aqueous phase. In contrast, the insertion of a fraction of hydrophobic poly(butyl acrylate) arms into the star structure significantly changed the surfactant behavior of the star copolymers, leading to the formation of stable water-in-oil emulsions. Additionally, in both cases, an extremely low surfactant concentration, <0.01 wt % vs total weight of water and xylene used for emulsion formation, was sufficient to generate stable emulsions.
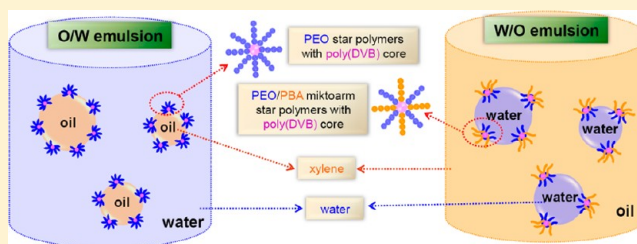
INTRODUCTION

The use of amphiphilic block copolymers, consisting of a water-soluble hydrophilic block and water-insoluble hydrophobic block, as surfactants for the generation of a stable emulsion has been well documented in the literature.[1] Because of the specific solubility characteristics of each segment of the copolymer, the block copolymers are driven to adsorb to the interface and stabilize the dispersed droplets. These block copolymers can also serve as surfactants for biphasic polymerization, allowing the preparation of stable polymer particles with tunable size. Polymeric surfactants show several unique features when compared to low molar mass surfactants, such as lower surfactant loading for the generation of a stable emulsion, a lower critical micelle concentration (cmc), and low molecular mobility, which is important when they are used to stabilize latexes, since the reduced desorption of surfactants from particle surfaces helps improve the latex stability during the potential application process. In addition, one can also easily adjust the composition of the block copolymers for a given application through the introduction of a (non)ionic anchoring block, functional sites, or even a stimuli-responsive block, aiming to tailor the interaction between the polymeric surfactants and the dispersed phase that is to be stabilized.[1]

The development of controlled radical polymerization[2−4] techniques during the past two decades, such as atom transfer radical polymerization,[5−9] enables control over the molecular weight and compositions of block copolymers and provides accessibility to a series of copolymers with complex topologies, including brush polymers, branched polymers, star polymers, and even cross-linked polymer networks.[10−12] Star poly-mers,[13−15] with multiple arms radiating from a central branching point, or core, represent one of the simplest branched topologies. The core−shell microstructure of star polymers leads to several unique properties, including tunable star polymer solubility by control of the composition of the arm and core or the introduction of multiple functionalities on the periphery to tune its affinity to different substrates.[16−24] These properties provide an opportunity to use star-shaped polymers as surfactants for emulsion applications or other biphasic polymerizations.[25] However, when compared to the extensive studies on utilization of amphiphilic block copolymers in a series of emulsification applications, there are a limited number of reports on star polymer-based emulsifier systems.[26−34] Nevertheless, these limited studies showed some promising results: (1) Star polymers are very efficient stabilizers, and generally a lower level of surfactant loading is needed for star polymer based surfactants to reduce the interfacial tension compared to their linear counterparts. (2) The composition of star copolymers significantly affects their interfacial behavior: more hydrophilic star polymers are good stabilizers for oil-in-water (O/W) emulsions, and more hydrophobic star polymers lead to the formation of water-in-oil (W/O) emulsions.

Herein, we report the design and use of a series of PEO-based star polymers as stabilizers/surfactants for the generation of stable oil-in-water or water-in-oil emulsions. The effects of several parameters on the emulsification behavior of the star
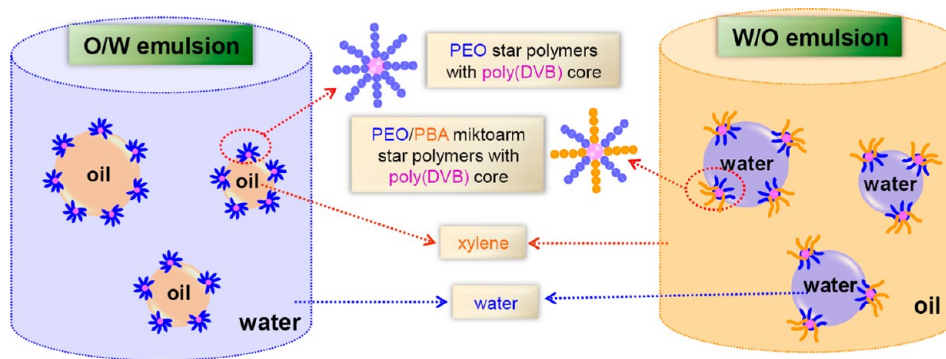
Scheme 1. PEO Star Polymers as Stabilizers for O/W or W/O Emulsions

polymers were studied, including arm composition/hydrophobicity, star size, and compactness. Xylene-in-water and water-in-xylene emulsions with long-term stability (3–6 months) were generated with a concentration of star emulsifiers as low as ca. 0.005 wt % by optimization of the star polymer composition.

■ EXPERIMENTAL SECTION

Materials. Divinylbenzene (DVB) was purchased from Aldrich. The cross-linker was purified by passing through a basic alumina column to remove the inhibitor. Poly(ethylene oxide) methyl ether methacrylate macromonomer (PEO MM) with M_n = 2080 and M_w/M_n = 1.05, obtained as a 50 wt % solution in water (Aldrich), was extracted from water with methylene chloride, followed by the rotary evaporation of methylene chloride. Poly(ethylene oxide)-based macroinitiators (PEO MI, M_n = 2200 or 5200) and poly(butyl acrylate)-based macroinitiators (PBA MI, M_n = 7800 and M_w/M_n = 1.10) were prepared according to the previously published procedures.[22] CuBr (98%, Acros) was purified by stirring in acetic acid, it was then filtered, washed with 2-propanol, and then dried under vacuum. Tris[(2-pyridyl)methyl]amine (TPMA) was prepared according to a previously published procedure.[35] All other reagents—CuBr$_2$, N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA), ethyl 2-bromoisobutyrate (EBiB), and solvents—were purchased from Aldrich and used as received.

Synthesis of PEO–Poly(DVB) Star Polymers (S$_D$64) via Cross-Linking of Macromonomers. Polymerization conditions were set at [PEO MM]$_0$/[EBiB]$_0$/[DVB]$_0$/[CuBr]$_0$/[TPMA]$_0$ = 5/1/15/1/1 and [PEO MM]$_0$ = 0.167 mM in anisole. PEO MM (5.11 g, 2.5 mmol), DVB (1.3 mL, 7.4 mmol), TPMA (143 mg, 0.49 mmol), and anisole (15 mL) were added to a clean dry Schlenk flask. The flask was degassed by five freeze–pump–thaw cycles. During the final cycle, the flask was filled with nitrogen and CuBr (0.070 g, 0.49 mmol) was quickly added to the frozen mixture. The flask was sealed with a glass stopper and then evacuated and backfilled with nitrogen five times before it was immersed in an oil bath at 80 °C. Finally, the N$_2$-purged initiator EBiB (0.072 mL, 0.49 mmol) was injected into the reaction system, via a syringe, through the side arm of the Schlenk flask. The reaction was stopped after 116 h via exposure to air and dilution with THF.

Synthesis of PEO-Based Star Polymers via Cross-Linking of Macroinitiators. A typical procedure for the synthesis of PEO–PBA–poly(DVB) miktoarm star polymers (MS$_{PBA50}$) is listed below. Polymerization conditions were set at [PEO MI]$_0$/[PBA MI]$_0$/[DVB]$_0$/[CuBr]$_0$/[PMDETA]$_0$ = 0.5/0.5/12/0.8/0.8 and [PEO]$_0$ = 0.015 mM in anisole. A clean and dry Schlenk flask was charged with PEO MI (1 g, 0.19 mmol initiating sites), PBA MI (1.48 g, 0.19 mmol initiating sites), DVB (0.82 mL, 4.6 mmol), PMDETA (0.080 mL, 0.38 mmol), and anisole (12 mL). The flask was degassed by five freeze–pump–thaw cycles. During the final cycle the flask was filled with nitrogen, and CuBr (0.200 g, 1.4 mmol) was quickly added to the frozen mixture. The flask was sealed with a glass stopper and then

evacuated and backfilled with nitrogen five times before it was immersed in an oil bath at 110 °C. The reaction was stopped after 22 h via exposure to air and dilution with THF.

Two other PEO–PBA–poly(DVB) miktoarm star polymers, sample MS$_{PBA30}$, [PEO MI]$_0$/[PBA MI]$_0$/[DVB]$_0$ = 0.7/0.3/12, and sample MS$_{PBA10}$, [PEO MI]$_0$/[PBA MI]$_0$/[DVB]$_0$ = 0.9/0.1/12, and two additional PEO–poly(DVB) homoarm star polymers sample S$_L$35 with [PEO MI]$_0$/[DVB]$_0$ = 1/5 and sample S$_L$30 with [PEO MI]$_0$/[DVB]$_0$ = 1/3 were prepared using similar procedures, by simply changing the molar ratio between arm precursors and cross-linker.

Generation of Emulsions. The water/oil ratio was set at 1:1 by weight, and emulsions were formed using a vortex mixer (Fisher Scientific Analogue Vortex Mixer, 120 V at 3000 rpm) for 30 s. Unless otherwise indicated, the star copolymers were dispersed in water before homogenization. After emulsification, the height of each phase, emulsion, neat water, and/or neat oil, was measured to calculate the volume percentages of oil and water in the emulsion phase. A drop test was conducted to determine the emulsion type by placing one drop of the emulsion phase into neat water or into neat oil. An O/W emulsion droplet disperses readily in water but not in oil and vice versa. All emulsions were stored in closed vials at room temperature, and the emulsion phase fraction was checked regularly to characterize emulsion stability.

Characterization. Apparent molecular weight and dispersity were measured by GPC (Polymer Standards Services (PSS) columns (guard, 10^5, 10^3, and 10^2 Å), with THF eluent at 35 °C, flow rate 1.00 mL/min, and differential refractive index (RI) detector (Waters, 2410)). Toluene was used as the internal standard to correct for any fluctuation of the THF flow rate. The apparent molecular weights and dispersity were determined with a calibration based on linear polystyrene standards using WinGPC 6.0 software from PSS. The detectors employed to measure the absolute molecular weights were a triple-detector system containing a RI detector (Wyatt Technology, Optilab REX), a viscometer detector (Wyatt Technology, ViscoStar), and a multiangle laser light scattering (MALLS) detector (Wyatt Technology, DAWN EOS) with the light wavelength at 690 nm. Absolute molecular weights were determined using ASTRA software from Wyatt Technology. The average hydrodynamic diameter of star polymers (D_n) was measured by dynamic light scattering (DLS) on a high performance zeta-sizer from Malvern Instruments, Ltd. Diluted emulsion droplets were imaged with an inverted bright-field microscope (Leica DMI 6000) at 40× magnification. Interfacial tensions of star polymers at the xylene/water interface were measured by the DuNouy ring method.

■ RESULTS AND DISCUSSION

As discussed in the Introduction, when star-shaped polymers are used as emulsifiers, one can control the type of emulsion formed by tuning the compositions of star polymers, i.e., the hydrophilicity of the star polymers: more hydrophilic star polymers favor the formation of oil-in-water (O/W) emulsions, while star polymers containing a large fraction of hydrophobic

Table 1. PEO Star Polymers as Stabilizers for Xylene-in-Water Emulsion

star polymer[a]	arm	DVB core (wt %)	$M_{w,star,RI}$[b]	$M_{w,star,MALLS}$[c]	$M_{w,star,MALLS}/M_{w,star,RI}$	N_{arm}[d]	HLB	surfactant amount[e] (wt %)	emulsion phase fraction[f] (%)	dispersed phase fraction[g] (%)
S_D64^a	PEO 2000	21	4.93×10^4	1.76×10^5	3.57	64	16	0.5, 0.25, 0.1, or 0.05	64	84
								0.01	46	80
								0.005	not stable	n/a
S_L35^a	PEO 2000	28	3.97×10^4	9.98×10^4	2.51	35	14	0.5	75	72
								0.25, 0.1, or 0.05	71	76
								0.01 or 0.005	not stable	n/a
S_L30^a	PEO 2000	22	3.59×10^4	8.29×10^4	2.31	30	16	0.5	75	72
								0.25 or 0.1	71	76
								0.05, 0.01, or 0.005	not stable	n/a

[a]$S_{L or D}X$; D represents dense star, L represents loose star, and X is the average arm number per star. PEO arms have an average molecular weight around 2000. [b]Weight-average molecular weight of star polymers determined by THF GPC with RI detector, calibration with linear polystyrene as standard. [c]Weight-average molecular weight of star polymers determined by THF GPC with MALLS detector. [d]Average arm number per star polymer calculated according to the equations shown in a previous paper.[22] [e]Surfactant amount was calculated based on the total weight of water and xylene used for the emulsion formation. [f]Volume fraction of emulsion phase as compared to total volume of emulsion plus neat water phase. [g]Volume fraction of the dispersed phase in the emulsion phase itself.

units would lead to the formation of a water-in-oil (W/O) emulsion.[33] Nevertheless, in prior work that established these principles,[33] the long-term stability of the generated emulsion was not evaluated, and a relatively high surfactant concentration was used, 1 wt %.

In this paper, we explored the effect of star polymer composition and size/compactness of the star on the preferred emulsion type and the emulsifying efficiency. As shown in Scheme 1, two classes of star polymers were prepared and used as emulsifiers: PEO−poly(DVB) homoarm star polymers and PEO−PBA−poly(DVB) miktoarm star polymers. The use of PEO−poly(DVB) homoarm star polymers led to the formation of an O/W emulsion due to the presence of hydrophilic PEO arms, resulting in better affinity of the star polymers to the aqueous phase. In contrast, the introduction of a certain percentage of hydrophobic PBA arms to the star structure significantly reduced the affinity of the star polymers to water, and when these star polymers were used as emulsifiers, stable W/O emulsions were obtained, due to the increased hydrophobicity of star polymers and the good affinity of PEO and PBA arms to xylene. It was previously reported that a stable emulsion could be formed with the concentration of a star surfactant as low as 0.02 wt % vs aqueous phase.[34] In the current study, we set out to determine the lowest level of star polymer-based surfactants that would generate either an O/W or W/O emulsion with long-term stability.

PEO−Poly(DVB) Homoarm Star Polymers as Stabilizers for O/W Emulsions. A series of star polymers with PEO arms and a cross-linked hydrophobic poly(DVB) core were synthesized through the cross-linking of either PEO MM or PEO MI arm precursors via the "arm-first" method by ATRP. Polymerization conditions and results are summarized in Table 1. The formed star polymers, samples S_D64, S_L35, and S_L30, have an average number of arms per star molecule ranging from 30 to 64 and also different degrees of compactness. The ratio of absolute molecular weight determined by MALLS to apparent molecular weight determined by GPC (using linear polymer standards) correlates with the compactness of the star polymer structure. Higher ratios indicate a more compact star structure.[16] The synthesized PEO homoarm star polymers have similar hydrophile−lipophile balance (HLB) values between 14 and 16, in the HLB range where conventional

surfactants are expected to be able to emulsify oil-in-water. These star polymers were then evaluated as stabilizers for generation of emulsions with a weight ratio of xylene and water set at 1/1. In all cases, O/W emulsions, which were stable for more than 6 months, were obtained, although the amount of star polymers required for the generation of a stable emulsion and the formed emulsion phase fraction varied slightly for the different star polymer surfactants.

All three of the PEO homoarm star polymers produced oil-in-water emulsions, consistent with their HLB of 14−16. Using PEO−poly(DVB) star polymers with a higher number of arms, 64, and a more compact structure, $M_{w,star,MALLS}/M_{w,star,RI} = 3.57$,[36] S_D64, as stabilizer, a stable xylene-in-water emulsion could be formed when the concentration of the star polymer was set at 0.01 wt % (relative to the total weight of water and xylene used for emulsion formation), which corresponds to an overall concentration of ca. 5.26×10^{-4} mM star polymers in the system. The formed emulsion phase occupied 46 vol % of the total mixture (Table 1 and Figure 1) with a neat water layer present at the bottom of the vial and a neat oil layer on top.
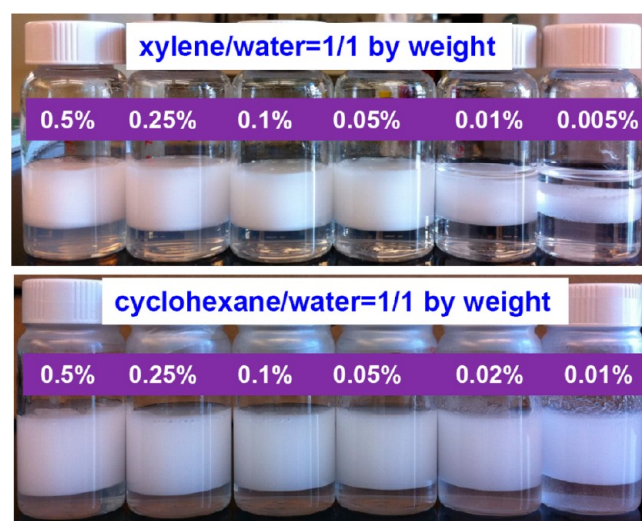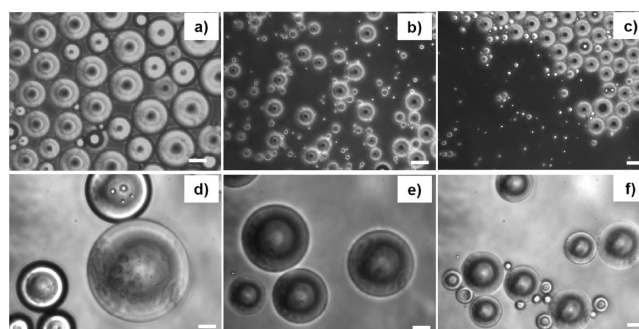

Figure 1. Images of oil-in-water emulsions stabilized by different amounts of PEO star polymer, S_D64.

The volume fraction of xylene droplets dispersed in the emulsion phase was 80 vol %. The emulsion phase fraction increased to ca. 64 vol %, with the emulsion phase containing a dispersed xylene volume fraction of 84 vol %, when the star concentration was increased to 0.05 wt %. However, only a thin layer of emulsion phase was formed at the oil/water interface when the concentration of the star stabilizer was reduced to 0.005 wt %. A similar trend was observed when the other PEO star polymers with different numbers of PEO arms, samples S_L35 and S_L30, were used. A slight increase of the emulsion phase fraction was observed with an increase in the concentration of star stabilizer.

The HLB can indicate the capability of forming a certain preferred emulsion type, but it does not capture differences in the emulsifying efficiency of a surfactant. Despite having similar HLB values as S_D64 (HLB 16), when the S_L35 (HLB 14) and S_L30 (HLB 16) PEO homoarm star polymers were used as stabilizers, the star polymer concentration required for the formation of a stable O/W emulsion was higher than that required for sample S_D64. For instance, 0.05 wt % of S_L35 PEO star polymers stabilizer was required to form a stable emulsion, compared to 0.01 wt % for S_D64. The different emulsification behavior reflects differences in the star polymer structure, namely star size and compactness, that are not captured by the HLB convention. The S_L35 star polymer has a smaller size/hydrodynamic volume than sample S_D64, as indicated by the relatively lower apparent molecular weight, which may lead to a less efficient coverage of the emulsion droplets resulting in the need for a larger amount of star polymers for the generation of a stable emulsion. On the other hand, once a stable emulsion was generated, for the same amount of star polymer, such as 0.05 or 0.1 wt %, a higher volume fraction of emulsion phase was obtained when using the smaller but less compact S_L35 PEO star polymer, $M_{w,star,MALLS}/M_{w,star,RI} = 2.51$. A less compact structure has less densely packed PEO arms in the star, which may affect how the PEO star polymer adsorbs at the interface, by analogy to the different emulsifying behaviors exhibited by polymer-grafted silica nanoparticles that were prepared with varying polymer grafting densities.[37] Stars with a lower number of arms and less compact structure would lead to a higher probability for the hydrophobic poly(DVB) core to be exposed to the oil/water interface, which may improve the stabilization effectiveness of the adsorbed layers produced at higher star polymer concentrations. This explanation is also supported by the results obtained using the S_L30 star polymer with an even lower number of arms, 30, and a less compact structure, $M_{w,star,MALLS}/M_{w,star,RI} = 2.31$, as stabilizer. In this case, an even higher concentration of the star surfactant, 0.1 wt %, was needed for the formation of a stable emulsion, but a larger fraction of emulsion phase was still obtained compared to the S_D64-stabilized emulsion.

An optical microscope was utilized to image the emulsion droplets after dilution and check the droplet size in emulsions stabilized by S_D64. As shown in Figure 2, although emulsion droplets with a broad distribution of size were formed, one could still clearly observe a decrease of average droplet diameter from ca. 50 to ca. 15 μm, when the concentration of the star surfactant was increased from 0.01 to 0.1 wt %, since a concentration of only 0.01 wt % of the star polymers was not sufficient to stabilize the larger surface area of smaller droplets. The droplet size did not change significantly when the star polymer concentration was further increased. This could be caused by the emulsion generation method; the vortex mixer

Figure 2. Micrographs at 40× magnification of diluted oil-in-water emulsions formed using the PEO star polymer S_D64 as stabilizer: (a–c) xylene in water (star polymer amount: (a) 0.01, (b) 0.1, and (c) 0.5 wt %); (d–f) cyclohexane in water (star polymer amount: (c) 0.01, (d) 0.1, and (e) 0.5 wt %). Scale bar 50 μm.

could not provide sufficient power to break dispersed droplets to an even smaller size.

Stable cyclohexane-in-water emulsions were also prepared using PEO–poly(DVB) S_D64 star polymers as stabilizers (Figure 1). The weight ratio of cyclohexane and water was also set at 1/1. Similar to the xylene-in-water emulsion, one could use a low concentration of the PEO star polymers, 0.01 wt %, to generate a stable emulsion. However, emulsion droplets with much larger size were formed when cyclohexane was used as the dispersed phase with the same amount of star polymer stabilizers (Figure 2) compared to the xylene case. Even when the star concentration was set at 0.5 wt %, the majority of the emulsion droplets have a diameter ca. 100 μm, which could be clearly observed in the optical microscope images. This can be attributed to the different solubility of the PEO star polymers in xylene and cyclohexane. The PEO star polymers are soluble in both xylene and water; thus, they could be efficiently anchored at the xylene/water interface, resulting in the formation of small emulsion droplets, while the PEO star polymers may adopt conformations at the cyclohexane/water interface that are less favorable for stabilizing emulsion droplets against coalescence and are thereby unable to stabilize small droplets with high surface area. With required HLB values for emulsification of 14 and 15, respectively, xylene and cyclohexane are nearly indistinguishable in the HLB convention.[38] These differences in emulsion performance for the same star polymer for these two oils demonstrates the importance of polymer solubility in the oil in the case of polymeric emulsifiers.

PEO–PBA–Poly(DVB) Miktoarm Star Polymers as Stabilizers for Water-in-Xylene Emulsions. The PEO homoarm star polymers are amphiphilic, having hydrophilic PEO arms and a cross-linked hydrophobic poly(DVB) core. However, the hydrophobic DVB core is buried inside the shell of the star polymers and may not be easily accessible to the environment due to the "protection" provided by the multiplicity of PEO arms. Therefore, the changes in star compositions or DVB core fraction, detailed in Table 1, of the PEO homoarm star polymers had relatively modest affects on the emulsifying performance of these polymers.

In order to more efficiently change the amphiphilicity of the star polymers, or their affinity to different phases of an emulsion system, a series of PEO–PBA–poly(DVB) miktoarm star polymers were prepared via the "arm-first" method[22] by using a mixture of PEO MI and a certain percentage of hydrophobic PBA MI as arm precursors. The introduction of

Table 2. PEO−PBA−Poly(DVB) Miktoarm Star Polymers as Stabilizers for Water-in-Xylene Emulsion

star polymer[a]	$[PEO]_0/[PBA]_0$[b]	DVB core (wt %)	$M_{w,star,RI}$[c]	$M_{w,star,MALLS}$[d]	$M_{wMALLS}/M_{w\ RI}$	N_{arm}[e]	HLB	surfactant amount[f] (wt %)	emulsion phase fraction[g] (%)	dispersed phase fraction[h] (%)
MS$_{PBA50}$[a]	5/5	22	8.87×10^4	3.2×10^5	3.61	39	6	0.5 or 0.25	67	69
								0.1, 0.05,0.01 or 0.005	58	80
MS$_{PBA30}$[a]	7/3	26	9.35×10^4	3.9×10^5	4.2	49	9	0.5	60	77
								0.25, 0.1, 0.05, or 0.01	55	84
								0.005	51	91
MS$_{PBA10}$[a]	9/1	30	9.01×10^4	4.2×10^5	4.67	54	12	0.5, 0.25, 0.1, or 0.05	58	80
								0.01 or 0.005	52	89

[a]MS$_{PBAX}$; X represents the initial molar fraction of PBA MI in arm precursors. [b]The initial molar ratio of PEO and PBA arm precursors for star polymer preparation, PEO MI, M_n = 5200, PBA MI, M_n = 7800, and M_w/M_n = 1.10. [c]Weight-average molecular weight of star polymers determined by THF GPC with RI detector, calibration with linear polystyrene as standard. [d]Weight-average molecular weight of star polymers determined by THF GPC with MALLS detector. [e]Average arm number per star polymer calculated according to the equations shown in a previous paper.[22] [f]Surfactant amount was calculated based on the total weight of water and xylene used for the emulsion formation. [g]Volume fraction of emulsion phase as compared to total volume of emulsion plus neat xylene phase. [h]Volume fraction of the dispersed phase in the emulsion phase itself.

more accessible hydrophobic components, the PBA arms, to the "surface" of star polymers would reduce the solubility of the formed star polymers in water, thereby affecting their adsorption behaviors and performance for emulsification. When PEO−PBA−poly(DVB) miktoarm star polymers were used as stabilizers for a water/xylene emulsion, a water-in-oil emulsion was expected to be formed for a sufficient degree of PBA incorporation into the star polymer due to the increased affinity of these star stabilizers to the oil phase and decreased affinity for the aqueous phase.

Three PEO−PBA−poly(DVB) miktoarm star polymers with different ratios of PEO arms to PBA arms were synthesized and evaluated as stabilizers for a water-in-xylene emulsion. It had been previously demonstrated by ^{1}H NMR and gradient polymer elution chromatography (GPEC) analysis that composition of the miktoarm stars prepared by ATRP using the "arm-first" method with PBA and PEO macroinitiators corresponds to the initial molar ratios of macroinitiators.[22] The compositions and molecular weight/arm number of the three PEO−PBA−poly(DVB) star polymers are summarized in Table 2. They have HLB ranging from 6 to 12, depending on the fraction of PEO arms. An HLB of 6 falls near the upper limit where conventional surfactants are expected to be able to stabilize water-in-oil emulsions. HLB of 8−16 is the range normally associated with the capability to emulsify oil-in-water, rather than water-in-oil, emulsions. A turbid and milky solution was obtained when these star polymers were dispersed in water, and as expected, the solubility of the miktoarm star polymers in water was progressively improved with an increase in the fraction of PEO in the arms.

Water-in-xylene emulsions, with the weight ratio of xylene and water set at 1/1, were successfully prepared using all three of the PEO−PBA−poly(DVB) miktoarm star polymers at concentrations of as low as 0.005 wt % vs total weight of water and xylene, corresponding to a concentration of ca. 1.4×10^{-4} mM star polymers in the system. A neat xylene layer could be observed on top of the emulsion (Figure 3). The formed emulsions were stable for more than 3 months. Adjusting the ratio between the PEO and PBA arms did not affect the generated emulsion type or the stability, but the volume fraction of emulsion phase varied slightly with different star polymers. When PEO−PBA−poly(DVB) miktoarm star polymers containing 50% PEO arms were employed as the
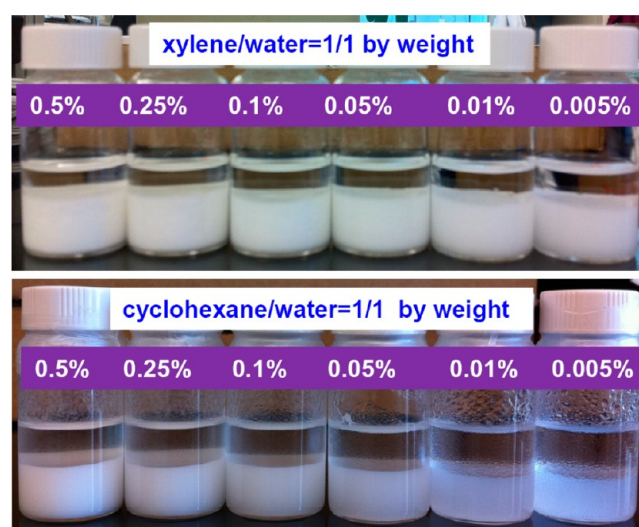

Figure 3. Images of water in xylene emulsions stabilized by different amount of PEO−PBA−poly(DVB) miktoarm star polymers (MS$_{PBA50}$).

stabilizer, sample MS$_{PBA50}$ in Table 2, ca. 58% emulsion phase was formed with 0.005 wt % star polymer surfactant. Increasing the amount of the star polymer surfactant to 0.25 wt % led to an increase in the emulsion phase fraction to ca. 67%. While in the case of using star polymers containing 70% PEO arms, sample MS$_{PBA30}$ in Table 2, 55 vol % emulsion phase was found when using 0.005−0.25 wt % star polymers stabilizer. This may be caused by the improved solubility of the star polymers in water. The different packing/adsorption of miktoarm star polymers at the interface would affect the formation of the emulsion. Further increase of PEO percentage to 90%, sample MS$_{PBA10}$, did not significantly affect the emulsification performance, and only a slightly lower fraction of emulsion phase was obtained with the same amount of star stabilizers, as compared to the emulsions formed by using MS$_{PBA50}$ or MS$_{PBA30}$ as stabilizers. This observation could be attributed to the migration of some star polymers containing a large percentage of PEO arms to the aqueous phase, resulting in a less efficient stabilization. Moreover, the fraction of xylene and water in the formed emulsion phase, using 0.005 wt % of MS$_{PBA50}$ star polymer as surfactant, was calculated to be ca. 20 vol % of

xylene and 80 vol % of water, respectively. The formation of stable water-in-oil emulsions by all three of the miktoarm star polymers, even though only one of them had an HLB value close to the range normally associated with W/O emulsions, is a further indication that the conventional HLB scale originally developed for less complex surfactant structures is insufficient to capture the effects of varying the structure and composition of star polymer emulsifiers.

When the star polymers were originally dispersed in xylene before emulsion generation, water-in-oil emulsions with similar fraction of emulsion phase were obtained, as when star polymers were originally dispersed in the aqueous phase. It appeared that the PEO−PBA−poly(DVB) miktoarm polymers were sufficiently mobile, and they could easily migrate to the xylene/water interfaces and further stabilize the formed dispersed water droplets even when they were originally dispersed in the aqueous phase that would become the discontinuous phase of the emulsion.

Cyclohexane was also used as continuous phase for the generation of water-in-oil emulsions with PEO−PBA−poly-(DVB) miktoarm star polymers as stabilizers. However, in this case, a much higher concentration of star polymers, 0.05 wt %, was needed for the generation of a stable emulsion. As was the case with PEO homoarm stars, the insolubility of PEO and PBA in cyclohexane affected the star adsorption to the oil/water interface that was less favorable for emulsion stabilization. The emulsion droplets observed in the optical microscope further support this conclusion. Although stable emulsions were formed when a higher concentration of the star copolymer, >0.05 wt %, was used, the generated emulsion droplets are large, up to 1 mm, even with 0.5 wt % star polymer, due to the relatively less effective interface stabilization by star surfactants with a collapsed morphology.

The droplet sizes in the diluted water-in-xylene emulsions were followed using an optical microscope. Similar to the xylene-in-water emulsions formed with PEO homoarm star polymers as stabilizers, a decrease in the size of the droplets, from ca. 100 to ca. 10 μm, could be clearly observed when the star polymer concentration was increased from 0.005 to 0.1 wt % (Figure 4) due to the increasing inventory of star polymers
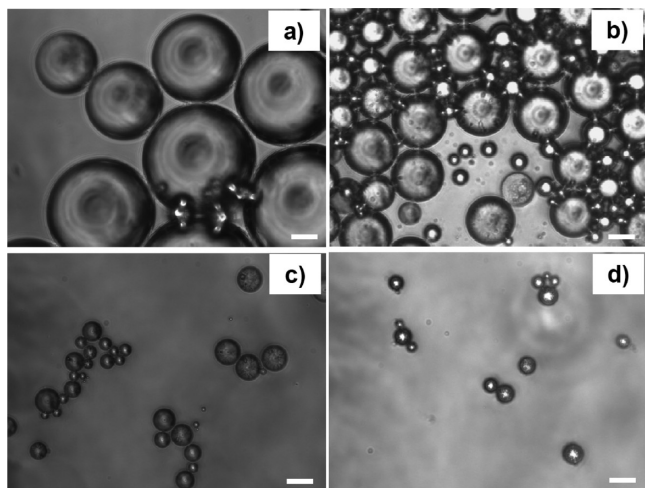
available to stabilize the larger surface area associated with smaller droplets. However, the droplet size did not change significantly when the star surfactant concentration was further increased from 0.1 to 0.5 wt %. A sample was then carefully taken from the neat xylene layer on top of the emulsion formed by using 0.5 wt % star polymers and analyzed by DLS. Star polymers with diameter ca. 10 nm could be found in the xylene solution, the pure miktoarm star polymer MS$_{PBA50}$ showed an average diameter of ca. 12 nm in xylene, while star polymers could rarely be detected on the top xylene layer in the emulsion formed using 0.005 wt % star polymers. It is possible that the water/oil interface was saturated by the star polymers, when larger amounts of star polymers were used for the emulsion generation using a vortex mixer; thus, some free star polymers could be detected in the continuous oil phase. As is known, one could tune the emulsion droplet size not only by changing star surfactant concentration but also by using different emulsion generation techniques. Thus, these free star polymers could be used for stabilization of even smaller emulsion droplets formed in a higher shear environment.

Thus, in a separate experiment, ultrasonication was used for the generation of emulsions containing smaller droplets, a Misonix sonicator S-4000 amplitude set at 70%, sonication for 30 s in ice/water bath. Similar to the cases of using a vortex mixer for emulsion generation, phase separation occurred with a neat xylene layer appearing on top of emulsions a couple of hours after sonication. However, smaller emulsion droplets were indeed obtained by using ultrasonication. With 0.5 wt % of star polymer, sample MS$_{PBA50}$, the formed emulsion droplets showed an average diameter of ca. 1.6 μm by volume distribution determined by DLS analysis, and this value increased to ca. 5.2 μm, when only 0.1 wt % of the star polymer was used as the surfactant. These emulsions were stable for more than 2 weeks. Meanwhile, as expected, if the star concentration was further decreased to 0.01 wt %, although smaller droplets were formed, with size ca. 20 μm after the sonication, the formed emulsion was not stable, and much larger droplets started to form after 1 day due to the limited amount of star polymers available to stabilize the smaller droplets.

Interfacial Tensions. Star polymers of both the PEO homoarm type (S$_D$64, S$_L$35, S$_L$30) and the PEO/PBA miktoarm type (MS$_{PBA50}$, MS$_{PBA30}$, MS$_{PBA10}$) demonstrated excellent interfacial tension lowering behavior at the xylene/water interface, as summarized in Table 3. This is consistent

Figure 4. Micrographs at 40× magnification of diluted water in xylene emulsion formed by using PEO−PBA−poly(DVB) miktoarm star polymers (MS$_{PBA50}$) as stabilizers, star polymer amount: (a) 0.005, (b) 0.01, (c) 0.1, and (d) 0.5 wt %. Scale bar 50 μm.

Table 3. Xylene/Water Interfacial Tensions (mN/m) for 0.01 and 0.1 wt % Star Polymer Solutions at 21 °C[a]

	S$_D$64	S$_L$35	S$_L$30	MS$_{PBA50}$	MS$_{PBA30}$	MS$_{PBA10}$
0.01 wt %	15.5	10.8	4.0	3.8	26.7	16.1
0.1 wt %	12.8	10.1	2.1	2.1	4.4	3.4

[a]Uncertainty is ±0.1 mN/m. The pure xylene/water interfacial tension is 36.6 mN/m.

with the interfacial tension lowering behavior of other nanoparticulate brush systems.[37] The most effective interfacial tension lowering PEO homoarm star polymer was S$_L$30, which decreased the xylene/water interfacial tension from the clean interface value of 36.6 mN/m to just 2.1 mN/m at a concentration of 0.1 wt %. This was a substantially lower interfacial tension than the values achieved by the other two PEO homoarm star polymers, all three of which had similar

HLB. S$_L$30 stands out as the least compact of the PEO homoarm star polymers. The greater exposure of the hydrophobic PDVB core in this structure may be responsible for the superior interfacial tension lowering performance. Nevertheless, S$_D$64 was the most efficient emulsifier of the three PEO homoarm stars. Interfacial tension lowering alone cannot predict emulsifying efficiency.

All three PEO−PBA miktoarm star polymers decreased the xylene/water interfacial tension to low values, 2.1−3.4 mN/m, at a 0.1 wt % concentration. The main distinction between the three was the ability of MS$_{PBA50}$ to also produce this level of interfacial tension lowering at the lower bulk concentration of 0.01 wt %. This was the least compact of the three PEO−PBA miktoarm star polymers. The correlation of more effective interfacial tension lowering with decreasing compactness mirrors the PEO homoarm results.

■ CONCLUSIONS

PEO-based star polymers, either PEO−poly(DVB) or PEO−PBA−poly(DVB) miktoarm star polymers, were prepared and utilized as stabilizers for generation of emulsions with long-term stability (3−6 months) at extremely low polymer concentration, <0.01 wt %, corresponding to submicromolar concentrations. The more hydrophilic PEO−poly(DVB) star copolymer favored the formation of xylene-in-water emulsions while the use of more hydrophobic PEO−PBA−poly(DVB) miktoarm star polymers as stabilizers resulted in the formation of water-in-xylene emulsions. The high surface activity of the star polymers was confirmed by their ability to produce extremely low interfacial tensions in dilute solutions. In addition, both cyclohexane-in-water (using PEO homoarm stars) and water-in-cyclohexane (using PEO−PVB miktoarm stars) emulsions were also successfully prepared using the PEO-based star polymer stabilizers. Emulsions with larger droplet size were formed in these cases where neither PEO nor PBA was soluble in the oil, unlike the situation with xylene where both PEO and PBA were soluble in the oil. Structural variations in the star polymers, especially the compactness of the structure, proved to correlate better with emulsifying tendencies than did the conventional HLB system. The successful generation of stable water-in-oil emulsions using low concentrations of star polymers offers the potential of using such PEO-based star polymers as stabilizers for diesel fuel emulsion application and high internal phase emulsions,[39] which are currently under investigation in our groups.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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