Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 46 (2005) 2433–2442

polymer

www.elsevier.com/locate/polymer

Synthesis, characterization and evaluation of amphiphilic star copolymeric emulsifiers based on methoxy hexa(ethylene glycol) methacrylate and benzyl methacrylate

Stella C. Hadjiyannakou, Aggeliki I. Triftaridou, Costas S. Patrickios*

Department of Chemistry, University of Cyprus, P.O. Box 20537, 1678 Nicosia, Cyprus

Received 21 April 2004; received in revised form 7 February 2005; accepted 8 February 2005

Abstract

Amphiphilic star copolymers were synthesized by sequential monomer and cross-linker additions using group transfer polymerization (GTP). Benzyl methacrylate (BzMA) and methoxy hexa(ethylene glycol) methacrylate (HEGMA) served as the hydrophobic and hydrophilic monomers, respectively, whereas the also hydrophobic ethylene glycol dimethacrylate (EGDMA) was used as the cross-linker. In total, twelve star copolymers were prepared, covering three different overall hydrophobic compositions, 39, 53 and 70% w/w, and four different architectures, AB star-block, BA star-block, heteroarm star and random star. The theoretical molecular weight of each arm was kept constant at 5000 g mol^{-1}. The molecular weights and molecular weight distributions of the linear precursors and of all the star copolymers were characterized by gel permeation chromatography (GPC) in tetrahydrofuran (THF), while their compositions were confirmed by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. Moreover, all the star copolymers were characterized by static light scattering (SLS) in THF to determine the absolute weight-average molecular weight, M_w, and the weight-average number of arms. After polymer characterization, xylene–water and diazinon (pesticide)–water emulsions were prepared using these star copolymers as stabilizers at 1% w/w copolymer concentration and at different overall organic phase/water ratios. The most important factor in determining the emulsion type was the star copolymer composition in hydrophobic units. The four most hydrophilic star copolymers (39% w/w hydrophobic composition) always formed o/w emulsions, while the four most hydrophobic star copolymers (70% w/w hydrophobic composition) always formed w/o emulsions. The type of the emulsion in the case of the star copolymers with the more balanced composition, 53% w/w hydrophobic units, also depended on the emulsion content in the organic solvent, similar to particulate-stabilized emulsions. Considering that the best o/w emulsifier is that star copolymer which can emulsify the largest quantity of organic phase in water resulting in low viscosity, o/w emulsions without excess oil or water phase, it appeared that the most hydrophilic random copolymer star is the optimal emulsifier. Moreover, this star copolymer presented the smallest droplet size in its emulsions. It is also noteworthy that the resulting emulsions almost never had high viscosity, a feature attributable to the compact nature of star polymers.

Keywords: Group transfer polymerization; Amphiphilic star copolymers; Emulsions

1. Introduction

Emulsion formation (or emulsification) is an industrially relevant process in which either oil is dispersed in water (oil-in-water emulsions, o/w) or water is dispersed in oil (water-in-oil emulsions, w/o) [1–3]. Emulsification necessitates the presence of a third component, the emulsifying agent or emulsifier, which is adsorbed at the liquid–liquid interface and reduces the oil–water interfacial tension. The emulsifier has traditionally been a low molecular weight (MW) surfactant. However, in recent years, amphiphilic polymeric stabilizers, such as linear block [4], graft [5], and star copolymers, have started to replace low MW surfactants because these copolymers are more effective stabilizers than the surfactants as manifested by the smaller amount of copolymer required for emulsification [6]. More recently, solid nano- and micro-particles also attract the attention for use as emulsifiers (Pickering-type emulsifiers) [7].

Linear diblock [8,9] and ABA triblock [9,10] copolymers have been tested in a variety of emulsification applications,

---

* Corresponding author. Tel.: +357 22 892768; fax: +357 22 892801.
E-mail address: costasp@ucy.ac.cy (C.S. Patrickios).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.02.008

with an increasing recent focus on use as stabilizers in emulsion polymerization [6,11–13]. Graft copolymers are often the choice in industrial applications [14–16]. To date, star copolymers have attracted much less attention, and there are only a very small number of studies on their use as emulsifiers. In some early investigations, Huynh-Ba-Gia and co-workers [17–20] prepared amphiphilic three-arm heteroarm star copolymers of polydiene and poly(ethylene oxide) (PEO) and used them for emulsion formation between water and a variety of organic solvents. Subsequently, Xie and Xia [21] showed that amphiphilic four-arm heteroarm star polystyrene-PEO (PS-PEO) copolymers, synthesized by anionic polymerization, were better benzene/water emulsifiers than their three-arm heteroarm star and linear diblock counterparts. Matyjaszewski and co-workers [6] employed atom transfer radical polymerization (ATRP) to prepare amphiphilic three-arm PS-poly(acrylic acid) (PS-PAA) star-block copolymers, which were evaluated as stabilizers in emulsion polymerization and were found to be as efficient as their linear counterparts. Kukula and colleagues [22] employed anionic polymerization to prepare amphiphilic heteroarm star copolymers with one hydrophobic PS and eight hydrophilic poly(sodium glutamate) arms. These star copolymers proved to be better emulsion polymerization stabilizers than their linear diblock counterparts at low stabilizer loadings.

We are interested in the preparation of stable o/w emulsions of liquid pesticides in water, stabilized by amphiphilic copolymers. To this end, we have used group transfer polymerization (GTP) [23–26] and prepared a series of linear amphiphilic diblock polymethacrylates, which we subsequently evaluated as xylene–water and diazinon (pesticide)–water emulsifiers [27]. Given the small number of studies on star copolymers as emulsifiers and the reported circumstantial superiority of star over linear copolymers, the present investigation aimed at the preparation by GTP of star copolymers based on non-ionic hydrophilic–non-ionic hydrophobic units and their evaluation for the emulsification of pesticides in water.

2. Experimental section

2.1. Synthesis

2.1.1. Materials

The GTP initiator 1-methoxy-1-trimethylsiloxy-2-methyl propene (MTS), the hydrophobic monomer benzyl methacrylate (BzMA), the hydrophobic cross-linker ethylene glycol dimethacrylate (EGDMA), the free radical inhibitor 2,2-diphenyl-1-picrylhydrazyl (DPPH), calcium hydride (CaH_2), potassium metal, tetrabutylammonium hydroxide, benzoic acid, and *p*-xylene were all purchased from Aldrich, Germany. Sodium metal was purchased from Fluka, and tetrahydrofuran (THF, both HPLC and AR grade) was purchased from Labscan, Ireland. Methoxy hexa(ethylene glycol) methacrylate (HEGMA), a nonionic hydrophilic monomer, was kindly donated by Laporte Performance Chemicals, UK. Diazinon (a pesticide of Syngenta) was provided by Premier Chemical Co. Ltd, Cyprus. Fig. 1 depicts the chemical structures and names of the two monomers, the cross-linker and the GTP initiator used for the synthesis of the star copolymers.

2.1.2. Methods

BzMA and EGDMA were passed twice through basic alumina columns to remove the polymerization inhibitor and protic impurities. Subsequently, BzMA and EGDMA were stirred over CaH_2 (to remove the last traces of moisture and protic impurities) for one hour in the presence of the free radical inhibitor DPPH, and were vacuum-distilled just prior to use. Due to the high viscosity of the neat monomer, a 50% v/v solution in (freshly distilled) THF of the HEGMA monomer [28] was used for the processing with basic alumina. The HEGMA monomer solution was also passed twice through basic alumina columns. The HEGMA solution was then stirred over CaH_2 (without DPPH) for one hour and was filtered through a 0.45 μm PTFE syringe filter directly into the polymerization flask. The MTS initiator was distilled just before use. The polymerization solvent, THF, was refluxed over a potassium/sodium alloy for 3 days and was freshly distilled prior to use. The polymerization catalyst, tetrabutylammonium bibenzoate (TBABB), was prepared from the reaction of tetrabutylammonium hydroxide with benzoic acid according to Dicker et al. [25] and was kept under vacuum until use.

2.1.3. Polymer synthesis

A typical polymerization procedure yielding the $HEGMA_{10}$-*b*-$BzMA_{10}$-*star* copolymer is detailed below. To a 100 mL round bottom flask containing a small amount (∼10 mg, 20 μmol) of TBABB were syringed 50 mL of freshly distilled THF and 0.6 mL MTS initiator (0.51 g, 2.93 mmol), in this order. 19.2 mL of the 50% v/v solution of HEGMA in THF (10.1 g of HEGMA, 28.8 mmol) was slowly added under stirring. The polymerization exotherm (25.4–29.6 °C) abated within 10 min, a sample for GPC was extracted, and 4.8 mL BzMA (4.99 g, 28.0 mmol) was added which produced an exotherm (28.2–33.3 °C). A sample for GPC of the linear HEGMA-BzMA diblock copolymer was extracted. Finally, 1.1 mL EGDMA (1.14 g, 5.83 mmol) was added which produced an exotherm (31.6–33.4 °C). A GPC sample of the final star copolymer was then extracted for analysis. All the star copolymers were recovered by precipitation in *n*-hexane and dried in a vacuum oven at room temperature for one week. For the synthesis of star copolymers with BzMA-HEGMA diblock copolymer arms (BA star-block) the same procedure was followed, with the only difference being that the order of monomer addition was reversed. For the synthesis of the star copolymer with random copolymer arms, the two monomers were added simultaneously, while for the preparation

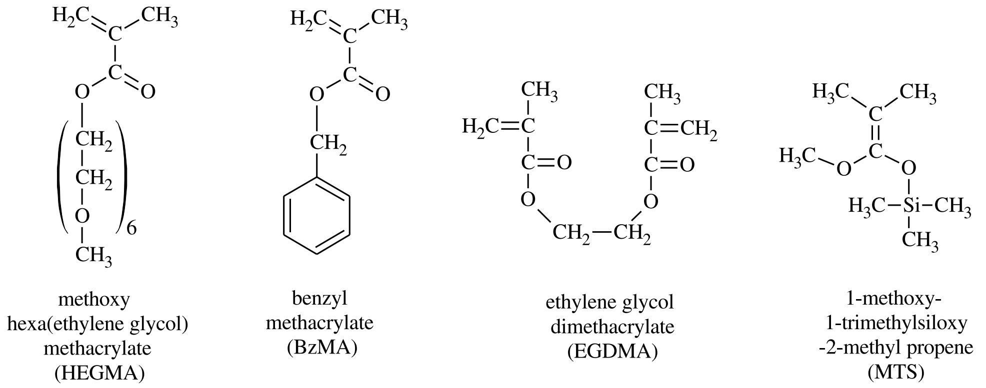

Fig. 1. Chemical structures and names of the two monomers, the cross-linker and the initiator.

of the heteroarm star copolymer the cross-linker was added between the additions of the first and second monomers. Fig. 2 shows the synthetic routes followed for the preparation of the four different star architectures.

2.2. Solubility tests

The solubilities in deionized water, *p*-xylene and diazinon of all star copolymers at a 1% w/w concentration were tested by attempting to dissolve 0.05 g of the star copolymer in 5.00 g of each of the three solvents.

2.3. Polymer characterization in organic solvents

2.3.1. Gel permeation chromatography (GPC)

Molecular weights (MWs) and molecular weight distributions (MWDs) were determined by gel permeation chromatography (GPC) on a Polymer Laboratories system equipped with a PL-LC1120 isocratic pump, an ERC-7515A refractive index detector and a PL Mixed ‘D’ column. The eluent was THF, pumped at 1 mL min^{-1}. The MW calibration was based on seven narrow MW (630, 2680, 4250, 13,000, 22,650, 128,000 and 260,000 g mol^{-1}) poly(methyl methacrylate), PMMA, standards also supplied by Polymer Laboratories.

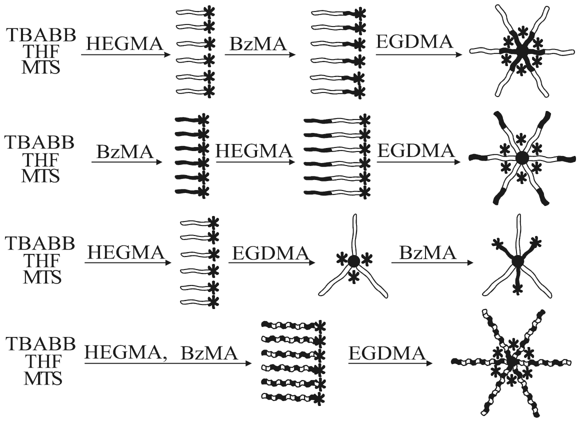

Fig. 2. Schematic representations of the synthetic routes followed for the preparation of the four different star architectures. The HEGMA units are drawn in white, whereas the BzMA units are painted black. The black circle in the center of each star copolymer indicates the hydrophobic EGDMA core, while the small star symbols denote the active sites of the polymerization.

2.3.2. Proton nuclear magnetic resonance (^1H NMR) spectroscopy

A 300 MHz AVANCE Bruker spectrometer equipped with an ultrashield magnet was used to acquire the proton NMR spectra of star copolymer solutions in $CDCl_3$ using TMS as a reference.

2.3.3. Static light scattering (SLS)

The absolute weight-average MW, M_w, of the star copolymers was determined by SLS on star copolymer solutions in THF using a BIMwA Brookhaven spectrophotometer equipped with a 30 mW red diode laser operating at 673 nm. Scattered intensities were measured at seven different angles, 35, 50, 75, 90, 105, 130 and 145°, and at six different star copolymer concentrations ranging from 8×10^{-5}–8×10^{-3} g mL^{-1}. Toluene (refractive index = 1.4740, Rayleigh ratio = 3.51×10^{-5}) was used as the calibration liquid. The weight-average number of arms of the star copolymers was estimated by dividing the star M_w by the M_w of the linear arms as determined by GPC.

2.4. Preparation of emulsions

After star copolymer characterization, xylene–water and diazinon–water emulsions were prepared using the star copolymers as emulsifiers. The star copolymer concentration was kept constant at 1% w/w of the total emulsion, while the oil content was varied at six values: 20, 40, 50, 60, 80 and 90% w/w of the total emulsion. Emulsions were prepared by first dissolving the proper amount of star copolymer in oil (xylene or diazinon) and then by adding dropwise the organic phase to deionized water under vigorous stirring. After the addition of all the amount of the organic phase, each emulsion was vigorously stirred for an additional 10 min. The samples were then allowed to stand for 48 h at 25 °C and observations were made regarding their appearance and phase separation. To obtain the type of the emulsion (o/w or w/o emulsion), two drops from each sample were diluted in 10 mL of solvent (xylene, diazinon or water). Emulsion drops dispersed uniformly in the solvent indicated that that solvent was the continuous phase of the emulsion [29]. When the emulsion drops precipitated in the form of coagulated spherical drops in that solvent, this implied that that solvent was not the continuous phase of the emulsion [29]. For example, if the emulsion was of the o/w type, the drops would be dispersed uniformly in water but they would coagulate in xylene (or diazinon). Finally, the size of the droplets of the xylene–water emulsions was measured using an Axiolab Zeiss optical microscope.

3. Results and discussion

3.1. Confirmation of polymer structure

Twelve star copolymers covering three different compositions and four different architectures were synthesized, and their schematic representations are given in Fig. 3. The color code was given in the legend of Fig. 2. All the star copolymers were characterized in terms of their MWs and compositions by GPC and ^{1}H NMR in THF and $CDCl_3$, respectively.

3.1.1. M_ns and PDIs

The number-average MWs, M_ns, and polydispersity indices (PDIs, M_w/M_n) of all the star copolymers and their linear precursors as determined by GPC are listed in Table 1. The same Table also shows the theoretical polymer formulas, with the subscripts indicating the theoretical degrees of polymerization (DPs), and the theoretical MWs, along with the star copolymer theoretical and ^{1}H NMR compositions. The MW analysis for the linear homopolymer and block-copolymer precursors to the stars are shown in the row above the corresponding star copolymer. Due to the calibration based on the linear PMMA MW standards, the M_ns determined for both the linear and the star polymers represent only apparent values. The apparent M_ns of the star copolymers were several times higher than those of their linear precursors and ranged between 50,000 and 120,000 g mol^{-1}. However, as will be shown below in the SLS section, these apparent star M_ns substantially underestimate the true polymer MWs due to the more compact nature of the star copolymers than that of the linear PMMA MW standards. The PDIs of the star copolymers were always lower than 1.3 and those of the linear polymers lower than 1.4.

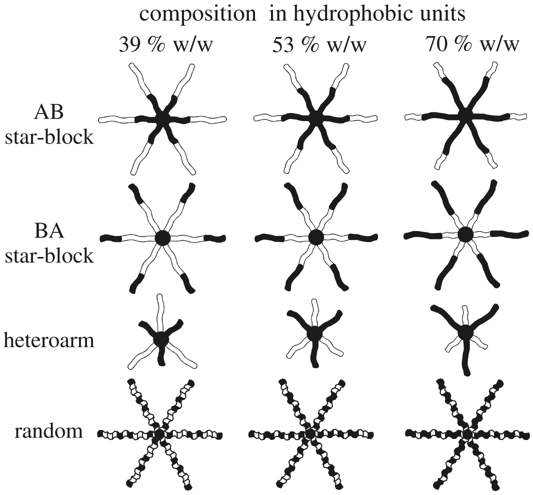

Fig. 3. Schematic representation of the twelve star copolymers prepared and studied in this investigation. The color code is the same as that in Fig. 2.

3.1.2. Composition

Fig. 4 shows the ^{1}H NMR spectrum of HEGMA$_{10}$-*star*-BzMA$_{10}$ in $CDCl_3$. The signals from protons e and f of the monomer repeat units of HEGMA and BzMA, respectively, were chosen to calculate the copolymer composition. The results of these calculations are also presented in Table 1. The star copolymer % w/w composition in BzMA calculated from ^{1}H NMR is in excellent agreement with that expected theoretically from the comonomer feed ratio during synthesis. Thus, for each of the four different star copolymer architectures, there were three star copolymers with w/w compositions in BzMA of 33, 50 and 67%. These compositions are expressed in terms of mass of BzMA units divided by the total mass of the two comonomer units, BzMA plus HEGMA. We must recognize, however, that BzMA was not the only hydrophobic component present in these star copolymers. The EGDMA core and the fragment from the MTS initiator in the star copolymers are also hydrophobic. By correcting the composition calculation to take into account all the types of hydrophobic units, the three overall hydrophobic compositions are modified to 39, 53, 70% w/w. These modified compositions are more appropriate for the interpretation of the emulsification data, and are the ones reported in section 3.3.

3.1.3. M_ws and number of arms

The results are presented in Table 2. The M_ws of the star copolymers obtained by SLS in THF ranged from 130,000 to 720,000 g mol^{-1}, approximately 2–13 times higher than the corresponding M_n values obtained by GPC in THF, as expected. The number of arms of each star copolymer was estimated by dividing its M_w obtained from SLS by the corresponding M_w of the linear copolymer precursor obtained by GPC, and taking into account the weight of the EGDMA cross-linker in the star copolymer. The number of arms of the star copolymers ranged between 20 and 82, in agreement with the number of arms observed in similar star polymers also synthesized by GTP [30,31].

Table 1
Molecular weight and composition analysis of the HEGMA-BzMA star copolymers

No.	Polymer formula	Theor. MW[a]	GPC Results		% w/w BzMA	
			M_n	M_w/M_n	Theor.	^{1}H NMR
1	HEGMA$_5$	1850	3500	1.19	–	–
	HEGMA$_5$-*b*-BzMA$_{20}$	5370	8600	1.24	–	–
	HEGMA$_5$-*b*-BzMA$_{20}$-*star*	–	116,000	1.19	67	67
2	HEGMA$_{10}$	3600	6600	1.19	–	–
	HEGMA$_{10}$-*b*-BzMA$_{10}$	5360	9000	1.23	–	–
	HEGMA$_{10}$-*b*-BzMA$_{10}$-*star*	–	81,500	1.16	33	32
3	HEGMA$_8$	2900	4600	1.20	–	–
	HEGMA$_8$-*b*-BzMA$_{15}$	5540	9000	1.24	–	–
	HEGMA$_8$-*b*-BzMA$_{15}$-*star*	–	89,000	1.19	50	48
4	BzMA$_{10}$	1860	3000	1.18	–	
	BzMA$_{10}$-*b*-HEGMA$_{10}$	5360	14,400	1.09	–	
	BzMA$_{10}$-*b*-HEGMA$_{10}$-*star*	–	67,000	1.11	33	34
5	BzMA$_{15}$	2740	2800	1.25	–	
	BzMA$_{15}$-*b*-HEGMA$_8$	5540	12,300	1.06	–	
	BzMA$_{15}$-*b*-HEGMA$_8$-*star*	–	61,300	1.12	50	52
6	BzMA$_{20}$	3620	3600	1.24	–	
	BzMA$_{20}$-*b*-HEGMA$_5$	5370	12,400	1.02	–	
	BzMA$_{20}$-*b*-HEGMA$_5$-*star*	–	65,000	1.14	67	69
7	HEGMA$_{10}$	3600	5300	1.24	–	
	HEGMA$_{10}$-*star*	–	32,000	1.16	–	
	HEGMA$_{10}$-*star*-BzMA$_{10}$	–	53,000	1.15	33	32
8	HEGMA$_8$	2900	3700	1.22	–	
	HEGMA$_8$-*star*	–	24,500	1.21	–	
	HEGMA$_8$-*star*-BzMA$_{15}$	–	55,000	1.17	50	49
9	HEGMA$_5$	1850	2900	1.21	–	
	HEGMA$_5$-*star*	–	20,000	1.28	–	
	HEGMA$_5$-*star*-BzMA$_{20}$	–	68,000	1.23	67	67
10	HEGMA$_{10}$-*co*-BzMA$_{10}$	5360	6000	1.37	–	
	HEGMA$_{10}$-*co*-BzMA$_{10}$-*star*	–	53,500	1.15	33	34
11	HEGMA$_8$-*co*-BzMA$_{15}$	5540	6200	1.32	–	
	HEGMA$_8$-*co*-BzMA$_{15}$-*star*	–	67,100	1.17	50	51
12	HEGMA$_5$-*co*-BzMA$_{20}$	5370	5400	1.25	–	
	HEGMA$_5$-*co*-BzMA$_{20}$-*star*	–	60,000	1.18	67	67

[a] Contribution from initiator fragment of 100 g mol^{-1} included.

3.2. Solubilities

All the star copolymers were soluble in *p*-xylene and diazinon, while none of them dissolved in water. The water-insolubility of the star copolymers is in marked contrast with the water-solubility of their linear counterparts (similar arm MWs and composition) investigated recently by our group [27]. In particular, the most hydrophilic linear

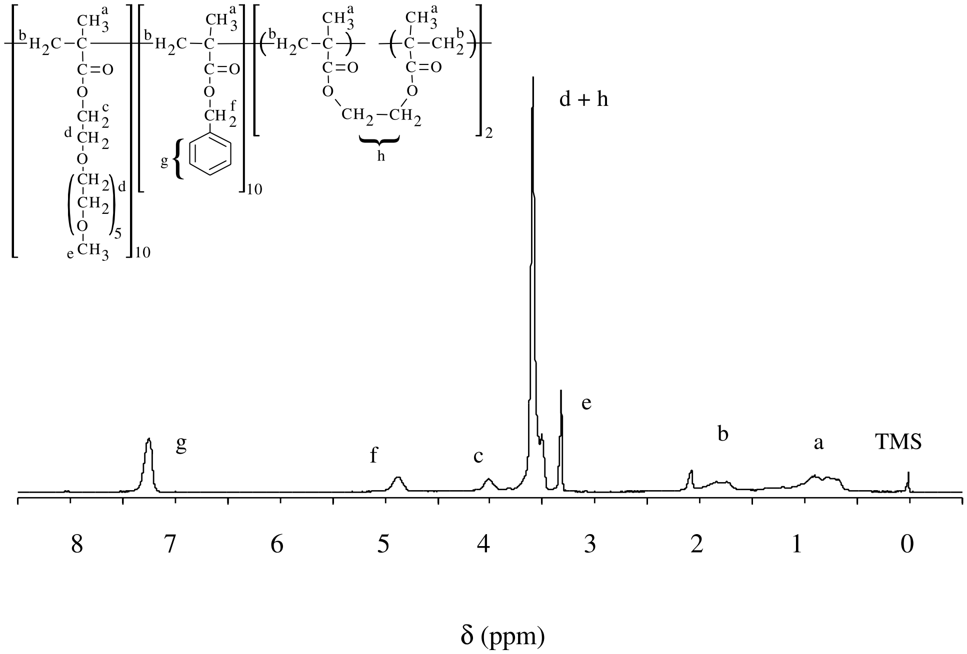

Fig. 4. ^{1}H NMR spectrum of the heteroarm star copolymer HEGMA$_{10}$-*star*-BzMA$_{10}$ in CDCl$_3$.

HEGMA-BzMA diblocks (33% w/w BzMA) readily dissolved in water, while the more hydrophobic linear HEGMA-BzMA diblocks with 50 and 67% w/w BzMA dissolved in water after intense mechanical stirring or ultrasonication, respectively. This difference can be attributed to the higher MWs and slightly greater hydrophobic composition (39, 53 and 70%) of the star copolymers compared to those of their linear counterparts.

3.3. Emulsion phase diagrams for the HEGMA-BzMA star copolymers

The twelve HEGMA-BzMA star copolymers were used to produce xylene–water and diazinon–water emulsions at different % w/w of the organic phase. The results for the xylene–water emulsions are shown in Fig. 5, whereas those for the diazinon–water emulsions in Fig. 6. One particular characteristic of these star copolymers was that the resulting emulsions were not always of the o/w type as was the case with the emulsions prepared using the linear diblock copolymeric emulsifiers prepared and studied recently in our laboratory [27]. As with the water-solubilities discussed above, this difference might also be due to the greater hydrophobicities and the higher MWs of the star copolymers compared to those of the linear diblock copolymers. Polymer surfactant hydrophobicity is known to be a crucial characteristic for the resulting type of emulsions. For example, linear amphiphilic copolymers of poly(sodium acrylate) grafted with dodecylamine must have a minimum composition in hydrophobic dodecyl units of at least 75% w/w to stabilize a w/o water–dodecane emulsion [32,33].

Fig. 5(a)–(c) present the phase diagrams for the xylene–water emulsions as a function of the % w/w xylene content in the formulation and the four different architectures for three different overall hydrophobic compositions of the star copolymers: (a) 39% w/w, (b) 53% w/w and (c) 70% w/w.

Table 2
Calculation of the M_w and the weight-average number of arms of the star copolymers

No.	Polymer formula	Arm M_w by GPC	Star M_w by SLS	Number of arms
1	HEGMA$_{10}$-*b*-BzMA$_{10}$-*star*	11,200	544,000	45
2	HEGMA$_8$-*b*-BzMA$_{15}$-*star*	11,000	670,000	58
3	HEGMA$_5$-*b*-BzMA$_{20}$-*star*	10,700	719,000	62
4	BzMA$_{10}$-*b*-HEGMA$_{10}$-*star*	11,800	302,000	24
5	BzMA$_{15}$-*b*-HEGMA$_8$-*star*	13,100	280,000	20
6	BzMA$_{20}$-*b*-HEGMA$_5$-*star*	12,700	468,000	34
7	HEGMA$_{10}$-*star*-BzMA$_{10}$	6500	181,000	38
8	HEGMA$_8$-*star*-BzMA$_{15}$	4500	131,000	30
9	HEGMA$_5$-*star*-BzMA$_{20}$	3500	363,000	67
10	HEGMA$_{10}$-*co*-BzMA$_{10}$-*star*	8100	716,000	82
11	HEGMA$_8$-*co*-BzMA$_{15}$-*star*	8200	231,000	27
12	HEGMA$_5$-*co*-BzMA$_{20}$-*star*	6800	390,000	54

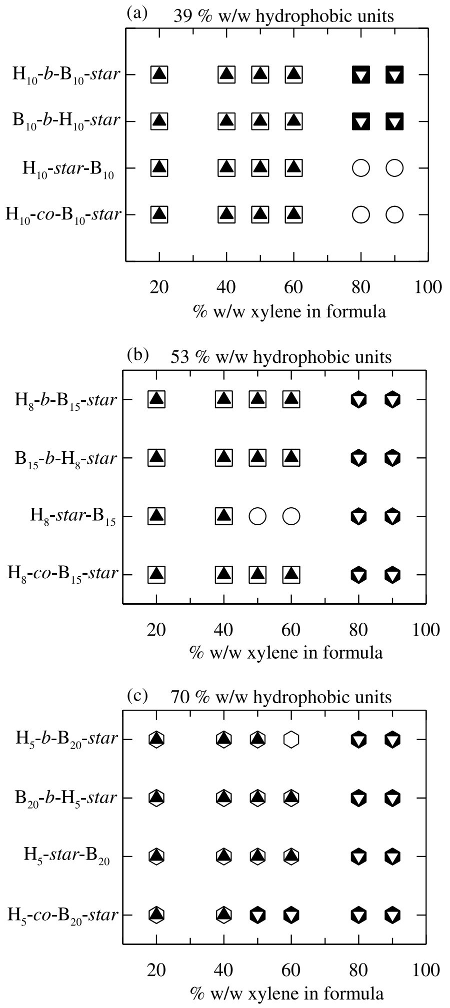

Fig. 5. Phase diagrams for the emulsions as a function of the % w/w xylene content in the total formulation and the four different architectures of the star copolymers for three different compositions in hydrophobic (BzMA plus EGDMA plus MTS) units: (a) 39% w/w, (b) 53% w/w and (c) 70% w/w. Symbols used for o/w emulsions are as follows. Open circles: stable, low-viscosity o/w emulsions without excess organic or aqueous phase; closed circles: stable, high-viscosity (gels) o/w emulsions without excess organic or aqueous phase; closed triangles within open squares: o/w emulsions co-existing with excess aqueous phase; open inverted triangles within closed squares: o/w emulsions co-existing with excess organic phase. Symbols used for w/o emulsions are as follows. Open hexagons: stable, low-viscosity w/o emulsions without excess aqueous or organic phase; closed hexagons: stable, high-viscosity (gels) w/o emulsions without excess aqueous or organic phase; closed triangles within open hexagons: w/o emulsions co-existing with excess aqueous phase; open inverted triangles within closed hexagons: w/o emulsions co-existing with excess organic phase.

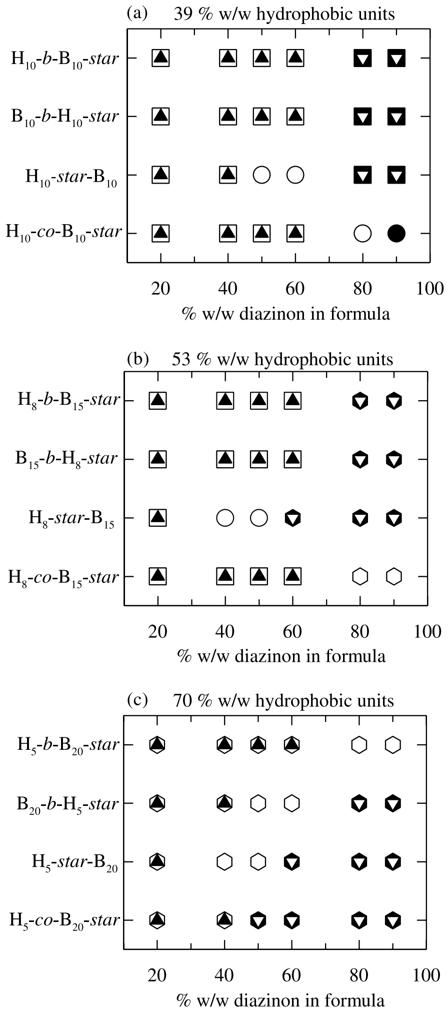

Fig. 6. Phase diagrams for the emulsions as a function of the % w/w diazinon content in the total formulation and the four different architectures of the star copolymers for three different compositions in hydrophobic (BzMA plus EGDMA plus MTS) units: (a) 39% w/w, (b) 53% w/w and (c) 70% w/w. The symbols used are the same as those in Fig. 5.

The main features of the phase diagram presented in Fig. 5(a) (based on star copolymers with 39% w/w hydrophobic composition) were the following: at values between 1/4 and 3/2 w/w of the xylene/water ratio, only o/w emulsions coexisting with excess water phase in the bottom were observed. The depth of the top emulsion phase (cream layer) was dependent on the weight fraction of the oil in the emulsion. In particular, as the weight fraction of xylene increased, the height of the cream layer also increased. For xylene/water mass ratios of 4/1 and 9/1, the cream layer in the emulsions of two star copolymers expanded to occupy the whole height of the system. The heteroarm star copolymer and the star copolymer comprising random copolymer arms were the two star copolymers, which provided emulsions without excess oil or aqueous phase. The other two star copolymers, both composed of block copolymer arms, gave two-phase systems with an o/w emulsion in the bottom and excess oil on the top. Thus, two out of the four star copolymers gave low viscosity o/w emulsions without excess organic or aqueous phase when the xylene/water ratios were 4/1 and 9/1 w/w.

The emulsion phase behavior of the star copolymers with 53% w/w overall hydrophobic composition is displayed in Fig. 5(b). With the exception of the heteroarm star copolymer, all other star copolymers gave o/w emulsions coexisting with excess water phase in the bottom at values between 1/4 and 3/2 w/w of the xylene/water ratio. The depth of the top emulsion phase was again dependent on the weight fraction of the oil in the emulsion. As the weight fraction of the xylene increased, the height of the cream layer also increased. The heteroarm star gave low-viscosity o/w emulsions without excess organic or aqueous phase when the % w/w content of the formula in xylene was 50 and 60%, while the star copolymer in Fig. 5(a) with the same architecture but a lower composition in hydrophobic units gave low-viscosity o/w emulsions without excess organic or aqueous phase at higher values of the xylene/water ratio (4/1 and 9/1 w/w). At even higher values of the xylene/water ratio (4/1 and 9/1 w/w), all star copolymers with 53% w/w hydrophobic composition gave two-phase systems with emulsions of the w/o type in the bottom and excess oil on the top. The existence of emulsions coexisting with excess oil and the fact that they formed reverse emulsions denoted the inability of these star copolymers to emulsify in water this large amount of xylene. The phase inversion observed in the emulsions stabilized with the star copolymers of this balanced composition (53% w/w hydrophobic units) when the oil/water ratio changes is similar to particulate-stabilized emulsions which can be inverted from w/o to o/w simply by increasing the water/oil ratio [7]. This similarity can be understood by considering the compact nature of both star polymers (especially when the number of arms is large, between 20 and 80, as in this case) and solid particles, and their similar size ∼10–25 nm.

Fig. 5(c) shows the phase behavior of emulsions stabilized by star copolymers with overall hydrophobic composition of 70% w/w. All emulsions appearing in Fig. 5(c) are of the w/o type. For the values 1/4 and 2/3 w/w of the xylene/water ratio, all the star copolymers gave w/o emulsions coexisting with excess water phase in the bottom. At 1/1 w/w, three out of the four star copolymers gave w/o emulsions coexisting with excess water phase in the bottom, while the fourth gave w/o emulsions coexisting with excess oil on the top. At higher values (3/2 w/w) there were three possibilities: either a low viscosity w/o emulsion without excess aqueous or organic phase, or w/o emulsions coexisting with excess water phase in the bottom, or a w/o emulsion co-existing with excess xylene on the top. Finally, for values 4/1 and 9/1 w/w of the xylene/water ratio, all the star copolymers gave w/o emulsions coexisting with excess oil on the top.

The size of the droplets of the xylene–water emulsions that provided emulsions without excess aqueous or organic phase was measured using optical microscopy and found to be in the range between 5 and 20 μm with unimodal size distributions. This size is smaller than the size of emulsion droplets stabilized by the linear HEGMA-BzMA diblock copolymers of our previous study, which ranged between 10 and 30 μm [27]. This indicates that the star copolymers are capable of stabilizing a greater surface area than their linear counterparts and are, therefore, more efficient emulsifiers. In particular, the following sizes were measured for the droplets of the emulsions stabilized by the star copolymers. The largest droplets, of 20 μm, were observed in the w/o emulsions stabilized by the most hydrophobic HEGMA-BzMA diblock star copolymer, HEGMA_5-*b*-BzMA_{20}-*star*. The two more hydrophilic heteroarm star copolymers, HEGMA_{10}-*star*-BzMA_{10} and HEGMA_8-*star*-BzMA_{15}, provided o/w emulsions with xylene droplets of 10 μm size (range from 1 to 15 μm). Finally, the most hydrophilic random copolymer star, HEGMA_{10}-*co*-BzMA_{10}-*star*, resulted in o/w emulsions with the smallest xylene droplets with a size of 5 μm (0.5–10 μm), suggesting that, from the star copolymers, this was the most effective emulsion stabilizer.

Fig. 6(a)–(c) present the phase diagrams for the diazinon–water emulsions as a function of the % w/w diazinon content in the formulation and the different architectures at three different % w/w compositions in hydrophobic units. The symbols used here are the same as those used in Fig. 5. The main features of the phase diagram in Fig. 6(a) were the following: at values between 1/4 and 3/2 w/w of the diazinon/water ratio, with the exception of the heteroarm star copolymer, all other star copolymers gave o/w emulsions coexisting with excess water, as was the case with the xylene/water emulsions in Fig. 5(a). However, the diazinon/water emulsions differed from the xylene/water at these organic phase/water ratios in that the excess water was in the top phase in the former type of emulsion due to the higher density of diazinon ($\rho = 1.117$ g mL^{-1} [34a]) than water compared to the lower density of xylene ($\rho = 0.861$ g mL^{-1} [34b]) than water. At higher values of the ratio (4/1 w/w) three out of the four star copolymers gave o/w emulsions coexisting with excess oil, while the random copolymer star was the exception, giving a low viscosity o/w emulsion without excess oil or aqueous phase. At the highest diazinon/water ratio, 9/1 w/w, the same three star copolymers gave again o/w emulsions co-existing with excess diazinon, whereas the random copolymer star provided in this case a high viscosity o/w emulsion without excess oil or aqueous phase. This was the only high viscosity emulsion observed with the star copolymers of this study. All other emulsions stabilized by the present star copolymers were of low viscosity, an expected characteristic given the compact nature of star polymers. It is noteworthy that linear HEGMA-BzMA diblock copolymers studied recently as emulsifiers in our research group [27] gave frequently high viscosity emulsions when the organic phase to water weight ratio was high. Thus, the architecture of star copolymers results in an important advantage for their use as emulsifiers over their linear counterparts: that of lower emulsion viscosity.

Similar to Fig. 5(b), the star copolymers in Fig. 6(b) gave mostly o/w emulsions coexisting with excess water for values from 1/4 through 3/2 w/w of the diazinon/water ratio. The only exceptions were the emulsions formed using the heteroarm star copolymer as stabilizer. This star copolymer gave stable, low viscosity o/w emulsions without excess oil or aqueous phase for values of the diazinon/water ratio of 2/3 and 1/1, and a w/o emulsion coexisting with excess diazinon for a 3/2 w/w diazinon/water ratio. At higher values of the diazinon/water ratio, 4/1 and 9/1 w/w, three out of the four star copolymers stabilized w/o emulsions coexisting with excess diazinon, while the random copolymer star was the exception, producing stable, low viscosity w/o emulsions without excess aqueous or oil phase. The emulsion inversion observed here at diazinon contents above 60% w/w was the same as that observed in Fig. 5(b) at xylene contents above 60% w/w using the same star copolymers (53% w/w hydrophobic composition) as stabilizers and this is reminiscent of the particulate-stabilized emulsions [7].

The main features of the phase diagram in Fig. 6(c) were the following: at 1/4 w/w of the diazinon/water ratio, only w/o emulsions coexisting with excess water phase were observed. At 2/3 w/w of the diazinon/water ratio, three out of the four star copolymers resulted again in w/o emulsions coexisting with excess water phase, while the heteroarm star copolymer gave a stable, low viscosity w/o emulsion without excess aqueous or oil phase. At values of the diazinon/water ratio of 1/1 and 3/2 w/w, three possibilities existed: either w/o emulsions coexisting with excess water phase, or stable, low viscosity w/o emulsions without excess aqueous or oil phase, or w/o emulsions coexisting with excess diazinon. Finally, at higher values (4/1 and 9/1 w/w) of the diazinon/water ratio, three out of the four star copolymers gave w/o emulsions coexisting with excess diazinon, except for HEGMA_5-*star*-BzMA_{20} that gave stable, low viscosity w/o emulsions without excess aqueous or organic phase.

Considering that the best o/w emulsifiers are those star copolymers that can emulsify the largest quantity of organic phase in water, resulting in low viscosity o/w emulsions without excess oil or aqueous phase, it appears from Figs. 5 and 6 that the random copolymer star with 39% w/w composition in hydrophobic units is the optimal emulsifier. Moreover, this star copolymer displays the smallest oil droplets in its emulsions.

4. Conclusions

The successful synthesis of twelve star copolymers of different architectures and compositions based on the nonionic, hydrophilic monomer methoxy hexa(ethylene glycol) methacrylate (HEGMA), the hydrophobic monomer benzyl methacrylate (BzMA) and the hydrophobic cross-linker ethylene glycol dimethacrylate (EGDMA) was presented. The apparent molecular weights and molecular weight distributions of the linear precursors were characterized by gel permeation chromatography (GPC) in tetrahydrofuran (THF), while their compositions were confirmed by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. Moreover, all the star copolymers were characterized using static light scattering (SLS) in THF, from which the absolute weight-average molecular weight, M_w, was calculated, and the weight-average number of arms was estimated. After polymer characterization, xylene–water and diazinon (pesticide)–water emulsions were prepared using the above star copolymers as stabilizers at 1% w/w polymer concentration and at different overall organic phase/water ratios. Unlike their linear counterparts, the emulsions of the star copolymers displayed low viscosities. Among the star copolymers, the most hydrophilic (bearing 39% w/w hydrophobic units) random star and heteroarm star copolymers exhibited the highest capacities in organic phase in their o/w emulsions, with the former being more efficient because it resulted in smaller droplet sizes. The more hydrophobic star copolymers (70% composition in hydrophobic units) proved to be appropriate for the stabilization of w/o emulsions. The star copolymers with the balanced composition (53% w/w hydrophobic units) displayed a particulate-emulsifier behavior in which the emulsion type was determined from the organic/water ratio.

Acknowledgements

We are grateful to Cyprus Research Promotion Foundation (PENEK2002, project ‘POLYFYTO’), Premier Chemical Co. Ltd, Cyprus, and D. J. Shukuroglou Ltd, Cyprus, for funding. The A. G. Leventis Foundation, Cyprus, is gratefully acknowledged for a generous donation, which enabled the purchase of the NMR spectrometer of the University of Cyprus. The University of Cyprus Research Committee is thanked for providing a grant (grant 2000–2003), which enabled the purchase of the static light scattering spectrophotometer. Finally, we thank Laporte Performance Chemicals, UK, for kindly donating to us the HEGMA monomer.

References

[1] Becher P. Emulsions: theory and practice. 2nd ed. New York: Krieger; 1977.

[2] Hunter RJ. Foundations of colloid science. vol. 2. Oxford: Oxford University Press; 1992. Chapter 16, pp. 908–947.

[3] Evans DF, Wennerström H. The colloidal domain: where physics, chemistry, biology and technology meet. 2nd ed. New York: Wiley-VCH; 1999. Chapter 11, pp. 539–597.

[4] Takahashi S, Saito T, Kasemura T. J Adhes 2003;79:287–309.

[5] Xie HQ, Xie D. Prog Polym Sci 1999;24:275–313.

[6] Burguière C, Pascual S, Bui C, Vairon JP, Charleux B, Davis K, et al. Macromolecules 2001;34:4439–50.

[7] Aveyard R, Binks BP, Clint JH. Adv Colloid Interface Sci 2003;100–102:503–46.

[8] Riess G, Nervo J, Rogez D. Polym Eng Sci 1977;17:634–8.

[9] Verdonck B, Goethals EJ, Du Prez FE. Macromol Chem Phys 2003;204:2090–8.

[10] Schmolka IR. J Am Oil Chemists’ Soc 1977;54:110–6.

[11] Riess G. Colloids Surf A 1999;153:99–110.

[12] Spinelli HJ. Prog Org Coat 1996;27:255–60.

[13] Gaillard N, Guyot A, Claverie J. J Polym Sci: Part A: Polym Chem 2003;41:684–98.

[14] Hasslin HW. US Patent No. 5 674 514 (Oct 7, 1997).

[15] Narayanan KS, Jon D, Prettypaul D. US Patent No. 6 033 681 (Mar 7, 2000).

[16] Kostka SJ, Pan R. US Patent No. 6 039 966 (Mar 21, 2000).

[17] Huynh-Ba-Gia, Jérôme R, Teyssié P. J Polym Sci: Part A: Polym Chem 1980;18:3483–98.

[18] Huynh-Ba-Gia, Jérôme R, Teyssié P. Colloid Polym Sci 1979;257: 1294–6.

[19] Huynh-Ba-Gia, Jérôme R, Teyssié P. J Polym Sci: Part B: Polym Phys 1980;18:2391–400.

[20] Huynh-Ba-Gia, Jérôme R, Teyssié P. J Appl Polym Sci 1981;26: 343–51.

[21] Xie H, Xia J. Makromol Chem 1987;188:2543–52.

[22] Kukula H, Schlaad H, Tauer K. Macromolecules 2002;35:2538–44.

[23] Webster OW, Hertler WR, Sogah DY, Farnham WB, RajanBabu TV. J Am Chem Soc 1983;105:5706–8.

[24] Sogah DY, Hertler WR, Webster OW, Cohen GM. Macromolecules 1987;20:1473–88.

[25] Dicker IB, Cohen GM, Farnham WB, Hertler WR, Laganis ED, Sogah DY. Macromolecules 1990;23:4034–41.

[26] Webster OW. J Polym Sci: Part A: Polym Chem 2000;38:2855–60.

[27] Hadjiyannakou SC, Vamvakaki M, Patrickios CS. Polymer 2004;45: 3681–92.

[28] Vamvakaki M, Armes SP, Billingham NC. Polymer 1999;40: 5161–71.

[29] Pons R, Solans C, Tadros ThF. Langmuir 1995;11:1966–71.

[30] Vamvakaki M, Hadjiyannakou SC, Loizidou E, Patrickios CS, Armes SP, Billingham NC. Chem Mater 2001;13:4738–44.

[31] Vamvakaki M, Patrickios CS. Chem Mater 2002;14:1630–8.

[32] Perrin P, Monfreux N, Dufour AL, Lafuma F. Colloid Polym Sci 1998;276:945–8.

[33] Perrin P, Monfreux N, Lafuma F. Colloid Polym Sci 1999;277:89–94.

[34] (a) Budavari S, O'Neil MJ, Smith A, editors. The Merck Index. 11th ed. Rahway, NJ: Merck Co., Inc.; 1989. p. 472.
(b) Budavari S, O'Neil MJ, Smith A, editors. The Merck Index. 11th ed. Rahway, NJ: Merck Co., Inc; 1989. p. 1590.