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

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Abstract

Linear, amphiphilic diblock copolymers based on the nonionic, hydrophilic monomer methoxy hexa(ethylene glycol) methacrylate (HEGMA) and the hydrophobic monomer benzyl methacrylate (BzMA) of different molecular weights and compositions were synthesized by group transfer polymerization. The molecular weights and comonomer compositions of these copolymers were characterized by gel permeation chromatography and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy, respectively. Dynamic light scattering on aqueous solutions of the diblock copolymers indicated that all the copolymers formed aggregates whose size increased with the % w/w BzMA composition and with the overall molecular weight of the linear chains. Turbidimetry on 1% w/w aqueous copolymer solutions was used to determine the cloud points, which were found to increase with the composition in hydrophilic units and the linear chain molecular weight. After polymer characterization, xylene/water and diazinon (pesticide)/water emulsions were prepared using the above polymers as stabilizers at 1% w/w polymer concentration and at different overall organic phase/water ratios. At an organic phase/water mass ratio of 4/1, the lower molecular weight (2500 and 5000 g mol^{-1}) diblock copolymers provided stable single-phase o/w emulsions, matching the behavior of commercially available hydrophilic Pluronics.

Keywords: Group transfer polymerization; Amphiphilic diblock copolymers; Emulsions

1. Introduction

Macroemulsions or, simply, emulsions, are thermodynamically unstable oil–water dispersions, in which either water or oil can be the continuous phase, called oil-in-water (o/w) and water-in-oil (w/o) emulsions, respectively [1,2a,3]. Emulsions are of great economic significance because of the frequent need in industry to enable the mixing of mutually incompatible liquids. The paints, pesticides, pharmaceuticals, cosmetics and food industries are examples of industries making extensive use of emulsions. Emulsions are usually prepared by the vigorous mixing of the two incompatible liquids in order to deform and break large droplets into smaller ones. The mixing is done in the presence of added low molecular weight (MW) surfactant, which is adsorbed at the liquid–liquid interface, thus conferring to the emulsion kinetic stability. Although the low MW surfactants have been historically the most frequently used type of stabilizer, in recent years, polymeric stabilizers, mainly graft, block and star copolymers, have started to replace low MW surfactants. These polymeric surfactants are more effective stabilizers than the conventional low MW ones as manifested by the smaller amount of polymer required for emulsification.

The availability of a number of ‘living’ polymerization methods enables the synthesis of new graft, block and star copolymers. Thus, it is possible to prepare a large number of such copolymers and evaluate their performance as polymeric emulsifiers in order to accurately map the dependence of emulsification potential on copolymer structure. Due to the great current interest in emulsion polymerization, there are several recent studies where such series of copolymers were prepared using anionic [4], group transfer (GTP) [5], atom transfer radical [6] and reversible addition fragmentation chain transfer [7] polymerization

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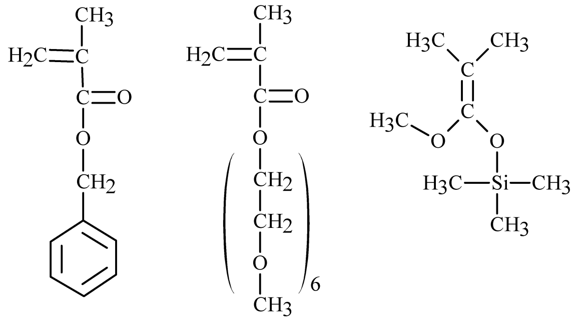
and evaluated as emulsion polymerization emulsifiers/stabilizers. There are also some older studies on the preparation of series of block copolymers by anionic polymerization and their evaluation as emulsifiers for the stabilization of water/organic solvent systems [8].

We are interested in the preparation of stable o/w emulsions of liquid pesticides in water, stabilized by block copolymers. To the best of our knowledge, there are no systematic studies on such a system, using a whole series of block copolymers. However, there are several patents reporting the occasional use of block copolymers for the stabilization of pesticide formulations [9–11]. The aim of this investigation was the synthesis of several nonionic amphiphilic diblock copolymers containing aromatic hydrophobic and ethylene oxide (EO) hydrophilic units, their characterization, and their evaluation as stabilizers in the preparation of pesticide emulsion formulations. The most common method to prepare such copolymers is sequential anionic polymerization [12]. In this work, polymer synthesis was accomplished by GTP [13–16], which, like anionic polymerization, secures a narrow size distribution of the polymers and their block structure, but it is also a simple and fast technique for the polymerization of methacrylates [16].

2. Experimental section

2.1. Materials and methods

Four Pluronics, which are commercially available linear, ABA, triblock copolymers of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), PEO-PPO-PEO, were kindly donated by BASF, Piscataway, NJ, USA, and provided through our colleague Professor P. Alexandridis of SUNY University at Buffalo, NY, USA. In particular, L92, P123, P105 and L64 Pluronic triblock copolymers were provided. Moreover, PPO (MW = 2500 g mol^{-1}) and PEO (MW = 2000, 3000, 6000 and 18,300 g mol^{-1}) homopolymers were purchased from Aldrich, Germany, and Polymer Laboratories, UK, respectively. The low MW surfactant hepta(ethylene glycol) monododecyl ether ($C_{12}E_7$) was purchased from Fluka, Germany. 1-Methoxy-1-trimethylsiloxy-2-methyl propene (MTS), benzyl methacrylate (BzMA, hydrophobic monomer), 2,2-diphenyl-1-picrylhydrazyl (DPPH), calcium hydride (CaH_2), potassium, tetrabutylammonium hydroxide, benzoic acid, and *p*-xylene were purchased from Aldrich. Sodium was purchased from Fluka, and tetrahydrofuran (THF, both HPLC and AR grade) was purchased from Labscan, Ireland. Methoxy hexa(ethylene glycol) methacrylate (HEGMA, nonionic hydrophilic monomer) was kindly donated by Laporte Performance Chemicals, UK. Fig. 1 depicts the chemical formulas and names of the two monomers, BzMA and HEGMA, and the GTP initiator, MTS. Diazinon (a pesticide of Syngenta) was provided by Premier Chemical Co. Ltd, Cyprus. Fig. 2 shows the chemical formulas and names of *p*-xylene and diazinon.


benzyl methacrylate (BzMA)

methoxy hexa(ethylene glycol) methacrylate (HEGMA)

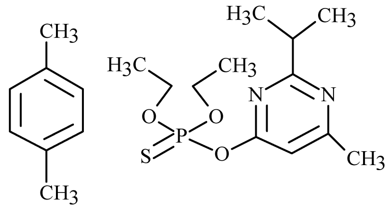
1-methoxy-1-trimethylsiloxy-2-methyl propene (MTS)

Fig. 1. Chemical formulas and names of the two monomers and the GTP initiator.

Both monomers were passed twice through basic alumina columns to remove the polymerization inhibitor and protic impurities. Due to the high viscosity of the neat monomer, a 50% v/v solution in freshly distilled THF of the HEGMA monomer [17] was used for the processing with basic alumina. Subsequently, BzMA was stirred over CaH_2 (to remove the last traces of moisture and protic impurities) for 3 h in the presence of the free radical inhibitor DPPH, and was vacuum-distilled just prior to use. The HEGMA solution was stirred over CaH_2 (without DPPH) 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. [15] and was kept under vacuum until use.

2.2. Polymer synthesis

A typical polymerization procedure yielding the HEGMA-BzMA diblock copolymer with a composition of 50% w/w BzMA and a nominal MW 5000 g mol^{-1}


p-xylene

diazinon

Fig. 2. Chemical formulas of xylene and the active pesticide ingredient diazinon.

(polymer nominal formula: HEGMA$_7$-*b*-BzMA$_{14}$) is detailed below. To a 100 ml round bottom flask containing a small amount (~10 mg) of TBABB (20 μmol) was syringed 40 ml of freshly distilled THF and 0.4 ml MTS initiator (0.34 g, 2.0 mmol), in this order. Subsequently, 9.5 ml of a 50% v/v solution of HEGMA in THF (4.99 g of neat HEGMA, 14 mmol) was slowly added under stirring. The polymerization exotherm (24–29 °C) abated within 10 min, and a sample for gel permeation chromatography (GPC) was extracted. Finally, 4.8 ml BzMA (4.99 g, 28 mmol) was added, which produced an exotherm (28.4–41 °C) and a sample for GPC of the final HEGMA-BzMA diblock copolymer was extracted. A similar procedure was followed in the homopolymer synthesis where, however, the addition of only one monomer was necessary. Both the copolymers and the homopolymers were recovered by precipitation in *n*-hexane and dried for three days in a vacuum oven at room temperature.

2.3. Solubility tests

The solubilities in deionized water, *p*-xylene and diazinon of all polymers and the low MW surfactant at a 1% w/w concentration were tested by attempting to dissolve 0.05 g of material in 5.00 g of each of the three solvents. In particular, all nine HEGMA-BzMA diblock copolymers, the HEGMA and BzMA homopolymers, the $C_{12}E_7$ low MW surfactant, the four Pluronics and the EO and PO homopolymers were tested.

2.4. Characterization in organic solvents

2.4.1. Gel permeation chromatography (GPC)

MWs and molecular weight distributions (MWDs) were determined by GPC on a Polymer Laboratories system equipped with a PL–LC1120 isocratic pump, an ERC–7515A refractive index detector and a PL Mixed 'E' column. The eluent was THF, pumped at 1 ml min^{-1}. The MW calibrations were based either on six narrow MW (630, 1400, 2400, 4250, 7600 and 13,000 g mol^{-1}) poly(methyl methacrylate), PMMA, standards (for the characterization of the methacrylate diblock copolymers and their homopolymer precursors) or on six narrow MW (400, 1500, 3000, 6000, 10,000 and 20,000 g mol^{-1}) PEO standards (for the characterization of the Pluronics), all supplied by Polymer Laboratories.

2.4.2. Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy

A 300 MHz AVANCE Bruker spectrometer equipped with an ultrashield magnet was used to acquire the proton NMR spectra of polymer solutions (both the methacrylates and the Pluronics) in $CDCl_3$ using TMS as a reference.

2.5. Characterization in water

All the experiments were performed at room temperature using polymer solutions prepared in deionized water obtained from a Milli-Q system (Millipore).

2.5.1. Dynamic light scattering

The hydrodynamic size of the copolymers in 1% w/w aqueous solutions was measured by dynamic light scattering using a 90Plus Brookhaven spectrophotometer with Particle Sizing Software Version 2.31 equipped with a 30 mW red diode laser operating at 673 nm. The measurements were performed at an angle of 90° and at room temperature. Five two-minute runs were performed for each polymer solution and the data were averaged. The data were processed using multimodal size distribution analysis based on non-negatively constrained least squares. Prior to the light scattering measurements the polymer solutions were filtered through 0.45 μm PTFE syringe filters three times to remove any existing dust particles, and were left at rest for about 1 h so that any air bubbles could escape.

2.5.2. Turbidimetry

A 3.0 ml aliquot of a 1% w/w diblock copolymer aqueous solution was transferred to a 10 mm path-length quartz cuvette containing a small stirring bar. The cuvette was placed in the sample compartment of a Lambda 10 Perkin–Elmer UV/vis Spectrometer and stirring was initiated using a miniature magnetic stirrer. A small temperature probe was immersed in the upper part of the solution, which was heated slowly from 25 to 90 °C. The optical density at 500 nm and the temperature were monitored using the software package TemLab (version 1.56) along with UVWinLab (version 2.7). The cloud point was taken as the temperature where the first large increase in optical density occurred.

2.5.3. Surface tension measurements

The surface tension of solutions of all copolymers within the concentration range from 10^{-8} to 10^{-4} mol l^{-1} was measured at room temperature using an instrument equipped with a du Noüy ring. At each concentration of a given sample four measurements of the surface tension were taken and the average was calculated.

2.6. Preparation of emulsions

After polymer characterization, xylene/water and diazinon/water emulsions were prepared using the diblock copolymers, the two HEGMA and BzMA homopolymers, the four Pluronics and the $C_{12}E_7$ surfactant as emulsifiers. The polymer 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 polymer in oil (xylene or diazinon) and then by adding dropwise the organic phase to deionized water under vigorous stirring (preliminary experiments had shown that this procedure maximizes the chances for the formation of o/w emulsions). After the addition of all the amount of 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. Two drops from each sample were then diluted in 10 ml of solvent (xylene, diazinon or water), so as to obtain the type of the emulsion (o/w or w/o emulsion). Emulsion drops dispersed uniformly in the solvent indicated that that solvent was the continuous phase of the emulsion. 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. 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. Polymer synthesis and confirmation of polymer structure

Nine diblock copolymers plus the two homopolymers, one of HEGMA and one of BzMA, were prepared, covering a wide spectrum of MWs and compositions. In particular, three different MWs, 2500, 5000 and 10,000 g mol^{-1}, and three different compositions in the hydrophobic component BzMA, 33, 50 and 67% w/w, were combined to give the nine diblock copolymers. A schematic representation of these diblock copolymers is given in Fig. 3. The polymerizations of this study were quantitative (yields close to 100%), allowed good MW control and resulted in products with satisfactorily narrow MWDs. The polymers were characterized in terms of their MWs and compositions by GPC and ^{1}H NMR in THF and CDCl$_3$, respectively.

3.1.1. MWs

The number-average MWs, M_ns, and polydispersities (M_w/M_n) of all polymers as determined by GPC are listed in Table 1. The same Table shows the theoretical polymer formulas, with the subscripts indicating the theoretical degrees of polymerization (DPs), and the theoretical MWs, along with the copolymer theoretical and ^{1}H NMR compositions. The M_ns are reasonably close to the theoretical MWs, although consistently higher, indicating some initiator de-activation and/or hydrodynamic differences between the present samples and the PMMA MW calibration standards. The polydispersities are higher at lower MWs but relatively low (<1.3) and decrease with increasing MW, as expected with polymers prepared by 'living' techniques such as GTP. The MW analysis for the homopolymer precursors to the diblocks is shown in the row above the corresponding diblock.

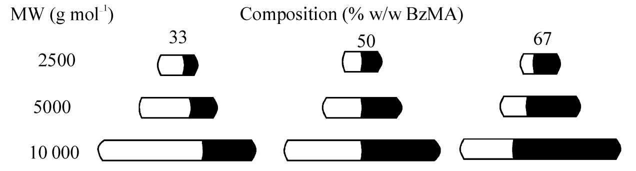


Fig. 3. Schematic representation of the nine diblock copolymers of this study. The BzMA hydrophobic units are indicated in black and the HEGMA hydrophilic units in white.

3.1.2. Composition

Fig. 4 shows the ^{1}H NMR spectrum of the HEGMA$_{19}$-b-BzMA$_{19}$ (MW 10,000 g mol^{-1}, 33% w/w BzMA) diblock copolymer. The signal from protons *e* and *f* of the monomer repeat units HEGMA and BzMA, respectively, were chosen to calculate the copolymer composition. The results of these calculations are also presented in Table 1. All diblock copolymers have a composition close to that expected from the comonomer feed ratio.

3.2. Solubilities

All polymers were soluble in *p*-xylene and diazinon except for the EO homopolymers. Although an organic polymer, PEO is very polar and is insoluble in non-polar organic solvents. PEO is soluble in the relatively polar solvent THF. Thus, the nine HEGMA-BzMA diblock copolymers, the HEGMA and BzMA homopolymers, the four Pluronics and the PO homopolymer were all soluble in both *p*-xylene and diazinon. All EO homopolymers were readily soluble in water, whereas the PO and BzMA homopolymers were water-insoluble. While only the three diblock copolymers bearing 67% w/w HEGMA hydrophilic units and the HEGMA homopolymer dissolved easily in water, the diblock copolymers with 50% and 33% w/w HEGMA units dissolved in water only after intense mechanical stirring or ultrasonication, resulting in clear and opaque solutions, respectively. The $C_{12}E_7$ surfactant was soluble both in *p*-xylene and water.

3.3. Aqueous solution aggregation

3.3.1. Hydrodynamic diameters

Fig. 5 displays a typical (copolymer 6, HEGMA$_7$-*b*-BzMA$_{14}$) histogram of the distribution of the hydrodynamic diameters of the block copolymers in aqueous solution. The distribution is bimodal with the smaller population being presumably that of well-defined micelles/small aggregates and the larger being that of non-equilibrium aggregates [18]. We tried to suppress the formation of the non-equilibrium aggregates by first dissolving the polymer samples in a small volume of a non-selective solvent, THF, so that all the aggregates could break up and all the polymer molecules be

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

Polym. No.	Polymer formula	Theor. MW[a]	GPC results		% w/w Composition in BzMA	
			M_n	M_w/M_n	Theoretical	^{1}H NMR
1	$BzMA_{20}$	3620	4900	1.13		
2	$HEGMA_{20}$	7100	9900	1.08		
3	$HEGMA_4$	1500	1650	1.28		
	$HEGMA_4$-*b*-$BzMA_7$	2730	3100	1.37	47	48
4	$HEGMA_2$	800	1950	1.24		
	$HEGMA_2$-*b*-$BzMA_9$	2400	3200	1.29	69	64
5	$HEGMA_5$	1850	2700	1.38		
	$HEGMA_5$-*b*-$BzMA_5$	2730	4350	1.11	33	31
6	$HEGMA_7$	2550	5000	1.09		
	$HEGMA_7$-*b*-$BzMA_{14}$	5000	8100	1.07	50	50
7	$HEGMA_5$	1850	4350	1.10		
	$HEGMA_5$-*b*-$BzMA_{19}$	5200	6900	1.16	66	69
8	$HEGMA_{10}$	3600	7100	1.07		
	$HEGMA_{10}$-*b*-$BzMA_{10}$	5360	8850	1.06	33	30
9	$HEGMA_{14}$	5000	8900	1.05		
	$HEGMA_{14}$-*b*-$BzMA_{28}$	9930	17850	1.09	50	51
10	$HEGMA_9$	3250	5950	1.07		
	$HEGMA_9$-*b*-$BzMA_{38}$	9940	16700	1.09	68	68
11	$HEGMA_{19}$	6750	12000	1.05		
	$HEGMA_{19}$-*b*-$BzMA_{19}$	10090	15950	1.05	33	30

[a] The MW of the initiator fragment of 100 g mol^{-1} was also included in the calculation.

molecularly dispersed as single chains. Subsequently, water was added slowly so that the hydrophobic units could associate to form the core of the micelles. Unfortunately, the hydrodynamic size distribution obtained with a 1% w/w aqueous solution of the most hydrophilic copolymer, $HEGMA_{19}$-*b*-$BzMA_{19}$, prepared by diluting in water its concentrated THF solution, gave again a bimodal size distribution. This indicates that the formation of the large aggregates might be due to intermicellar association, possibly driven by the hydrophobicity of the HEGMA backbone.

The maximum in the distribution of the hydrodynamic diameters of the smaller aggregates for all diblock copolymers is plotted in Fig. 6 as a function of their M_ns determined by GPC and their composition. The three straight lines plotted in the upper part of the figure indicate the dependence of the theoretical hydrodynamic diameters of spherical micelles of HEGMA-BzMA diblock copolymers with fully stretched

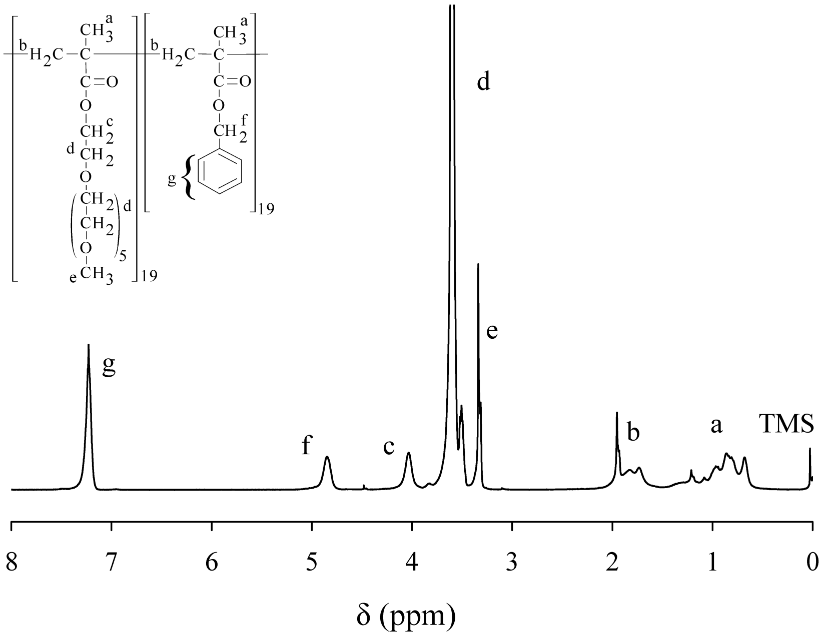


Fig. 4. ^{1}H NMR spectrum of the $HEGMA_{19}$-*b*-$BzMA_{19}$ copolymer.

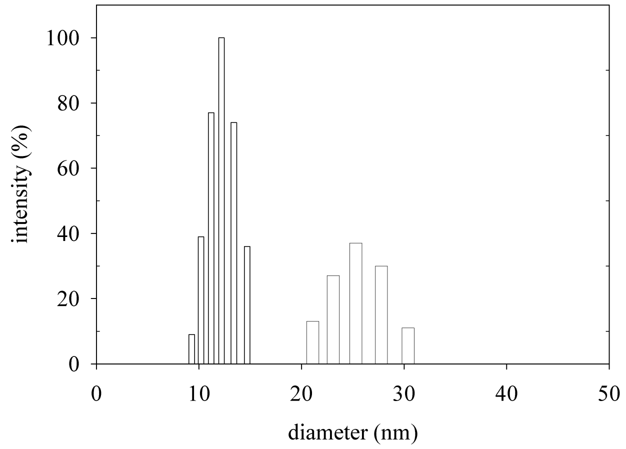


Fig. 5. Distribution of hydrodynamic diameters for diblock copolymer HEGMA$_7$-*b*-BzMA$_{14}$ in 1% w/w aqueous solution.

chains on GPC M_n, whereas the lines in the lower part of the figure represent the dependence of the theoretical hydrodynamic diameters of random coil unimers of the same diblock copolymers. These calculations enable us to determine the upper and lower limits of the size of such a diblock copolymer in aqueous solution. The straight lines plotted in the upper part of the figure were calculated using the equation:

$$d = 0.508 + 0.001451 \times (M_n - 100) \times (1 + 0.9886 x_{\mathrm{BzMA}}) \tag{1}$$

where d is an *upper limit* for the micelle diameter in nm (fully stretched chains assumed), M_n is the GPC M_n of the diblock copolymer, and x_{BzMA} is the copolymer weight fraction in BzMA. This calculation of d is based on doubling the chain contour length which is equal to the product of the overall DP, DP$_{\mathrm{total}}$, times the contribution of one monomer repeat unit to the contour length, which is 0.254 nm:

$$d = 2 \times 0.254 \times \mathrm{DP}_{\mathrm{total}} = 0.508 \times \mathrm{DP}_{\mathrm{total}} \tag{2}$$

DP_{total} is calculated from M_n and the MWs of the two monomer repeat units of 176 and 350 g mol^{-1} for BzMA and HEGMA, respectively, and also taking into account the incorporation of the initiator fragment into the copolymer, which corresponds to one extra monomer repeat unit:

$$\mathrm{DP}_{\mathrm{total}} = 1 + \left(\frac{M_n - 100}{350}\right) \times \left(1 + \frac{174}{176} x_{\mathrm{BzMA}}\right) \tag{3}$$

where the 100 g mol^{-1} subtracted from M_n is that of the initiator fragment in the copolymer, and 174 g mol^{-1} is the difference between the MWs of the two monomer repeat units. The combination of Eqs. (2) and (3) leads to Eq. (1).

The differentiation between the three theoretical straight lines for the micellar hydrodynamic diameters arises from the different MWs of the two monomer repeat units, and leads to higher predicted values of d for diblock copolymers with higher contents in the monomer with the lower MW, BzMA.

The HEGMA-BzMA diblock copolymer unimers in water (if any) comprise a collapsed BzMA globule and a swollen HEGMA random coil. Thus, the dimensions of the unimer are dominated by the size of the HEGMA hydrated block. However, it is difficult to calculate this size because of the unavailability of the stiffness factor [19] for HEGMA homopolymer. To circumvent this problem, the calculation was performed for linear PEO with the same MW as the HEGMA block, for which the stiffness factor can be assumed to be unity. Due to the arrangement of all carbon and oxygen atoms in the backbone of PEO, as opposed to the graft structure of the HEGMA units, the proposed calculation will provide an *upper estimate* for the unimer sizes of our experimental system. The DP of PEO with the same MW as the HEGMA block is calculated from:

$$\mathrm{DP}_{\mathrm{PEO}} = 1 + \left(\frac{M_n - 100}{44}\right) \times (1 - x_{\mathrm{BzMA}}) \tag{4}$$

where 44 is the MW of the EO monomer repeat unit. The swollen random coil size of the PEO block, d_{PEO}, is calculated using:

$$d_{\mathrm{PEO}} = 0.36 \times \alpha_{\mathrm{PEO}} \times (\mathrm{DP}_{\mathrm{PEO}})^{1/2} \tag{5}$$

where 0.36 nm is the contribution of one EO unit to the polymer contour length (EO monomer repeat unit comprises three bonds as compared to two in the methacrylate monomer repeat unit), and α_{PEO} is the polymer expansion factor from the θ-solvent state to a good solvent state, calculated from the modified Flory–Krigbaum theory [20]:

$$\alpha_{\mathrm{PEO}}^5 - \alpha_{\mathrm{PEO}}^3 = 0.88 \times (0.5 - \chi_{\mathrm{PEO-water}}) \times (\mathrm{DP}_{\mathrm{PEO}})^{1/2} \tag{6}$$

where the constant 0.88 was modified from the original

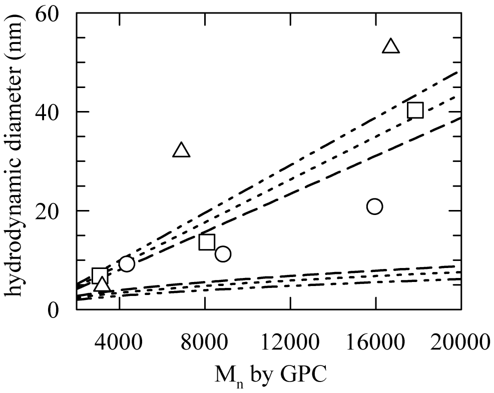


Fig. 6. Dependence of hydrodynamic diameters of the diblock copolymers in aqueous solution on their number average molecular weights and composition. The circles, squares and triangles correspond to copolymers bearing 33, 50 and 67% w/w BzMA, respectively. The three upper lines represent the theoretical prediction for spherical micelles with fully stretched chains, whereas the lower three lines show the random coil dimensions of EO homopolymers with the same molecular weight as the HEGMA block. Dashed, dotted and combined dashed-dotted lines correspond to copolymers bearing 33, 50 and 67% w/w BzMA, respectively.

value of 2.0 to secure better agreement with experimental data, and $\chi_{\text{PEO-water}}$ is the Flory–Huggins interaction parameter between PEO and water, found in literature to have a value of 0.3 [20]. An upper estimate of α_{PEO} from Eq. (6) was 1.4, which was used throughout the calculations.

With the exception of two points (which lie above the micelle regime), all measured hydrodynamic diameters in Fig. 6 lay in the area between the stretched spherical micelle model and the unimer model. For the samples to be unimers, their hydrodynamic diameters should be equal to or smaller (due to the overestimations made in the calculation) than the unimer model predictions. On the other hand, for the samples to be micellar, their hydrodynamic diameters should be equal to or smaller (because chain coiling was ignored in the calculations) than the micelle model predictions. Thus, we conclude from Fig. 6 that, in water, the block copolymers were in the micellar rather than in the unimer state.

More careful comparison between the experimental hydrodynamic diameters and the theoretical predictions for micelles revealed that, for the most hydrophilic diblock copolymers (33% w/w BzMA), the experimental diameters were smaller than the theoretical, for the most hydrophobic diblock copolymers (67% w/w BzMA) the experimental diameters were higher than the theoretical, and for the diblock copolymers with 50% w/w BzMA, the agreement between experiment and theory was very good. The overestimation of the theoretical diameters in the hydrophilic copolymers was probably due to chain coiling in the micelles of the experimental system (collapse of the hydrophobic blocks in the core and retraction of the hydrophilic blocks in the shell), not taken into account in the calculation. On the other hand, the underestimation of the theoretical diameters in the hydrophobic copolymers was probably due to the formation of multi-micellar aggregates in the experimental system, promoted by the pronounced hydrophobicity of these copolymers. Finally, the satisfactory agreement between the theoretical and experimental diameters for the diblock copolymers with 50% w/w BzMA was probably due to the cancellation of two opposite deviations in the calculations, namely that due to chain coiling and that due to multi-micellar aggregate formation.

3.3.2. Cloud points

Fig. 7 shows the cloud points of the HEGMA-BzMA diblock copolymers as a function of the % w/w composition in hydrophobic BzMA for the three different overall theoretical MWs. At constant overall MW, the cloud points decreased with the composition in BzMA, whereas, at constant composition, the cloud points increased with the overall MW. At constant overall MW, an increase in the BzMA composition implies both an increase in the number of hydrophobic units and a decrease in the number of HEGMA hydrophilic units. Given the micellization of the block copolymer chains in water, an increase in the BzMA content at constant overall MW led to a reduction in the cloud point for two reasons: first, a greater number of hydrophobic units resulted in longer hydrophobic blocks, a larger micellar hydrophobic core with a greater interfacial area between the core and water; and, second, a lower number of hydrophilic units resulted in shorter hydrophilic blocks and a less efficient steric stabilization of the micelles in water [2b]. At constant diblock copolymer composition, an increase in the overall MW led to an increase in the length of both blocks, which, based on the discussion in the preceding paragraph, would have opposite effects on the cloud points. From the above results, it appears that the effect of a longer hydrophilic block dominates that of a longer hydrophobic block.

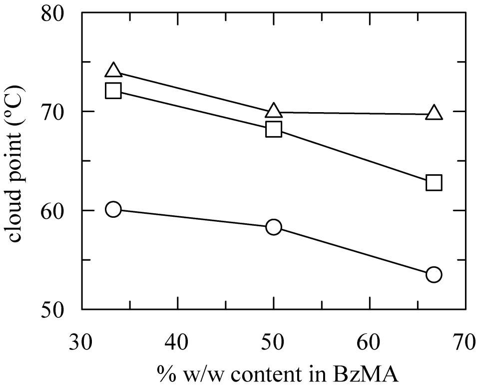


Fig. 7. Dependence of cloud points of 1% w/w aqueous diblock copolymer solutions on the % w/w composition in hydrophobic BzMA monomer and on the overall molecular weight. The circles, squares and triangles correspond to copolymers with molecular weights 2500, 5000 and 10,000g mol^{-1}.

3.3.3. Surface activity

To confirm their amphiphilic properties, the surface tension of all block copolymers in aqueous solution in a wide range of concentrations was measured. From the reduction of the surface tension with copolymer concentration, the critical micellization concentrations (cmcs) of all the block copolymers were found to be in the range from 10^{-6} to 10^{-5} mol l^{-1} (there were no clear trends with respect to polymer structure, possibly due to presence of impurities). These cmc values are comparable to those reported for other amphiphilic methacrylate block copolymers [21–23] and for the Pluronics [24]. On the other hand, the values of the surface tension at the cmc for all the diblock copolymers of this study were around 50 dyn cm^{-1}, higher than those of the Pluronics (of around 35 dyn cm^{-1}) but comparable to those of amphiphilic methacrylate block copolymers [21–23]. The lower surface activity of amphiphilic methacrylate copolymers might be due to the side chain of the methacrylate unit which renders packing at the air–water interface more difficult, compared to the Pluronics in which most of the atoms lie in the main chain.

3.4. Emulsion phase diagrams for HEGMA-b-BzMA

First, the homopolymers of HEGMA and BzMA were used to emulsify both xylene in water and diazinon in water at different organic/water weight ratios. In all cases, the system quickly separated into two clear phases without the formation of emulsion. Another experiment where a 50% w/w mixture of the two homopolymers was used had the same result. Thus, these homopolymers proved to be inefficient emulsifiers. Similarly, poor emulsification results were obtained when the low MW nonionic surfactant $C_{12}E_7$ was used to emulsify xylene in water.

Next, the nine HEGMA-BzMA diblock 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. 8, whereas those for the diazinon/water emulsions in Fig. 9. One particular characteristic of our diblock copolymers is that all resulting emulsions were of the o/w type (no w/o emulsion was observed).

Fig. 8(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 % w/w composition of copolymer in hydrophobic BzMA monomer for three different copolymer MWs: (a) 2500, (b) 5000 and (c) 10,000 g mol^{-1}. The symbols used are explained in the figure legend.

The main features of the phase diagrams, presented in Fig. 8, were the following: at low values (1/4 w/w) of the organic phase/water ratio, five out of the six copolymers of lower MW (2500 and 5000 g mol^{-1}) gave three-phase systems, comprising a polymer precipitate and the separated xylene and aqueous phases. Precipitation of the copolymer occurred because the xylene-swollen copolymer was insoluble in the excess water to which the xylene solution of the copolymer was added. The precipitated polymer lay in the bottom of the vial within the heavier water phase where, however, it could not dissolve because it was swollen in the water-immiscible xylene (note that all the HEGMA-BzMA diblock copolymers were water-soluble). This behavior was not observed with the higher MWs (10,000 g mol^{-1}) copolymers probably because the longer hydrophilic chains secured partial water-solubility even in the presence of xylene. At higher values (2/3 and 1/2 w/w) of the xylene/water ratio, no precipitation was observed with any copolymer, irrespective of MW, because of the larger amount of xylene (and, at the same time, the smaller amount of water) in the system than before. In this particular region, 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. As the weight fraction of xylene increased, the height of the cream layer also increased. When the xylene weight fraction became 80%, the cream layer in the emulsions of five copolymers expanded to occupy the whole height of the system. The emulsions of all three diblock copolymers of 5000 g mol^{-1} MW presented this one-phase system. The lower MW copolymers (2500 g mol^{-1}), bearing 33 and 50% w/w BzMA, also gave one-phase o/w emulsions, while the one bearing 67% w/w BzMA gave a two-phase system with an o/w emulsion in the bottom and excess oil on the top. The opposite trend was observed with copolymers of

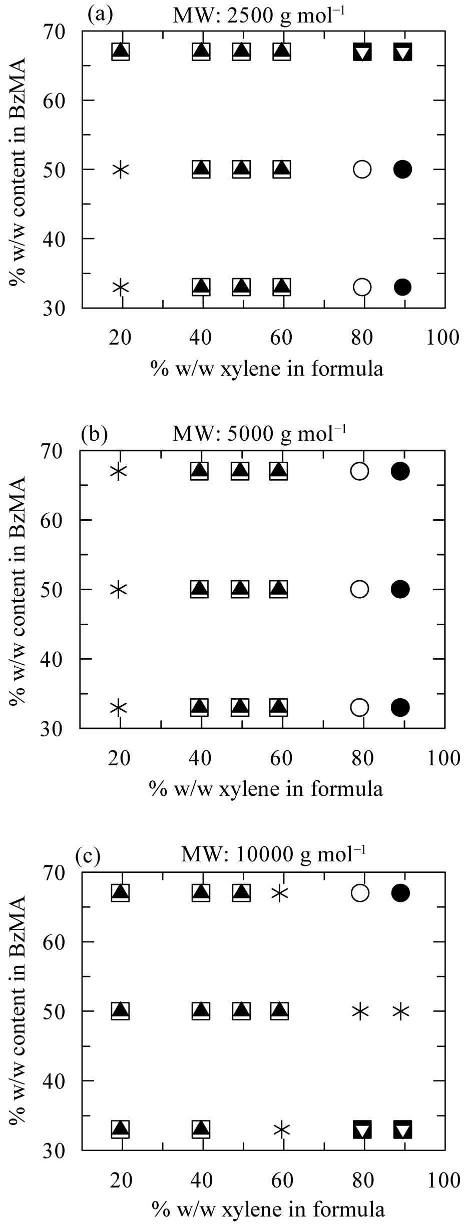


Fig. 8. Phase diagrams for the emulsions as a function of the % w/w xylene content in the total formulation and the % w/w composition of diblock copolymer in hydrophobic monomer for three different molecular weights: (a) 2500, (b) 5000 and (c) 10,000 g mol^{-1}. Open circles: stable, low-viscosity single-phase o/w emulsions; closed circles: stable, high-viscosity (gels) single-phase o/w emulsions; stars: systems that broke down to their 3 ingredients, polymer, xylene and water; black triangles within open squares: o/w emulsions coexisting with excess aqueous phase; open inverted triangles within closed squares: o/w emulsions coexisting with excess organic phase.

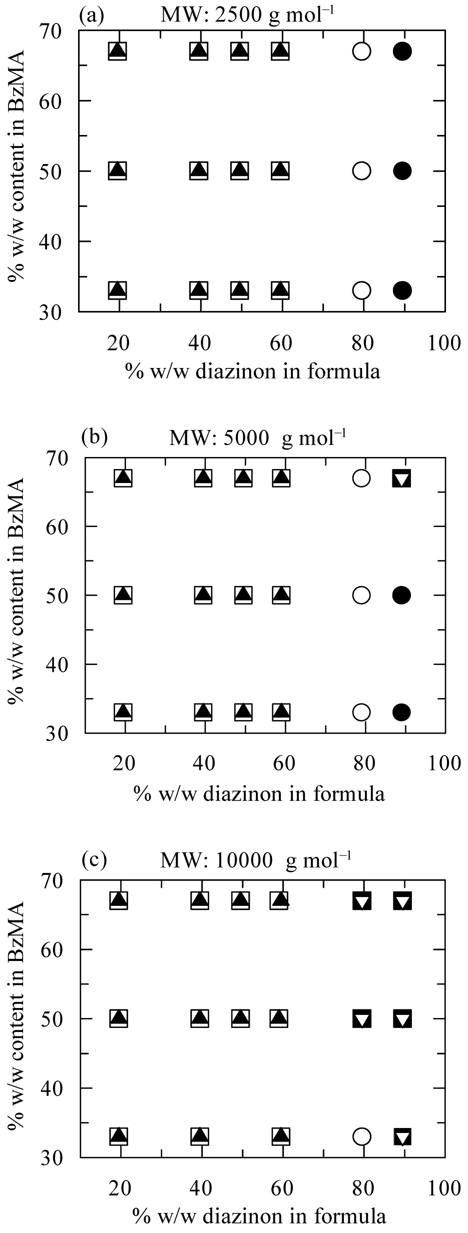


Fig. 9. Phase diagrams for the emulsions as a function of the % w/w diazinon content in the total formulation and the % w/w composition of diblock copolymer in hydrophobic monomer for three different molecular weights: (a) 2500, (b) 5000 and (c) 10,000 g mol^{-1}. Symbols are the same as those in Fig. 8.

10,000 g mol^{-1} MW, where only the most hydrophobic copolymer succeeded in providing a single-phase o/w emulsion. The poorer emulsification behavior of higher MW copolymers has been observed before [8] and it might be due to the slower diffusional characteristics of larger copolymers, which can reduce the emulsifier availability at the o/w interface. Thus, six out of the nine copolymers gave single-phase o/w emulsions of low viscosity when the xylene/water ratio was 4/1 w/w. This seemed to be the optimum capacity of our diblock copolymers because at higher values of the xylene/water ratio none of the copolymers resulted in a low-viscosity single-phase emulsion. In particular, when the xylene/water ratio was 9/1 w/w, three possibilities existed: either a polymer precipitate with the two separated neat liquid phases, or a two-phase system with an o/w emulsion in the bottom and an excess oil on the top, or a single-phase o/w emulsion of high viscosity (an undesirable feature for this type of formulations). The formation of the high viscosity o/w emulsion (emulsion gel) was probably due to the high concentration of oil droplets, which were in contact and adhered with one another, creating a network of droplets, while the existence of emulsions coexisting with excess oil denoted the inability of these copolymers to emulsify this large amount of xylene. It is noteworthy that the same six diblock copolymers that gave the low-viscosity single-phase emulsions at the 4/1 w/w xylene/water ratio gave the high-viscosity single-phase emulsions at the 9/1 w/w xylene/water ratio.

The size of the droplets of the emulsions was measured using optical microscopy and found to be in the range between 10 and 30 μm. It is likely that, in addition to the block copolymer adsorbed at the liquid/liquid interface, some copolymer migrates to the aqueous phase where it stays in the form of micelles [4], and some other polymer remains within the xylene droplets as unimers (both the HEGMA and BzMA homopolymers are soluble in xylene).

Fig. 9(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 % w/w polymer composition in hydrophobic BzMA monomer for three different MWs: (a) 2500, (b) 5000 and (c) 10,000 g mol^{-1}. The symbols used are the same as those used in Fig. 8. The first observation was the absence of star symbols anywhere in the phase diagrams in Fig. 9. Thus, in the diazinon/water system, no three-phase system with a polymer precipitate was observed, even at low values (1/4 w/w) of the organic phase/water ratio. This was due to the fact that diazinon has a higher density ($\rho = 1.117$ g ml^{-1} [25a]) than water as compared to the lower density of xylene ($\rho = 0.861$ g ml^{-1} [25b]) than water. Thus, when the copolymer solution in diazinon was added to water, if the copolymer precipitated, this would immediately redissolve in diazinon because diazinon was in the bottom. At higher values (2/3 to 3/2 w/w) of the diazinon/water ratio, o/w emulsions coexisting with excess water were observed as with the xylene/water emulsions. 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. Single-phase o/w emulsions of low viscosity resulted at the same values (4/1 w/w) of the diazinon/water ratio as with xylene. Thus, at an 80% w/w content of the formula in diazinon, seven copolymers gave single-phase o/w emulsions. These copolymers were all six copolymers of lower MW (2500 and 5000 g mol^{-1}) plus the most hydrophilic copolymer with MW of 10,000 g mol^{-1}. The two remaining block copolymers (MW 10,000 g mol^{-1}) gave o/w emulsions coexisting with excess oil. At even higher values (9/1 w/w) of the ratio, two possibilities existed: either emulsions coexisting with excess oil (especially in polymer with high MW), or single-phase o/w emulsions of high viscosity. Similar to Fig. 8, the block copolymers in Fig. 9 that resulted in high-viscosity single-phase emulsions at a 9/1 w/w diazinon/water ratio gave low-viscosity single-phase emulsions at a 4/1 w/w diazinon/water ratio.

Considering that the best emulsifiers are those block copolymers that can emulsify the largest quantity of organic phase in water, resulting in single-phase o/w emulsions of low viscosity, it appears from Figs. 8 and 9 that the lower MW copolymers (2500 and 5000 g mol^{-1}) are the optimal emulsifiers. It can also be concluded that, in many cases, xylene and diazinon behave similarly in terms of their emulsification with water using the HEGMA-BzMA diblock copolymers. However, there are cases when the behavior of the two differs markedly (diblock copolymer precipitation with xylene but not with diazinon), indicating that, in these emulsification experiments, xylene (organic solvent) cannot be a perfect substitute for the much more toxic diazinon (pesticide).

3.5. Emulsion phase diagrams for Pluronics

To compare the performance of our polymeric emulsifiers with that of commercially available polymeric emulsifiers, we evaluated the emulsification properties of four Pluronics using the same emulsion formation procedure as that used for our diblock copolymers. Pluronics are ABA triblock copolymers of EO-PO-EO. The four Pluronics used appear in Table 2 along with their names, molecular formulas and properties [26], including the hydrophilic-lipophilic balance (HLB), and theoretical and experimental MWs and compositions.

Fig. 10(a) and (b) show the emulsification behavior of the four Pluronics with xylene and diazinon, respectively. Pluronics formed both o/w emulsions, for which the same symbols were used as for the o/w emulsions in Figs. 8 and 9, and w/o emulsions, for which new symbols were used. The symbols used for the w/o emulsions are analogous to those employed for the o/w emulsions but they are hexagonal, as detailed in the legend of Fig. 10.

Fig. 10(a) and (b) show that the two hydrophilic Pluronics, L64 and P105, both with HLB values of 15, behaved as emulsifiers in a way similar to our diblock copolymers, in that they always resulted in o/w emulsions and in most cases gave single-phase emulsions at 80% w/w content in organic phase. In contrast, the two hydrophobic Pluronics, L92 and P123, with HLB values of 6 and 8, respectively, always gave w/o emulsions. Our most hydrophobic HEGMA-BzMA diblock copolymers never provided w/o emulsions possibly because

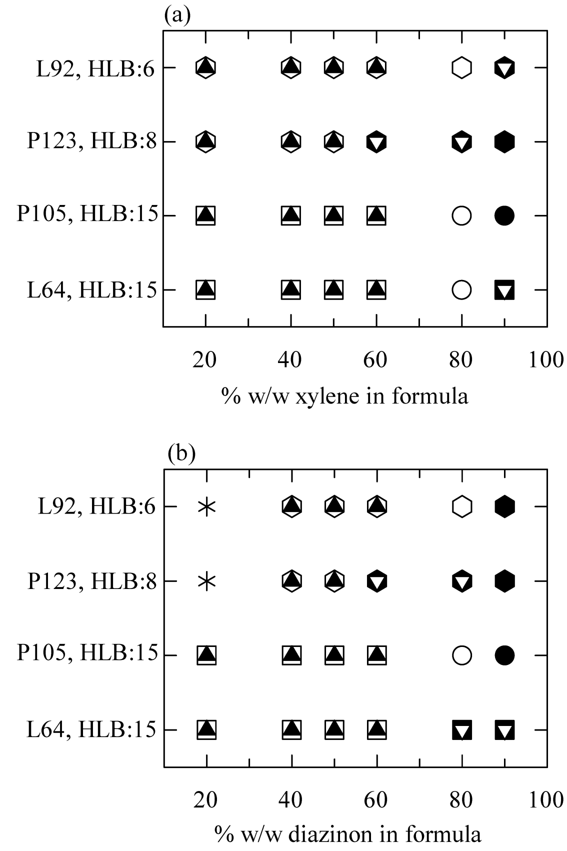


Fig. 10. Phase diagrams for the emulsions as a function of the % w/w organic phase content in the total formulation and the type of Pluronic copolymer. Organic phase: (a) xylene, and (b) diazinon. The symbols of Fig. 8 for o/w emulsions are used, plus the following symbols for w/o emulsions: open hexagons: stable, low-viscosity single-phase w/o emulsions; closed hexagons: stable, high-viscosity (gels) single-phase w/o emulsions; black triangles within open hexagons: w/o emulsions coexisting with excess aqueous phase; open inverted triangles within closed hexagons: w/o emulsions coexisting with excess organic phase.

Table 2
Names, molecular formulas and properties of the four Pluronics tested as emulsifiers

Polym. name	Polymer formula[a]	HLB[a]	Theor. MW[a]	GPC Results[b]		% w/w Composition in EO	
				M_n	M_w/M_n	Theor.[a]	^{1}H NMR[b]
L92	EO_8-b-PO_{50}-b-EO_8	6	3604	7650	1.04	20	24
P123	EO_{20}-b-PO_{70}-b-EO_{20}	8	5820	4200	1.31	30	36
P105	EO_{37}-b-PO_{56}-b-EO_{37}	15	6504	4790	1.27	50	49
L64	EO_{13}-b-PO_{30}-b-EO_{13}	15	2884	2490	1.06	40	40

[a] From Ref. [26].
[b] Measured in this study.

they were not hydrophobic enough (67% w/w hydrophobic units) as compared to the two Pluronics with 70 and 80% w/w content in hydrophobic units. For comparison, ionic amphiphilic copolymers of poly(sodium acrylate) grafted with dodecylamine used for the emulsification of the dodecane-water system required a content in hydrophobic dodecyl units of at least 75% w/w to stabilize a w/o emulsion [27,28].

Fig. 10(a) is the xylene–water emulsification phase diagram for the four Pluronics as a function of the content in xylene. For all xylene/water ratios, the two hydrophilic Pluronics gave o/w emulsions while the two hydrophobic Pluronics gave w/o emulsions. With the exception of P123 (which is a more balanced surfactant than the other Pluronics), for xylene/water ratios between 1/4 and 3/2, there was formation of emulsion, co-existing with excess water. Unlike the behavior of five of our diblock copolymers (Fig. 8), there was no precipitation of Pluronics at low xylene contents (high water contents), possibly due to the weaker incompatibility of PPO with water compared to that between BzMA homopolymer and water. Again with the exception of P123 (which, according to the manufacturer, is not as good emulsifier as wetting agent [29]), at the xylene/water ratio of 4/1, there was formation of low-viscosity, single-phase emulsions with the other three Pluronics. At the highest xylene/water w/w ratio, 9/1, there were two possibilities: either single-phase emulsions of high viscosity, or emulsions co-existing with excess xylene, similar to the emulsion phase behavior of our diblock copolymers at a 9/1 w/w xylene/water ratio depicted in Fig. 8.

Fig. 10(b) gives the emulsification behavior of diazinon-water with the four Pluronics as a function of the diazinon content. At a 1/4 w/w diazinon/water ratio, the two hydrophobic Pluronics, L92 and P123, precipitated. Precipitation was also observed in Fig. 8 with our HEGMA-*b*-BzMA copolymers in the xylene/water system. It is noteworthy that both L92 and P123 were soluble in both water and diazinon. However, the precipitation might be due to a combination of the insolubility of PPO (the majority component in these copolymers) in water (the liquid comprising 80% w/w of the emulsion), and the relatively low solubility of PPO in diazinon (the solvent in the bottom phase). It is reminded that, in Fig. 9, no precipitation of any of our HEGMA-BzMA diblock copolymers was observed in the diazinon-water system. This discrepancy might be due to the higher solubility of BzMA homopolymer in diazinon compared to that of PPO in diazinon.

For the rest of the points in the phase diagram in Fig. 10(b), the two hydrophilic Pluronics gave o/w emulsions, while the two hydrophobic Pluronics gave w/o emulsions. For diazinon/water ratios from 1/4 to 3/2, and with the exception of the two precipitation points discussed above, the phase diagram was identical to that in Fig. 10(a), confirming the similar properties of the two organic phases, diazinon and xylene. At a 4/1 w/w diazinon/water ratio, the emulsification behavior was again the same as that in Fig. 10(a), with the exception of L64 which resulted in an o/w emulsion in equilibrium with diazinon rather than a single-phase o/w emulsion. At a 9/1 w/w diazinon/water ratio, the emulsification behavior was once again the same as that in Fig. 10(a), with the exception of L92 which provided a single-phase w/o emulsion of very high viscosity rather than w/o emulsion in equilibrium with diazinon.

These emulsification phase diagrams for Pluronics confirm that the two Pluronics with high HLB values are best o/w emulsifiers, as recommended by the manufacturer. This behavior is matched by most of our HEGMA-BzMA diblock copolymers which can therefore be successfully used as o/w emulsifiers. It is noteworthy, however, that, unlike the hydrophobic Pluronics, none of the HEGMA-BzMA diblock copolymers was hydrophobic enough to stabilize w/o emulsions.

4. Conclusions

The successful synthesis of nine amphiphilic diblock copolymers of different molecular weights and compositions based on the nonionic, hydrophilic monomer methoxy hexa(ethylene glycol) methacrylate (HEGMA) and the hydrophobic monomer benzyl methacrylate (BzMA) was presented. In aqueous solution, the diblock copolymers formed micelles whose hydrodynamic diameters increased with the % w/w composition in BzMA hydrophobic units and the molecular weight. However, the cloud points of 1% w/w aqueous solutions increased with the % w/w composition in hydrophilic HEGMA units and the molecular weight. These diblock copolymers succeeded in emulsifying xylene in water and diazinon in water, similar to hydrophilic Pluronics, and unlike the homopolymers of HEGMA and BzMA.

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