Synthesis, Characterization, and Evaluation as Emulsifiers of Amphiphilic−Ionizable Aromatic Methacrylate ABC Triblock Terpolymers

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ABSTRACT: Four isomeric terpolymers based on benzyl methacrylate (BzMA, nonionic hydrophobic), 2-(dimethylamino)ethyl methacrylate (DMAEMA, ionizable hydrophilic), and methoxyhexa(ethylene glycol) methacrylate (HEGMA, nonionic hydrophilic) were synthesized using group transfer polymerization (GTP). The three of the terpolymers were the ABC block sequence isomers, ABC, ACB, and BAC, and the fourth was the statistical terpolymer. Their theoretical molecular weight was 5000 g mol^{-1}, and the theoretical w/w composition was 33% from each monomer. The success of the synthesis was confirmed by gel permeation chromatography (GPC), which showed that the experimental molecular weights were in reasonable agreement with the theoretical ones and the polydispersity indices were low (in most cases <1.1), and by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy, which provided experimental compositions very close to the theoretical ones. All the terpolymers were characterized in aqueous solution by dynamic light scattering at room temperature to determine their hydrodynamic diameters and turbidimetry to determine their cloud points. The results indicated that the behavior of the terpolymers in aqueous solution was profoundly affected by the monomer distribution in the polymer chain. After polymer characterization, the above terpolymers were used as stabilizers at a 1% w/w polymer concentration to prepare xylene−water and diazinon (pesticide)−water emulsions. All emulsions formed were of the o/w type (no w/o emulsion was observed), probably due to the hydrophilic nature of the terpolymers (66% w/w composition in hydrophilic units). From emulsion droplet size measurements, it appeared that the emulsification efficiency of the terpolymers was also affected by the monomer distribution in the polymer chain with the most efficient terpolymer being the triblock with a BzMA midblock and the least efficient being the statistical terpolymer.

Introduction

Emulsion formation is a widely applied industrial process allowing the mixing of two or more mutually incompatible chemical species by dispersing one in the other. There are mainly two kinds of liquid/liquid emulsions: the oil-in-water (o/w) emulsions where the continuous phase is water and the water-in-oil (w/o) emulsions where oil is the continuous phase.[1−3a] Emulsion formation requires the input of mechanical energy in order to deform and break large droplets into smaller ones and the addition of a third component called the emulsifying agent that usually is a low molecular weight (MW) surfactant. This emulsifying agent confers to the emulsion kinetic (as opposed to thermodynamic) stability being adsorbed at the liquid−liquid interface. Even though most of the emulsions are historically stabilized by low MW surfactants, there is a trend nowadays to replace them with polymeric emulsifiers such as amphiphilic linear, graft, and star copolymers.[4−10] These copolymers are more effective than the conventional low MW ones, as manifested by the smaller amount of polymer required for emulsification.[8]

A new type of linear polymeric surfactants is that of amphiphilic ABC triblock terpolymers, whose aqueous solution properties and potential applications have scarcely been investigated. The few examples in the literature to date are reviewed below. Triblock terpolymers of 2-phenylethyl methacrylate, poly(ethylene glycol) methacrylate, and potassium methacrylate were prepared by group transfer polymerization (GTP)[11−14] and tested as dispersants of pigment particles in water.[15,16] ABC triblock hydrophobic polyampholytes containing one hydrophobic, one positively charged, and one negatively charged block were prepared by GTP[17] and anionic polymerization[18,19] and studied in aqueous solution. One ABC triblock terpolymer of styrene, methyl methacrylate (MMA), and acrylic acid was prepared by anionic polymerization, and its morphologies in mixtures of water and organic solvents were studied.[20] One ABC triblock terpolymer of 2-ethylhexyl methacrylate, MMA, and acrylic acid was prepared by GTP and found to form micelles in water with a microphase-separated core.[21] Finally, an ABC triblock terpolymer based on styrene, acrylic acid, and *n*-butyl methacrylate was prepared by anionic polymerization and was studied as thickener.[22]

The properties of aqueous solutions of amphiphilic ABC triblock terpolymers depend on the monomer types, composition, and molecular weights, as is the case with diblock and ABA triblock copolymers, but also on block sequence. There are three possible block sequences for triblock terpolymers: ABC, ACB, and BAC. To date, the effect of this variable has been studied to an even smaller extent. Patrickios and co-workers[23] synthesized by “living” cationic polymerization ABC triblock terpolymers of methoxytri(ethylene glycol) vinyl ether, methyl vinyl ether, and ethyl vinyl ether with the three possible block sequences and determined that the cloud points of aqueous solutions and the extent of micelli-

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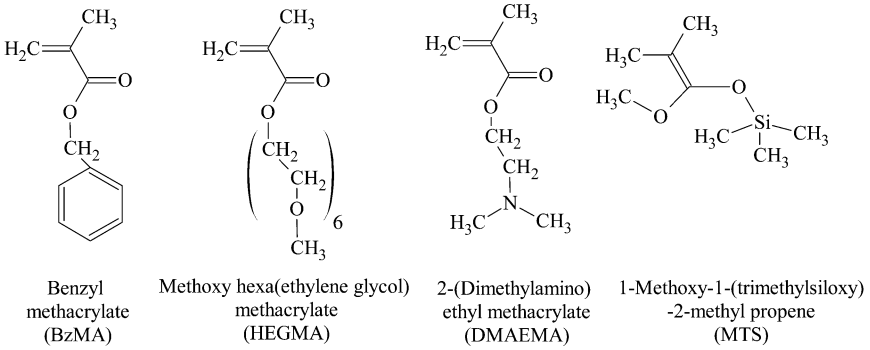

Figure 1. Chemical structures and names of the three monomers and the initiator used for the synthesis of the four isomeric terpolymers.

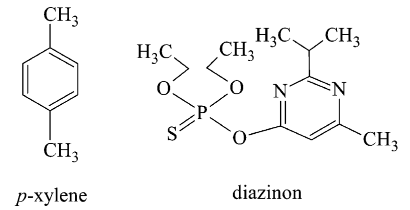

Figure 2. Chemical structures of *p*-xylene and diazinon (pesticide).

zation in aqueous salt solutions both depended on the block sequence. Nakahama and colleagues[24] prepared by anionic polymerization ABC triblock terpolymers of 2-hydroxyethyl methacrylate, *tert*-butyl methacrylate, and 2-(perfluorobutyl)ethyl methacrylate with the three possible block sequences and determined that terpolymer aggregation in methanolic solutions strongly depended on the block sequence. Along the same lines were the results of Patrickios et al.[25] and Triftaridou et al.[26] on ABC triblock hydrophobic polyampholytes[25] and ABC triblock terpolymers with two hydrophilic and one hydrophobic blocks,[26] respectively, who observed block-sequence-dependent micellar sizes.

The aim of this investigation was the preparation of linear amphiphilic ABC triblock terpolymer surfactants appropriate for the emulsification of aromatic oils in water. To this end, an aromatic monomer was employed for the synthesis of the hydrophobic block, while the other two blocks were hydrophilic. The emphasis in this study was placed on the effect of block sequence. Thus, all three block sequence isomers, ABC, ACB, and BAC, plus the statistical terpolymer, were synthesized. All four terpolymers were characterized in aqueous solution and evaluated as emulsifiers.

Experimental Section

Materials. The chemical structures and names of the three monomers, benzyl methacrylate (BzMA), methoxy hexa(ethylene glycol) methacrylate (HEGMA), and 2-(dimethylamino)ethyl methacrylate (DMAEMA), and the GTP initiator, 1-methoxy-1-(trimethysiloxy)-2-methyl propene (MTS), are shown in Figure 1. BzMA, DMAEMA, and MTS were purchased from Aldrich, Germany, whereas HEGMA was kindly donated by Laporte Performance Chemicals, UK. The free radical inhibitor 2,2-diphenyl-1-picrylhydrazyl (DPPH), calcium hydride (CaH_2), potassium metal, tetrabutylammonium hydroxide, benzoic acid, and *p*-xylene were also purchased from Aldrich. Tetrahydrofuran (THF, both HPLC and AR grade) was purchased from Labscan, Ireland. Sodium metal was purchased from Fluka, Germany. Diazinon (a pesticide of Syngenta) was provided by Premier Chemical Co. Ltd., Cyprus. Figure 2 shows the chemical structures of *p*-xylene and diazinon.

Methods. For the processing with basic alumina, the HEGMA monomer was handled as a 50% v/v solution in freshly distilled THF because of its high viscosity.[27] BzMA and the HEGMA solution were passed twice through basic alumina columns to remove the polymerization inhibitors and protic impurities, while DMAEMA was passed only once through a basic alumina column due to the higher initial purity of this monomer. BzMA and DMAEMA were 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 were vacuum-distilled just prior to use. The HEGMA solution was stirred over CaH_2 (without added DPPH) for 1 h and was filtered through a 0.45 μm PTFE syringe filter directly into the polymerization flask. The MTS initiator was vacuum-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 according to Dicker et al.[13] and was kept under vacuum until use.

Terpolymer Synthesis. The three triblock terpolymers were prepared by sequential monomer addition under GTP conditions, while the statistical terpolymer was prepared by the simultaneous GTP of all three monomers. A typical polymerization procedure yielding the ABC triblock terpolymer with block sequence HEGMA−DMAEMA−BzMA of theoretical molecular weight 5000 g mol^{-1} and 33% w/w compositions from each monomer is detailed below. TBABB catalyst (~10 mg, 20 μmol), freshly distilled THF (27 mL), and MTS initiator (0.4 mL, 0.34 g, 2.0 mmol) were added, in this order, to a 100 mL round-bottom flask kept under a dry nitrogen atmosphere and sealed with a rubber septum. Then, 6.4 mL of a 50% solution of HEGMA (3.4 g of neat monomer, 9.5 mmol) in THF was slowly added under stirring. The polymerization exotherm (27.9−33.0 °C) abated within 5 min, samples for GPC were extracted, and 3.6 mL of DMAEMA (3.36 g, 21.2 mmol) was added, which produced an exotherm (31.2−42.0 °C). Subsequently, a sample of the produced HEGMA−DMAEMA diblock copolymer was extracted for GPC analysis. Finally, 3.2 mL of BzMA (3.33 g, 19.6 mmol) was added to the solution, which produced an exotherm (37.7−45.6 °C), and a sample of the triblock terpolymer was extracted for GPC analysis. The syntheses of the other two triblock terpolymers followed similar procedures which differed only in the order of monomer addition. The statistical terpolymer was prepared by the slow simultaneous addition of the three monomers to a THF solution of TBABB catalyst and MTS initiator. Figure 3 illustrates the monomer addition sequences used to prepare the four isomeric terpolymers. The length of each block in Figure 3 is proportional to the respective mole fraction rather than the weight fraction. All terpolymers were recovered by precipitation in *n*-hexane and were dried in a vacuum oven at room temperature for 2 days.

Characterization by GPC and ^{1}H NMR. Samples of the three ABC triblock terpolymers and the statistical terpolymer were characterized in terms of their MW and composition using GPC and ^{1}H NMR. GPC was performed 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

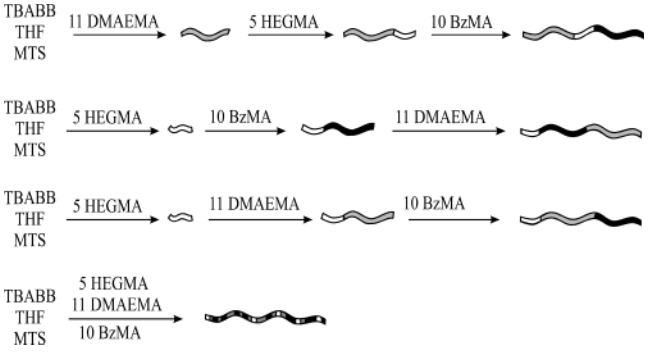

Figure 3. Schematic representation of the monomer addition sequences employed to afford the three ABC triblock terpolymers and the statistical terpolymer.

min^{-1}. The MW calibration was based on six narrow MW (630, 1400, 2400, 4250, 7600, and 22 650 g mol^{-1}) polyMMA standards also supplied by Polymer Laboratories. The terpolymer compositions were measured by ^{1}H NMR analysis in $CDCl_3$ using a 300 MHz AVANCE Bruker spectrometer equipped with an ultrashield magnet.

Aqueous Solution Characterization. 1% w/w salt-free solutions in deionized water (Millipore system) of the terpolymers were characterized in terms of their hydrodynamic diameters, cloud points, and effective p*K*s, using dynamic light scattering, turbidimetry, and hydrogen ion titration, respectively. A 90Plus Brookhaven dynamic light scattering spectrometer equipped with a BI9000 correlator and a 30 mW red diode laser operating at 673 nm was used for the scattering measurements at an angle of 90° and at room temperature. Five 2 min individual runs were performed for each terpolymer solution, and the data were averaged. The data were processed using multimodal size distribution (MSD) analysis based on nonnegatively constrained least squares (NNLS). Prior to the light scattering measurements, the terpolymer solutions were filtered through 0.5 μm PTFE syringe filters and were left at rest for approximately 1 h so that any air bubbles could escape. A single beam Lambda 10 Perkin-Elmer UV/vis spectrometer was used for the turbidity measurements. The terpolymer solution was placed in a 10 mm path length quartz cuvette containing a small magnetic bar set in motion with the aid of a miniature magnetic stirrer. A small temperature probe was immersed in the upper part of the solution, which was heated from 20 to 95 °C. The optical density at 500 nm and the temperature were monitored using the software package TempLab (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. For the hydrogen ion titrations, 5 mL of 1% w/w terpolymer solutions adjusted to pH 2 was placed in 15 mL glass vials and were titrated to pH 12 with a 0.5 M NaOH standard solution under continuous stirring. The pH was measured using a Corning PS30 portable pH meter. The effective p*K*s were calculated as the pH at 50% ionization.

Preparation of Emulsions. After terpolymer characterization, xylene–water and diazinon–water emulsions were prepared using the four terpolymers as emulsifiers. The terpolymer 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. First, the proper amount of terpolymer was dissolved in oil (xylene or diazinon). Next, this terpolymer solution was added dropwise to deionized water under vigorous stirring. (Preliminary experiments had shown that this procedure maximized the chances for the formation of o/w emulsions.[28]) After the addition of all the amount of the organic phase to water, each resulting emulsion was vigorously stirred for an additional 10 min, the samples were 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). When the emulsion drops were dispersed uniformly in the solvent being tested, then 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.

Results and Discussion

Polymer Synthesis and Confirmation of Structure. A schematic representation of the structure of the four terpolymers prepared is given in Table 1. The same table also lists the theoretical chemical formulas and the MW and composition characterization results of the terpolymers and their precursors. The number-average MWs, M_ns, are approximately 50% higher than the theoretical MWs, indicating partial initiator deactivation and/or hydrodynamic differences between the present

Table 1. Experimental and Theoretical Molecular Weights and Compositions of the Terpolymers and Their Precursors

Schematic Representation of Terpolymer Structure[a]	Theoretical Formula of Final Terpolymer	Blocks	Theoretical MW[b]	GPC Results		% mol composition	
				M_n	M_w/M_n	Theoretical	^{1}H NMR
	$HEGMA_5$-*b*-$DMAEMA_{11}$-*b*- $BzMA_{10}$	Homo	1850	2980	1.26		
		Diblock	3577	5650	1.10		
		Triblock	5337	7730	1.09	19–42–39	22–46–32
	$HEGMA_5$-*b*-$BzMA_{10}$-*b*-$DMAEMA_{11}$	Homo	1850	3950	1.11		
		Diblock	3610	5620	1.09		
		Triblock	5337	7420	1.09	19–39–42	20–37–43
	$DMAEMA_{11}$-*b*-$HEGMA_5$-*b*-$BzMA_{10}$	Homo	1827	2870	1.08		
		Diblock	3577	6380	1.08		
		Triblock	5337	8800	1.06	42–19–39	40–22–38
	$DMAEMA_{11}$-*co*-$HEGMA_5$-*co*-$BzMA_{10}$	Statistical	5337	8340	1.08	42–19–39	42–21–37

[a] The hydrophilic HEGMA units are shown in white, the marginally hydrophilic DMAEMA units are colored gray, and the hydrophobic BzMA units are painted black. [b] The MW of the initiator fragment of 100 g mol^{-1} is also included.

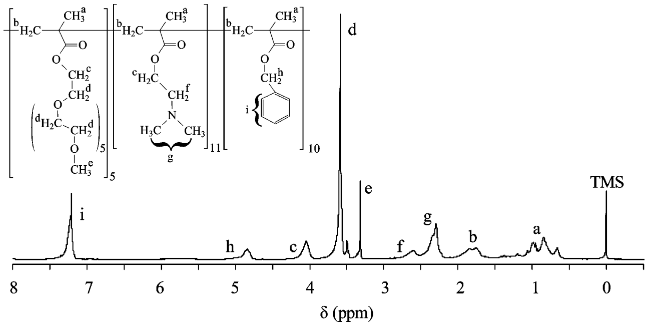

Figure 4. ^{1}H NMR spectrum of the HEGMA$_5$-*b*-DMAEMA$_{11}$-*b*-BzMA$_{10}$ triblock terpolymer in CDCl$_3$.

samples and the PMMA MW calibration standards. However, the polydispersities of the terpolymers are relatively low, in most cases <1.1.

The terpolymer compositions were calculated using ^{1}H NMR spectroscopy. Figure 4 shows the ^{1}H NMR spectrum and the theoretical chemical structure of the triblock terpolymer HEGMA$_5$-*b*-DMAEMA$_{11}$-*b*-BzMA$_{10}$, along with the relevant peak assignment. The characteristic peaks for each monomer repeat unit used for the calculation of the composition are as follows. For the HEGMA unit, the peak of the three methoxy protons **e** was chosen, whereas the six azamethyl protons **g** were the choice for DMAEMA. Finally, peak **h** of the two methylene protons next to the benzene ring was taken as the characteristic signal from BzMA. The molar compositions were calculated by ratioing the normalized areas of each of the three characteristic peaks to their sum. The results are shown in Table 1 and seem to agree well with the theoretical terpolymer compositions.

Aqueous Solution Characterization. The results from the characterization of aqueous solutions of the terpolymers are presented in Table 2 and assist in the elucidation of the structural organization of these materials in water.

Hydrodynamic Diameters. From previous studies on similar systems,[26] the three triblock terpolymers were expected to form micelles in aqueous solution, while the statistical terpolymer was expected to remain dissolved in the form of unimers in water. To confirm that the present terpolymers formed the expected structures, the relative magnitudes of the hydrodynamic diameters determined by dynamic light scattering were inspected. Moreover, the experimental hydrodynamic diameter of each terpolymer was compared to a theoretical estimation corresponding to the expected structure. These theoretical estimations are outlined in the following paragraph.

First, the calculations for the three triblocks are given. The two triblocks with the hydrophobic BzMA block at the end of the chain (and the other two hydrophilic blocks on the same side of the hydrophobic block) should form AB diblock copolymer type micelles, as shown in Figure 5. The triblock with the hydrophobic BzMA block in the middle of the chain should form ABA triblock copolymer type micelles which are smaller than the previous type of micelles and are also shown in Figure 5. The upper limit of the size of these two types of micelles, considering spherical shape, can be obtained by assuming fully stretched chains within the micelles. However, it must be recognized that the chains both in the shell and in the core are not fully stretched because of their natural trend to maximize configurational entropy. It is, therefore, stressed that the present calculation leads to a highest estimate for the size of the micelles.

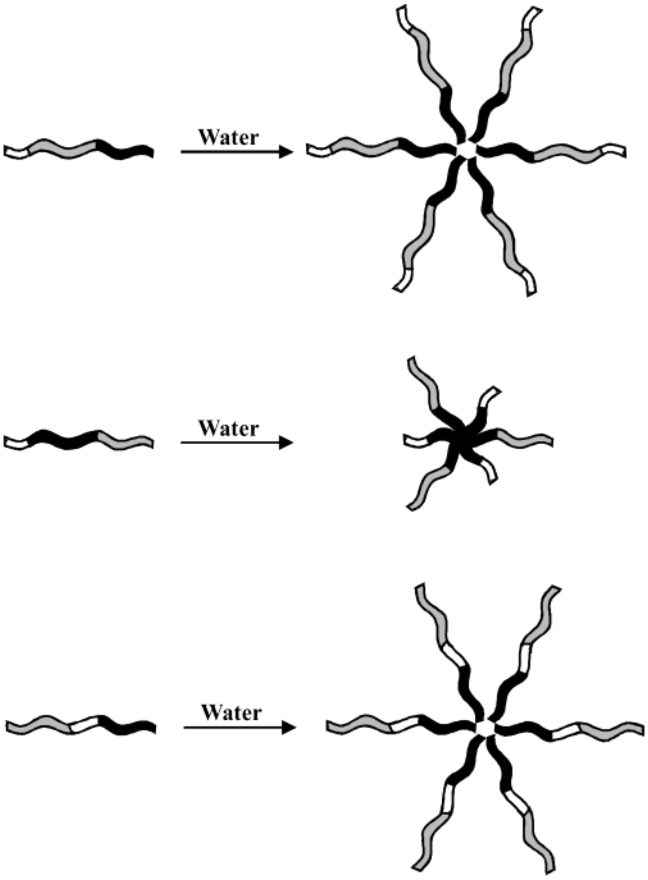

Figure 5. Schematic representation of the structures of the spherical micelles formed by the three ABC triblock terpolymers in aqueous solution.

In the case of AB diblock copolymer type micelles, the maximum theoretical spherical micellar diameter is equal to twice the contour length which can be calculated as the product of the overall degree of polymerization times 0.254 nm,[30a] the contribution of one monomer repeat unit to the chain length. This calculation gives maximum diameters of 13.2 nm, which are entered in Table 2. In the case of ABA triblock copolymer type micelles, the maximum theoretical spherical micellar diameter is equal to the sum of the contour length of the BzMA block plus twice the contour length of the longest block which is the DMAEMA block (note the compositional asymmetry in moles of these terpolymers; see also Figure 5). This calculation gives a maximum

Table 2. Results of Aqueous Solution Characterization of the Four Isomeric Terpolymers

	hydrodynamic diameter (nm)			
terpolymer theoretical formula	experimental	theoretical	cloud point (°C)	effective p*K*
HEGMA$_5$-*b*-DMAEMA$_{11}$-*b*-BzMA$_{10}$	8.9	13.2	65.8	6.4
HEGMA$_5$-*b*-BzMA$_{10}$-*b*-DMAEMA$_{11}$	7.3	8.1	59.6	6.8
DMAEMA$_{11}$-*b*-HEGMA$_5$-*b*-BzMA$_{10}$	9.0	13.2	66.6	6.5
DMAEMA$_{11}$-*co*-HEGMA$_5$-*co*-BzMA$_{10}$	5.5	3.2	47.5	6.5

diameter of 8.1 nm, which also appears in Table 2. Finally, to obtain an estimate for the size of the unimers formed by the statistical terpolymer, equations for random coils could be used. However, these equations require stiffness factors[30b] for each constituent monomer, and this factor is not available for HEGMA. Thus, the diameter of a solvent-free globule containing one collapsed terpolymer chain is calculated from the statistical terpolymer M_n and assuming spherical geometry, and it represents a lower limit for the size of the corresponding random coil. Using the measured value of 8340 g mol^{-1} for M_n, a globule diameter of 2.8 nm is calculated. To refine the result, a chain expansion parameter can be calculated using existing theories.[31] Using a value of 0.4 for the Flory−Huggins χ parameter for the interaction between water and the marginally water-soluble statistical terpolymer (its cloud point is 47.5 °C; see below), the value for the chain expansion parameter is determined to be 1.15, resulting in an estimate for the size of the unimer of 3.2 nm, which is entered in Table 2.

Comparing now the experimental hydrodynamic diameters with their theoretical estimates, both displayed in Table 2, we can see that there is an acceptable quantitative agreement between the two, although there are some deviations. In particular, for the triblocks the experimental diameters are always lower than the theoretical, reflecting some chain coiling within the micelles, whereas for the statistical terpolymer the experimental size is larger than the theoretical, indicating an underestimation for the theoretical value. However, the order in the experimental diameters is the same as that in the theoretical sizes, with the HEGMA-*b*-DMAEMA-*b*-BzMA and DMAEMA-*b*-HEGMA-*b*-BzMA triblocks exhibiting the largest diameters, followed by the HEGMA-*b*-BzMA-*b*-DMAEMA triblock, and with the statistical terpolymer having the smallest size. Thus, the agreement between experimentally measured and theoretically expected sizes is consistent with the originally assumed structures.

Cloud Points. The cloud points of the four terpolymers, as determined by turbidimetry, are also listed in Table 2. These values are lower by approximately 10 °C than those of a previous investigation[26] because of the greater hydrophobicity of the present terpolymers: these terpolymers have fewer HEGMA units and a BzMA rather than a MMA hydrophobic monomer repeat unit.[26] Triblock terpolymers HEGMA-*b*-DMAEMA-*b*-BzMA and DMAEMA-*b*-HEGMA-*b*-BzMA have the highest cloud points because they form the largest micelles, and they have the longest stabilizing segments composed of the HEGMA plus the DMAEMA blocks. According to the theory of steric stabilization of lyophobic colloidal particles (here the micelle is considered to be the particle), a greater length of the stabilizing chains confers better stability.[3b] The next lower cloud point is exhibited by the triblock terpolymer HEGMA-*b*-BzMA-*b*-DMAEMA which forms smaller micelles and has shorter stabilizing segments, the HEGMA and the DMAEMA blocks separately. The lowest cloud point is displayed by the statistical terpolymer which cannot form micelles at all.

Effective pKs. The effective p*K*s of the DMAEMA units in the terpolymers were determined to be around 6.5, although they were expected to be around 7.0, according to previous investigations on linear copolymers bearing DMAEMA units.[32] The lower values of the p*K*s might be due to the higher hydrophobicity of the terpolymers, which further lowers the local dielectric constant, rendering the ionization of the DMAEMA units more difficult.[32] For all the terpolymer solutions, no precipitation occurred during the titrations from pH 2 to 12.

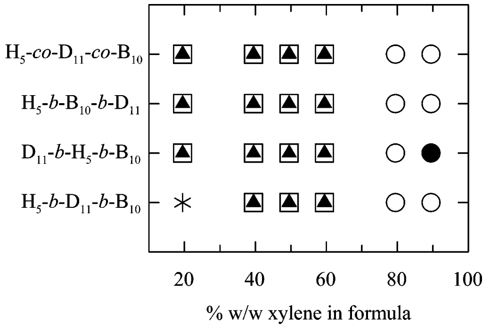

Figure 6. Phase diagram for xylene−water emulsions stabilized using 1% w/w terpolymer as a function of the % w/w emulsion content in xylene and the architecture of the terpolymer. Open circles: stable, low-viscosity, single-phase o/w emulsions; closed circles: stable, high-viscosity (gels), single-phase o/w emulsions; stars: systems that broke down to their three ingredients, terpolymer, xylene, and water; closed 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.

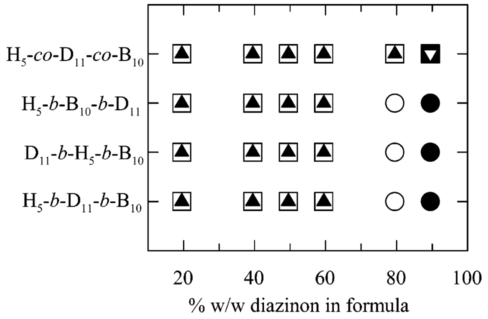

Figure 7. Phase diagram for diazinon−water emulsions stabilized using 1% w/w terpolymer as a function of the % w/w emulsion content in diazinon and the architecture of the terpolymer. The symbols used are the same as those used in Figure 6.

Emulsion Phase Diagrams. All four HEGMA−DMAEMA−BzMA terpolymers were used to produce xylene−water and diazinon−water emulsions at different ratios of the organic/water phase. The results for the xylene−water emulsions are shown in Figure 6, whereas those for the diazinon−water emulsions are shown in Figure 7. One general observation is that all resulting emulsions were of the o/w type (no w/o emulsion was observed), which is consistent with the hydrophilic character of the terpolymers,[2] bearing 66% w/w of hydrophilic (HEGMA plus DMAEMA) units.

Figure 6 is the phase diagram for the xylene−water emulsions as a function of the % w/w emulsion content in xylene and the terpolymer architecture. The symbols used in the figure are explained in the figure legend. The main features of the phase diagram presented in Figure 6 were the following: at values between 1/4 and 3/2 w/w of the xylene/water ratio, all terpolymers mostly gave o/w emulsions coexisting with excess water phase in the bottom. 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/water weight ratio became 4/1, the cream layer in the emulsions of all four terpolymers expanded to occupy the whole height of the system, resulting in stable, single-phase o/w emulsions of low viscosity. When the xylene/water ratio was increased to 9/1 w/w, most of the emulsions remained as before (xylene/water ratio of 4/1), indicating that this was the maximum capacity of the terpolymers in xylene. However, in the case of the DMAEMA-*b*-HEGMA-*b*-BzMA triblock terpolymer at the 9/1 xylene/water ratio, the resulting single-phase o/w emulsion was of high viscosity, which is 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 the oil droplets, which were in contact and adhered with one another, creating a network of droplets.[34] Thus, for the particular emulsion experiment, there is no significant discrepancy among the terpolymers.

The size of the droplets of the emulsions at the 4/1 xylene/water ratio, all of which led to single-phase systems, was determined using optical microscopy and provided a measure for the emulsification efficiency of each terpolymer. The triblock with a BzMA middle block resulted in emulsions with the smallest xylene droplets, 2−5 μm, and this is, therefore, the best emulsifier among the four terpolymers. The two triblocks with BzMA end blocks provided emulsions with xylene droplets of intermediate size, 5−10 μm. Finally, the statistical terpolymer led to emulsions with the largest xylene droplets, 10−20 μm, suggesting that this is the least efficient stabilizer. Thus, the droplet size measurements rank the terpolymers in the following order of decreasing emulsification efficiency: HEGMA$_5$-*b*-BzMA$_{10}$-*b*-DMAEMA$_{11}$ > HEGMA$_5$-*b*-DMAEMA$_{11}$-*b*-BzMA$_{10}$ ∼ DMAEMA$_{11}$-*b*-HEGMA$_5$-*b*-BzMA$_{10}$ > HEGMA$_5$-*co*-DMAEMA$_{11}$-*co*-BzMA$_{10}$.

Figure 7 is the phase diagram for the diazinon−water emulsions as a function of the % w/w emulsion content in diazinon and the terpolymer architecture. The symbols used here are the same as those used in Figure 6. The first observation was the absence of star symbols anywhere in Figure 7. Thus, in the diazinon−water system, no terpolymer precipitation was observed, even at low values (1/4 w/w) of the organic phase/water ratio. At values between 1/4 and 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 emulsions 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} [35a]) than water as compared to the lower density of xylene ($\rho = 0.861$ g mL^{-1} [35b]) than water. Single-phase, o/w emulsions of low viscosity were observed 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, the three triblock terpolymers gave single-phase o/w emulsions, while the statistical terpolymer gave an o/w emulsion coexisting with excess water. At a 9/1 w/w diazinon−water ratio, two possibilities existed: either emulsions coexisting with excess oil (statistical terpolymer) or single-phase, o/w emulsions of high viscosity (the three triblock terpolymers). From the results at 4/1 and 9/1 w/w diazinon/water ratios, we also observed that the triblock terpolymers are better stabilizers than the statistical terpolymer for the diazinon−water emulsions because the latter failed to stabilize single-phase o/w emulsions.

Conclusions

Three ABC triblock terpolymers and one statistical terpolymer were synthesized using group transfer polymerization and were characterized in aqueous solution. Because of the different distributions of the three monomer repeat units, each of the four isomeric terpolymers exhibited a unique behavior in aqueous solution, forming a different type of aggregates. These terpolymers succeeded in emulsifying xylene and diazinon in water. The emulsion droplet size measurements suggest that the emulsifier efficiency is in the order HEGMA$_5$-*b*-BzMA$_{10}$-*b*-DMAEMA$_{11}$ > HEGMA$_5$-*b*-DMAEMA$_{11}$-*b*-BzMA$_{10}$ ∼ DMAEMA$_{11}$-*b*-HEGMA$_5$-*b*-BzMA$_{10}$ > HEGMA$_5$-*co*-DMAEMA$_{11}$-*co*-BzMA$_{10}$.

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