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Amphiphilic diblock and ABC triblock methacrylate copolymers: synthesis and aqueous solution characterization

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Abstract

Three isomeric, linear, equimolar, amphiphilic ABC triblock copolymers comprising methyl methacrylate (MMA, nonionic hydrophobic), 2-(dimethylamino)ethyl methacrylate, (DMAEMA, ionizable hydrophilic) and hexa(ethylene glycol) methacrylate (HEGMA, nonionic hydrophilic) units (10 units in each block) were synthesized by group transfer polymerization (GTP). These were the three block sequence isomers, ABC, ACB and BAC. The corresponding random terpolymer was also prepared. The molecular weights and compositions of all the polymers were characterized by GPC and ^{1}H NMR. Measurements of the hydrodynamic diameters and cloud points of the copolymers in aqueous solution suggest that the various distributions of monomer units in the four terpolymers (the three triblocks and the random) result in different supramolecular structures with different colloidal stabilities. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: ABC triblock copolymers; Block sequence; Amphiphilic polymers

1. Introduction

Following the intense interest in the study of diblock and ABA triblock copolymers [1], the polymer community starts now to focus on a new type of block copolymers, that of ABC triblock copolymers [2] comprising three blocks, each made of a different monomer repeat unit. The presence of three different monomers placed in different blocks confers to these polymers, three rather than two functions. Thus, ABC triblock copolymers of sufficiently high molecular weight (MW) and sufficient incompatibility between the blocks can form three rather than two microphases in the bulk [2]. Although some of these morphologies are direct extensions of the type of microphases encountered in diblock and ABA triblock copolymers, such as trilamellae [3] and cylinders or spheres at dilamellar interfaces [4], some others are exotic patterns unique to ABC triblock copolymers, such as cylinders surrounded by rings [5] or helices [6] embedded in a continuous matrix.

The solution behavior of ABC triblock copolymers has been explored to a much smaller degree than their properties in the bulk [5,7,8]. A limited number of studies focus on the micellization of these copolymers in solvents, selective for one or two of the blocks [9,10]. In the former case, a micelle with a microphase-separated core was observed [11]. The composite core was created by the mutual incompatibility of the two solvent-insoluble blocks. Our own studies involved ABC triblock copolymers in solvents selective for two of the blocks [12–14]. The present work extends our previous studies with the aim to explore the effect of block sequence on the behavior of ABC triblock copolymers in water.

2. Experimental section

2.1. Materials and methods

The chemical formulas and names of the three monomers, methyl methacrylate (MMA), hexa(ethylene glycol) methacrylate (HEGMA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA), and the group transfer polymerization (GTP) initiator, 1-methoxy-1-trimethylsiloxy-2-methyl propene (MTS), are shown in Fig. 1. HEGMA is not a pure compound, and there is a distribution of ethylene glycol units in it, with their average number per monomer being between 6 and 7. DMAEMA and MTS were purchased from Aldrich, Germany, while HEGMA was kindly donated by Inspec, UK. All monomers were passed 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 tetrahydrofuran (THF) of the HEGMA monomer was used for processing with basic alumina. The HEGMA monomer

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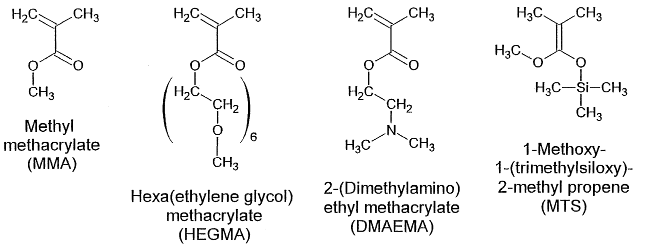


Fig. 1. Chemical formulas of the monomers and initiator used for the block copolymer synthesis.

solution was passed twice through basic alumina columns while DMAEMA and MMA were passed only once due to the high initial purity of these monomers. DMAEMA and MMA were stirred overnight over calcium hydride (to remove the last traces of moisture and protic impurities) in the presence of a free-radical inhibitor, 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH), and were vacuum-distilled just prior to use. The HEGMA solution was stirred over calcium hydride (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 catalyst used for the polymerization, tetrabutylammonium bibenzoate (TBABB) was prepared according to Dicker et al. [15] and kept under vacuum until use.

2.2. Polymer synthesis

A typical polymerization procedure yielding the ABC triblock with block sequence HEGMA–MMA–DMAEMA with 10 units in each block and overall theoretical MW 6170 g mol^{-1} is detailed later. To a 100 mL round bottom flask containing a small amount (~10 mg) of TBABB were syringed 15 mL of freshly distilled THF and 0.20 mL of MTS initiator (1.0 mmol) in this order. 6.6 mL of a 50% v/v solution of HEGMA (9.9 mmol) in THF were slowly added under stirring. The polymerization exotherm (26.3–31.6 °C) abated within 5 min, samples for GPC were extracted, and 1.0 mL of MMA (9.4 mmol) were added which produced an exotherm (30.7–35.8 °C). Samples for GPC of the HEGMA–MMA diblock copolymer were extracted. Finally, 1.7 mL of DMAEMA (10.0 mmol) were added to the polymerization solution, resulting in an exotherm from 34.0 to 37.8 °C. The polymer was recovered by precipitation in *n*-hexane and dried for three days in a vacuum oven at room temperature.

2.3. Characterization by GPC and ^{1}H NMR

Homopolymer, diblock and triblock copolymer samples 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 'D' column. The eluent was THF, pumped at 1 mL min^{-1}. The MW calibration was based on six narrow MW (630, 1400, 4250, 7600, 13000 and 28900 g mol^{-1}) polyMMA standards also supplied by Polymer Laboratories. The ^{1}H NMR spectra of polymer solutions in deuterated chloroform were recorded using a 300 MHz AVANCE Bruker spectrometer equipped with an Ultrashield magnet.

2.4. Aqueous solution characterization

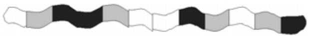
1% w/w aqueous salt-free solutions of the copolymers were characterized in terms of their hydrodynamic diameters, cloud points and effective p*K*s, using dynamic light scattering, turbidimetry, and hydrogen ion titration, respectively. In the dynamic light scattering and the turbidimetry experiments, the polymer solutions used were obtained by dissolving neutral polymer into deionized water so that the DMAEMA units were uncharged and the resulting pH ~ 8. A 90 Plus 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 runs were performed for each polymer 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 polymer solutions were filtered through 0.45 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 polymer 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 93 °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. 5 g of 1% w/w solutions of each polymer were titrated between pH 2 and 12 using a standard NaOH 0.5 M solution with 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.

3. Results and discussion

3.1. Polymer synthesis

ABC triblock copolymers have been synthesized using various 'living' polymerization techniques [16], including anionic [3,5,6,17,18], living cationic [13], GTP [11,12,14]

Table 1
MW and composition analysis of the copolymers and their precursors

No.	Polymer representation	Polymer theoretical formula	Theoretical MW[a]	M_n by GPC[b]	M_w/M_n by GPC	Theoretical composition (mol%)	Composition by NMR (mol%)
1		HEGMA_{10}	3600	5600	1.09		
		HEGMA_{10}-*b*-MMA_{10}	4600	6500	1.09	50–50	47–53
2		HEGMA_{10}	3600	5900	1.09		
		HEGMA_{10}-*b*-DMAEMA_{10}	5170	6150	1.09	50–50	48–52
3		DMAEMA_{10}	1670	1700	1.28		
		DMAEMA_{10}-*b*-MMA_{10}	2670	3600	1.10	50–50	47–53
4		DMAEMA_{10}	1670	3800	1.07		
		DMAEMA_{10}-*b*-HEGMA_{10}	5170	10100	1.15		
		DMAEMA_{10}-*b*-HEGMA_{10}-*b*-MMA_{10}	6170	11500	1.18	33–33–33	31–33–36
5		HEGMA_{10}	3600	7850	1.08		
		HEGMA_{10}-*b*-MMA_{10}	4600	9700	1.08		
		HEGMA_{10}-*b*-MMA_{10}-*b*-DMAEMA_{10}	6170	13050	1.09	33–33–33	34–30–36
6		HEGMA_{10}	3600	7550	1.08		
		HEGMA_{10}-*b*-DMAEMA_{10}	5170	9300	1.08		
		HEGMA_{10}-*b*-DMAEMA_{10}-*b*-MMA_{10}	6170	11250	1.09	33–33–33	34–35–31
7		(HEGMA-*co*-DMAEMA-*co*-MMA)$_{10}$	6170	13250	1.08	33–33–33	32–34–34

[a] Contribution from initiator fragment of 100 g mol^{-1} included.
[b] Based on a calibration using PMMA standards of narrow MWD.

and, more recently, living free-radical polymerization [19]. However, due to its main applicability to methacrylate monomers which present similar reactivities, GTP is the most appropriate synthetic method for the preparation of ABC triblock copolymers of all the possible block sequences as well as statistical (random) terpolymers. Thus, GTP was the polymerization method of choice for the present syntheses. The polymers synthesized, including a schematic representation of their structure, are shown in Table 1. The ABC, the ACB and the BAC triblocks, as well as the random terpolymer were prepared. The four terpolymers were equimolar isomers with a theoretical degree of polymerization 30, containing 10 repeat units from each of the three different monomers. The three diblock copolymers derived from the pairwise combinations of the three different monomer units were also prepared.

3.2. Analysis by GPC in THF

The number average MWs (M_ns) and polydispersities (M_w/M_n) of all copolymers and their precursors, as determined by GPC, are also shown in Table 1. The polydispersities of all samples are lower than 1.3, and those of the copolymers are about 1.1. The MW distributions of all samples are unimodal (data not shown). The M_ns are about twice as high as the theoretically predicted, because of differences of the DMAEMA and HEGMA units with the PMMA MW calibration standards and possible partial initiator deactivation.

3.3. ^{1}H NMR analysis in $CDCl_3$

Fig. 2 shows the ^{1}H NMR spectrum of a particular ABC triblock copolymer. The signals from protons c, i and f of the three monomer repeat units, MMA, DMAEMA and HEGMA, respectively, were chosen to calculate polymer composition. The signal from protons c of MMA was calculated by subtracting the contribution from HEGMA in the joint c, e peak at 3.7 ppm. The experimentally calculated copolymer compositions are presented again in Table 1 and seem to agree well with the theoretical copolymer compositions, also shown.

3.4. Hydrodynamic sizes in aqueous solution

The hydrodynamic diameters of aqueous polymer solutions measured at room temperature are displayed in Table 2. With the exception of polymers 2 and 7, all other polymers form micelles because their measured diameters are much higher than those corresponding to random coil dimensions of approximately 2 nm for the given MW range [20]. Diblock copolymer 2 lacks any hydrophobic MMA units, while the MMA hydrophobic units are randomly distributed in random terpolymer 7. Thus, there is none or not enough hydrophobic force to drive micellization in aqueous solutions of polymers 2 and 7. The size of the micelles of diblock copolymer 1 is larger than that of diblock copolymer 3 probably due to the bulky nature of the HEGMA units compared to DMAEMA. The micellar size of triblocks 4 and 6 is larger than that of diblocks 1 and 3 due to the greater overall degree of polymerization of the triblocks. Triblock 5 forms micelles with half the size of its isomers, triblocks 4 and 6, due to the placement of the hydrophobic MMA units in the midblock in the former case, while in the endblock in the latter (Fig. 3). Thus, the hydrodynamic diameter of the micelles formed by triblock 5

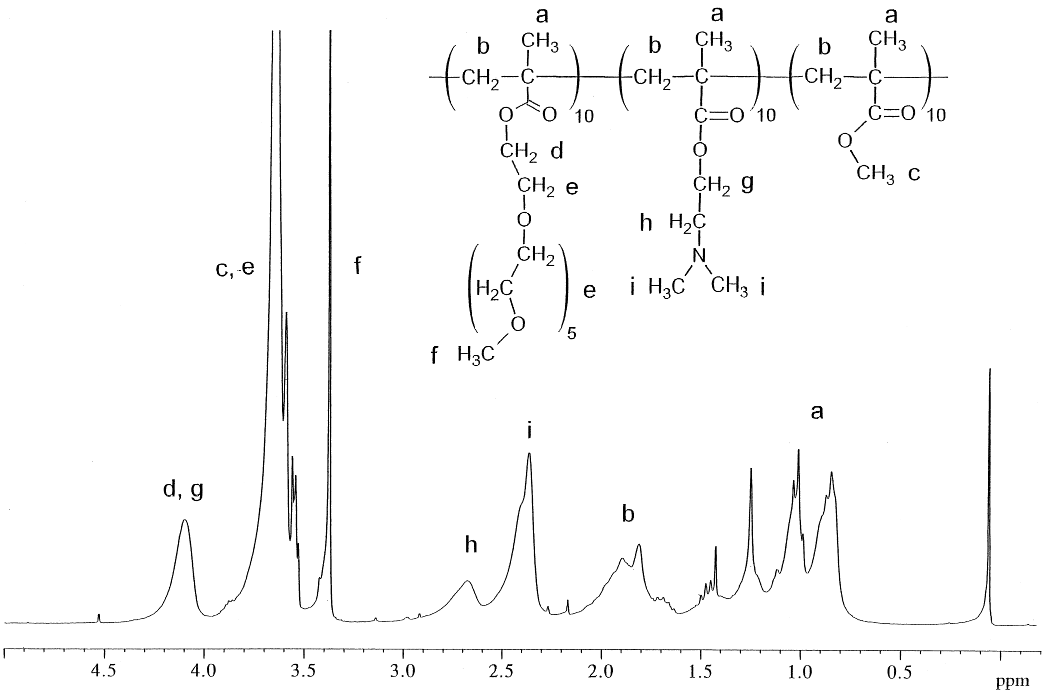


Fig. 2. ^{1}H NMR spectrum of the HEGMA–DMAEMA–MMA ABC triblock copolymer in CDCl$_3$.

is expected to be approximately equal to the chain contour length, while the hydrodynamic radius of the micelles of triblocks 4 and 6 should be approximately equal to the same chain contour length. This calculation assumes formation of spherical micelles and fully stretched chains within the micelles, justified by the tendency of the amphiphilic polymers to pack in a sphere and at the greatest possible numbers in order to minimize the interfacial area per chain. To test this simple model, Table 2 shows a calculation of the micellar diameters assuming fully stretched chains. The chain contour lengths were estimated as the product of the theoretical degree of polymerization times the contribution of one monomer repeat unit of 0.254 nm. All micellar diameters were calculated by doubling the contour lengths, except for triblock 5. The theoretically calculated hydrodynamic diameters are reasonably close to the experimentally measured ones, and consistently higher suggesting some chain coiling.

3.5. Cloud points in aqueous solution

The cloud points of all the copolymers are also listed in Table 2. The main observation from the table is that, with the exception of statistical terpolymer 7 and the most

Table 2
Hydrodynamic diameters and cloud points of 1% (w/w) aqueous solutions of the polymers

No.	Polymer formula	Hydrodynamic diameter (nm)		Cloud point (°C)
		Experimental[a]	Theoretical	
1	HEGMA$_{10}$-*b*-MMA$_{10}$	8.2	10.0[b]	72.3
2	HEGMA$_{10}$-*b*-DMAEMA$_{10}$	4.3	1.7[c]	79.8
3	DMAEMA$_{10}$-*b*-MMA$_{10}$	6.8	10.0[b]	36.1
4	DMAEMA$_{10}$-*b*-HEGMA$_{10}$-*b*-MMA$_{10}$	11.0	15.0[b]	80.0
5	HEGMA$_{10}$-*b*-MMA$_{10}$-*b*-DMAEMA$_{10}$	6.4	7.5[b]	80.7
6	HEGMA$_{10}$-*b*-DMAEMA$_{10}$-*b*-MMA$_{10}$	12.0	15.0[b]	89.5
7	(HEGMA-*co*-DMAEMA-*co*-MMA)$_{10}$	4.5	2.0[c]	57.2

[a] Determined from MSD analysis.

[b] Calculated assuming fully stretched chains within spherical micelles; the chain contour length was estimated as the product of the theoretical degree of polymerization times the contribution of one monomer repeat unit of 0.254 nm.

[c] Calculated using random flight statistics corrected for the carbon tetrahedral angle and using PMMA's stiffness factor of 2.20 [20]. In particular, the formula used to calculate the root mean-square diameter of gyration was $\langle d_g^2 \rangle^{1/2} = 2 \times (2 \times 2.20 \times \mathrm{DP}/3)^{1/2} \times 0.154$ nm, where DP is the degree of polymerization and 0.154 nm is the length of one carbon–carbon bond.

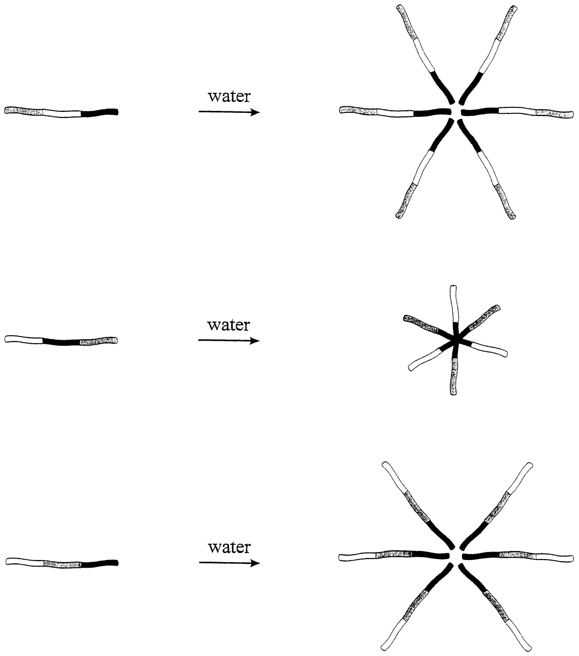


Fig. 3. Schematic representation of the structures of the spherical micelles formed by the three ABC triblock copolymers in aqueous solution.

hydrophobic diblock copolymer 3, all other copolymers have cloud points above 70 °C. The statistical terpolymer exhibited a cloud point of 57 °C. This polymer cannot form micelles, confirmed by dynamic light scattering, due to the random distribution of its hydrophobic units, which remain unshielded from the aqueous solvent, thereby facilitating its precipitation. Focusing now on the diblocks, they precipitate in the expected order. Their cloud points increase with their hydrophilicity. Thus, diblock 3 which is based on the two most hydrophobic components, MMA and DMAEMA precipitates more easily than polymers 1 and 2, while diblock 2 consisting only of hydrophilic units, has the highest cloud point of all three.

From the ABC triblocks, polymers 4 and 5 have similar cloud points while polymer 6 precipitates at a higher temperature. This difference in the cloud points is attributed to the location within the micelles of the temperature-sensitive DMAEMA block which has a precipitation temperature of 45 °C. As shown in Fig. 3, the micelles of triblocks 4 and 5 have DMAEMA in the outer region of their corona, while the DMAEMA is located between the core and the outermost HEGMA shell in the case of triblock 6. Given the very slow kinetics of polymer rearrangement within block copolymer micelles, particularly in the presence of a glassy PMMA micellar core, above 45 °C the hydrophobic DMAEMA units in the micelles of triblocks 4 and 5 will promote interparticle association, and therefore precipitation, to a greater extent than the protected DMAEMA units in the micelles of polymer 6. This explains the higher cloud point of triblock 6 compared to 4 and 5.

3.6. Hydrogen ion titrations

The effective p*K*s of the DMAEMA units in all the copolymers (except diblock 1 which is DMAEMA-free) were determined to be around 7.0, in agreement with previous investigations on DMAEMA-containing linear polymers [21]. All copolymer solutions remained optically clear during their titrations between pH 2 and 12.

4. Conclusions

In conclusion, this study involved the synthesis and aqueous solution characterization of the three block sequence isomers, triblock copolymers ABC, ACB and BAC, as well as their statistical isomer. The different distributions of monomer units in the four terpolymers are responsible for the different supramolecular structures observed in aqueous solution, which lead to different colloidal stabilities for the solution of each polymer. Future work will involve the synthesis of triblock copolymers based on different monomer combinations, such as two hydrophobic and one hydrophilic, and the investigation of the aqueous solution properties with respect to block sequence.

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