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Micelles and 'reverse micelles' with a novel water-soluble diblock copolymer

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ABSTRACT

A series of poly[2-(diisopropylamino)ethyl methacrylate]-*block*-poly[2-(*N*-morpholino)ethyl methacrylate], [PDPA-*b*-PMEMA], have been synthesized by using group transfer polymerization. These novel PDPA-*b*-PMEMA diblock copolymers dissolved molecularly in aqueous solution at low pH (<6.0) due to the protonation of all tertiary amine residues of both blocks and formed PDPA-core micelles at pH 7.5 by PMEMA block forming the micelle coronas. On the other hand, it was also observed that these diblock copolymers formed near-monodisperse 'reverse micelles', PMEMA-core micelles, in *n*-alkanes with or without requiring cosolvent depending on comonomer ratios. Dynamic light scattering studies indicated monodisperse or near-monodisperse micelles in both cases. The intensity-average radii of the PDPA-core and the PMEMA-core micelles were between 10 nm and 17 nm (polydispersity index, $\mu_2/\Gamma^2 < 0.08$) and between 10 nm and 13 nm in *n*-hexane ($\mu_2/\Gamma^2 < 0.09$), respectively.

1. Introduction

During the last decade, double-hydrophilic diblock copolymers having pH-, salt-, and temperature-responsive characters have attracted considerable interests due to their potential applications [1,2]. These applications have so far included drug carrier systems and gene therapy [3–5], switchable amphiphiles [6,7], mineralization templates [8] and crystal growth modifiers [9], induced nanoreactors for metal colloid synthesis [10], desalination membranes [11] and polymeric water-in-water emulsions of two incompatible polymers [12,13] just to name a few. Such diblock copolymers are fully soluble in water as unimers under certain conditions. But one of the blocks can be independently tuned to become hydrophobic by subtle adjustment of the solution temperature, solution pH or ionic strength, and thus, they form well-defined core–shell micelles in aqueous solution. For example, ethylene glycol-, (meth)acrylic acid- and *N*-isopropylacrylamide-based diblock copolymers have been reported as pH- and thermo-responsive diblock copolymers and studied in detail. Poly(ethylene glycol)-*block*-poly(*N*-isopropylacrylamide) (PEG-*b*-PNIPAM) [14] and poly(*N*-isopropylacrylamide)-*block*-poly(acrylic acid) (PNIPAM-*b*-PAA) [15] diblock copolymers form PNIPAM-core micelles at high temperatures (>32 °C) at neutral pH and alkaline solutions. Poly(styrenesulfonic acid)-*block*-poly(methacrylic acid) [16], and poly(ethylene glycol)-*block*-poly(methacrylic acid) (PEG-*b*-PMAA) [17], form PMAA-core micelles at low pH values due to desolvation of non-ionized carboxylic acid groups of PMAA.

Since 1997 numerous examples of novel water-soluble diblock copolymers having weak basic character of both blocks based on tertiary amine methacrylates and their selectively quaternized derivatives have also been reported [18–20]. Such diblock copolymers exhibit pH-, salt-, and temperature-responsive characters and show high surface activity. For instance, poly[2-(dimethylamino)ethyl methacrylate]-*block*-poly[2-(diethylamino)ethyl methacrylate], [PDMA-*b*-PDEA], poly[2-(dimethylamino)ethyl methacrylate]-*block*-poly[2-(diisopropylamino)ethyl methacrylate], [PDMA-*b*-PDPA], and poly[2-(dimethylamino)ethyl methacrylate]-*block*-poly[2-(*N*-morpholino)ethyl methacrylate], [PDMA-*b*-PMEMA], synthesized by using group transfer polymerization (GTP) are molecularly soluble in acidic solution due to the protonation of the tertiary amine residues [18–20]. But PDEA and PDPA blocks of the PDMA-*b*-PDEA and PDMA-*b*-PDPA diblock copolymers can be tuned to become hydrophobic by increasing the solution pH while the PMEMA block of the PDMA-*b*-PMEMA diblock copolymer can be tuned to become water-insoluble by the addition of electrolyte due to salting-out effect or by an increase on solution temperature. Thus, they form well-defined core–shell micelles (PDEA-core, PDPA-core and PMEMA-core micelles) in the absence of any organic cosolvent. Micelles of such diblock copolymers and their cationic derivatives spontaneously form an adsorbed layer at the mica and silica aqueous solution interface due to favorable electrostatic interactions [21–25].

One new class of such diblock copolymers were 'schizophrenic' diblock copolymers in which the individual blocks can be independently tuned to become either hydrophilic or hydrophobic by changing the solution pH, temperature and/or ionic strength

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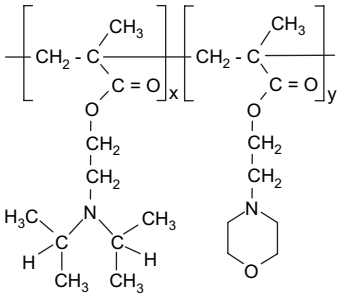

Fig. 1. Chemical structure of the PDPA-*b*-PMEMA diblock copolymer synthesized by using group transfer polymerization.

[26–33]. The original report in this new sub-field involved a tertiary amine methacrylate-based AB diblock copolymer, poly[2-(diethylamino)ethyl methacrylate]-*block*-poly[2-(*N*-morpholino)ethyl methacrylate] (PDEA-*b*-PMEMA) [7,26,27], synthesized by GTP, that was both pH- and salt-responsive, allowing the formation of either PMEMA-core micelles or PDEA-core 'reverse micelles' in aqueous solution with the diameter of 26 nm and 33 nm, respectively.

In recent years, there has been great interest on such 'schizophrenic' diblock copolymers. For instance, poly[*N*-(morpholino)ethyl methacrylate]-*block*-poly[4-(2-sulfoethyl)-1-(4-vinylbenzyl)pyridinium betaine] (PMEMA-*b*-PSVBP) was synthesized *via* reversible addition–fragmentation chain transfer polymerization and exhibited purely salt-responsive 'schizophrenic' micellization behaviour in aqueous media [31]. The same research group has also reported poly(*N*-isopropylacrylamide)-*block*-poly(L-glutamic acid) (PNIPAM-*b*-PLGA) as novel 'schizophrenic' diblock copolymer which molecularly dissolved in aqueous solution at alkaline pH and room temperature but supramolecularly self-assembled into PNIPAM-core micelles at alkaline pH and elevated temperatures and PLGA-core micelles at acidic pH and room temperature accompanied with coil-to-helix transition of the PLGA sequence [32].

A novel zwitterionic PMAA-*b*-PDEA diblock copolymer having only pH-responsive 'schizophrenic' micellization behaviour in aqueous media was reported by Mao et al. This block copolymer formed PMAA-core micelles at pH 2 and PDEA-core micelles at pH 12. In the presence of electrolyte (0.3 M NaCl), the size of the PMAA-core micelles reduced by almost half while the aggregation number was little changed. On the other hand, addition of NaCl had only a small effect on PDEA-core micelle diameter [33].

It is also well known that small molecule surfactants can form micelles and 'reverse micelles' in aqueous and nonaqueous media, respectively. It is also possible to obtain micelles and 'reverse micelles' from the same diblock copolymer by choosing appropriate selective solvents. For example, double hydrophobic polystyrene-*block*-polybutadiene diblock copolymers can form micelles with either polystyrene cores (in *n*-alkanes) or polybutadiene cores (in DMF or MEK) [34]. Similarly, hydrophobic–hydrophilic diblock copolymers, such as polystyrene-*block*-poly(methacrylic acid), polystyrene-*block*-poly(ethylene oxide), poly(methyl methacrylate)-*block*-poly(acrylic acid), can form micelles in aqueous media and 'reverse micelles' in non-polar system [1]. In both cases, near-monodisperse micelle formations require additional cosolvent.

Recently, Babin et al. have demonstrated the use of atom transfer radical polymerization (ATRP) to graft polymers onto preformed shell cross-linked reverse micelles (SCRM). Reverse micelles were first obtained in organic solvents and stabilized by cross-linking of the solvated shell using the photoinduced dimerization of coumarin groups in the PDMA-*block*-P(MMA-*co*-CMA) copolymer. The structurally locked SCRM is then used as micellar macroinitiators for further polymerization from their surface of monomers such as styrene and DMA *via* ATRP. The decoration of an outer corona of PDMA rendered the nanoparticles containing a hydrophilic core soluble in water, with the solubility being sensitive to solution pH and temperature [35].

Prior to our study we were not aware of any literature examples of double-hydrophilic AB diblock copolymers having weak basic character on both blocks, which are capable of forming both micelles in aqueous media (A block in the core) and 'reverse micelles' (B block in the core) in *n*-alkanes without requiring any cosolvent.

Herein we describe the synthesis of a series of double-hydrophilic diblock copolymers, poly[2-(diisopropylamino)ethyl methacrylate]-*block*-poly[2-(*N*-morpholino)ethyl methacrylate], (PDPA-*b*-PMEMA, Fig. 1), by GTP *via* sequential monomer addition. The PDPA-*b*-PMEMA diblock copolymers are completely soluble in acidic solution (pH < 6) and form PDPA-core micelles in aqueous media above pH 6.4. It also forms PMEMA-core micelles (reverse micelles) in *n*-alkanes with or without requiring cosolvent (see Fig. 2). In both cases, the DLS studies indicated monodisperse or near-monodisperse micelle formations.

2. Experimental

2.1. General protocols

Group transfer polymerization (GTP) was used to synthesize tertiary amine methacrylate-based diblock copolymers with narrow polydispersity indexes and well-controlled molecular weights and comonomer compositions in THF at 20 °C. All chemicals were purchased from Aldrich, unless otherwise stated. All glasswares and transfer needles were dried by storing in an oven overnight at 140 °C before use. All reactions were carried out under dry nitrogen. In order to eliminate surface moisture, all glasswares were directly assembled from the oven, flamed out under high vacuum (10^{-4}–10^{-5} Torr) and allowed to cool to room temperature. Nitrogen was passed through both a silica column and a P_2O_5 drying column prior to use.

Tetrahydrofuran (THF; Labscan) was initially dried over sodium wire and refluxed over potassium for three days before use. The

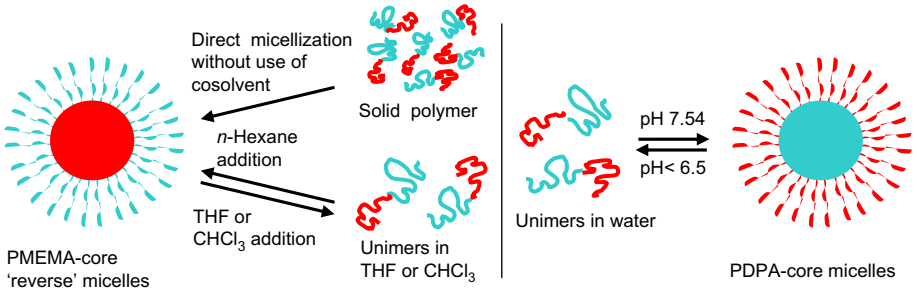

Fig. 2. Schematic representation of the micelle and 'reverse micelle' formation exhibited by a PDPA-*b*-PMEMA diblock copolymer in both dilute aqueous solution and *n*-alkanes: Micelles with PDPA-core are formed above pH 7.5 in aqueous solution, whereas PMEMA-core micelles can be formed in *n*-alkanes.

Table 1
Copolymer compositions, number average molecular weights (M_ns), polydispersity indexes (M_ws/M_ns) and degrees of polymerizations (DP_ns) for the PDPA-*b*-PMEMA diblock copolymers

Polymer code	M_n (g/mol, theory)	DPA content of the copolymer (mol%, theory)	M_n[a] (g/mol)	M_w/M_n[a]	DP_n[b]	DPA content of the copolymer[b] (mol%)
I	12,000	80	14,800	1.06	–	81
II	18,000	80	21,900	1.12	–	84
III	22,000	80	26,500	1.07	–	80
IV	10,000	20	10,241	1.10	13–55	19
V	10,300	23	12,100	1.12	15–57	21
VI	18,000	20	19,400	1.10	18–77	19
VII	18,000	30	19,000	1.14	36–74	33

[a] As determined by GPC [calibrated with poly(methyl methacrylate) standards].
[b] As determined by ^{1}H NMR spectroscopy using the GTP initiator fragment as an end group and relevant signals of both blocks.

dried THF was stored over 4 Å molecular sieves at room temperature and transferred into the reaction vessel *via* cannula. MEMA (Polyscience Inc.) and DPA (SP2) were each passed in turn through a basic alumina column to remove the hydroquinone methyl ether inhibitor, stirred over calcium hydride, the less volatile 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH) inhibitor was added and then stored at −20 °C. The monomers were each distilled under reduced pressure before transferring into the reaction vessel by cannula under a dry nitrogen atmosphere. 1-Methoxy-1-trimethylsiloxy-2-methyl-1-propane (MTS) was distilled and stored at −20 °C in a graduated Schlenk flask under dry nitrogen prior to use. Tetra-*n*-butyl ammonium bibenzoate (TBABB) was prepared by the method of Dicker et al. [36] and stored under dry nitrogen.

2.1.1. Synthesis of tertiary amine methacrylate-based diblock copolymers

To synthesize a PMEMA-rich PDPA-*b*-PMEMA diblock copolymer by group transfer polymerization (GTP), the solid TBABB catalyst (approximately 100 mg) was added from a side arm under a nitrogen purge into a 250 mL three-necked round bottom flask. THF (approximately 150 mL) was then transferred into the flask *via* cannula before the addition of MTS (0.30 mL). This solution was stirred for 15 min and then first monomer (4.0 mL DPA) was added by cannula. In the meantime, a contact thermocouple was attached to the side of the reaction vessel to monitor the exotherm during the addition of monomer. It was observed that the reaction temperature typically increased by 1.5 °C, which depends on monomer/solvent ratio. The reaction mixture was stirred until the solution temperature returned to room temperature (approximately 40 min). Then a 1.0 mL aliquot of the reaction mixture was extracted *via* syringe for GPC and proton NMR analyses. To produce an AB diblock copolymer (PDPA-*b*-PMEMA), after a 1.0 mL aliquot was extracted from the polymerizing DPA reaction mixture (as described above), the second monomer (MEMA, 11.00 mL) was added *via* cannula and a second exotherm was recorded (5 °C). The reaction mixture was stirred at room temperature until the exotherm had abated (approximately 50 min).

After extraction of a 1.0 mL aliquot for GPC and proton NMR analyses the reaction was terminated with methanol (2 mL) prior to recovery using a rotary evaporator. The resulting diblock copolymer was dried on a vacuum line at room temperature for 24 h after removing the little PDPA contaminations. The PDPA content of the resulting PDPA-*b*-PMEMA diblock copolymer (**V**) was calculated from ^{1}H NMR spectra as being 21 mol%.

Due to easy removal of possible PMEMA homopolymer contaminants of PDPA-rich diblock copolymer in methanol by simple precipitation of the diblock copolymer from its concentrated THF solution, MEMA monomer was polymerized first and then DPA monomer was added into the reaction vessel as second monomer for the PDPA-rich diblock copolymer synthesis. For the PMEMA-rich diblock copolymer synthesis (**V**, 21 mol% DPA), DPA monomer was polymerized first and then MEMA was added into the reaction vessel as second monomer due to the easy removal of possible PDPA homopolymer contaminants of PMEMA-rich diblock copolymer in cold *n*-hexane by simple precipitation of the diblock copolymer from its concentrated THF solution. Very high yields were obtained in all copolymerizations (>98%). A summary of the synthesized diblock copolymers, including their ^{1}H NMR spectroscopy and GPC data, is listed in Table 1.

2.2. Copolymer characterizations

2.2.1. Gel permeation chromatography (THF eluent)

Molecular weights and polydispersity indexes of all polymers were determined by using gel permeation chromatography (GPC). The GPC consisted of an Agilent Iso Pump, a refractive index detector, both Mixed 'D' and Mixed 'E' columns (ex. Polymer Labs), and calibration was carried out using PMMA calibration standards (ex. Polymer Labs), with M_n ranging from 680 g mol^{-1} to 218,600 g mol^{-1}. The GPC eluent was HPLC grade THF stabilized with BHT, at a flow rate of 1.0 mL min^{-1}.

2.2.2. Nuclear magnetic resonance spectroscopy (NMR)

Block copolymer compositions were determined using a Bruker 400 MHz Avance NMR instrument. All spectra were recorded in $CDCl_3$ solvent. The methoxy signal at δ 3.6–3.7 due to the MTS initiator fragment was used to estimate the actual DP_n of the first PDPA block (just before addition of second monomer) for PMEMA-rich diblock copolymer (**V**, 21 mol% DPA) [19]. Treating this PDPA block as an end group, not only the degree of polymerization of second block but also the copolymer compositions of the diblock copolymer were determined by comparing appropriate integrals

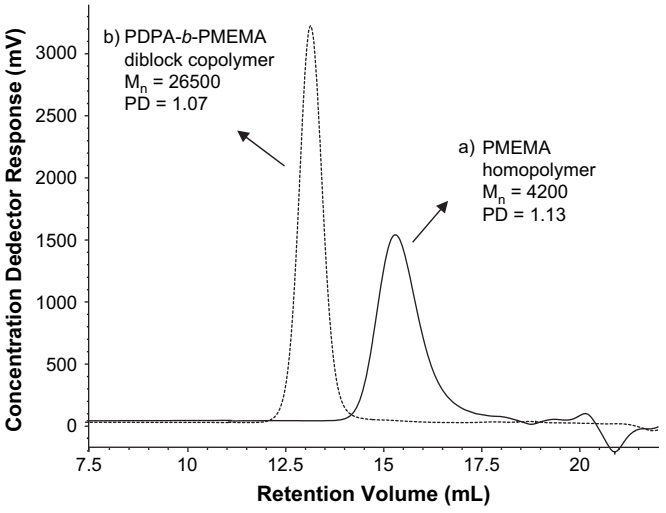

Fig. 3. GPC chromatograms of each step in the synthesis of PDPA-*b*-PMEMA diblock copolymer (**III**, 80 mol% DPA): (a) PMEMA homopolymer; (b) PDPA-*b*-PMEMA diblock copolymer.

assigned to the different comonomers. For the PDPA-rich diblock copolymers, only block copolymer compositions were calculated from proton NMR spectra. ^{1}H NMR studies with a Bruker 400 MHz Avance NMR instruments were also carried out to characterize the micellization behaviour of the diblock copolymers both in D_2O by adjusting the solution pH with DCl and NaOD and in *n*-hexane-d_{14} without using any cosolvent.

2.2.3. Dynamic light scattering studies

To determine the hydrodynamic radius and the polydispersity index (PDI $= \mu_2/\Gamma^2$) of the diblock copolymer micelles dynamic light scattering (DLS) studies were conducted using an ALV/CGS-3 compact goniometer system (Malvern, UK) equipped with a 22 mW He–Ne laser operating at λ_0 632.8 nm, an avalanche photodiode detector with high quantum efficiency, and an ALV/LSE-5003 multiple tau digital correlator electronics system. All measurements were performed on 0.5% (w/v) diblock copolymer solutions at 20 °C for aqueous solution and at 20 °C, 30 °C, 40 °C and 50 °C for *n*-hexane solutions using a fixed scattering angle of 90°, and the data were fitted using second-order cumulants' analysis.

2.2.4. Surface tension measurements

The surface tension measurements were carried out using a Kruss K11 surface tensiometer (platinum ring method) for the PDPA-*b*-PMEMA diblock copolymer solutions.

3. Results and discussion

3.1. Diblock copolymer syntheses and characterizations

The PDPA-*b*-PMEMA diblock copolymers were successfully synthesized in high yield using GTP and characterized by using GPC

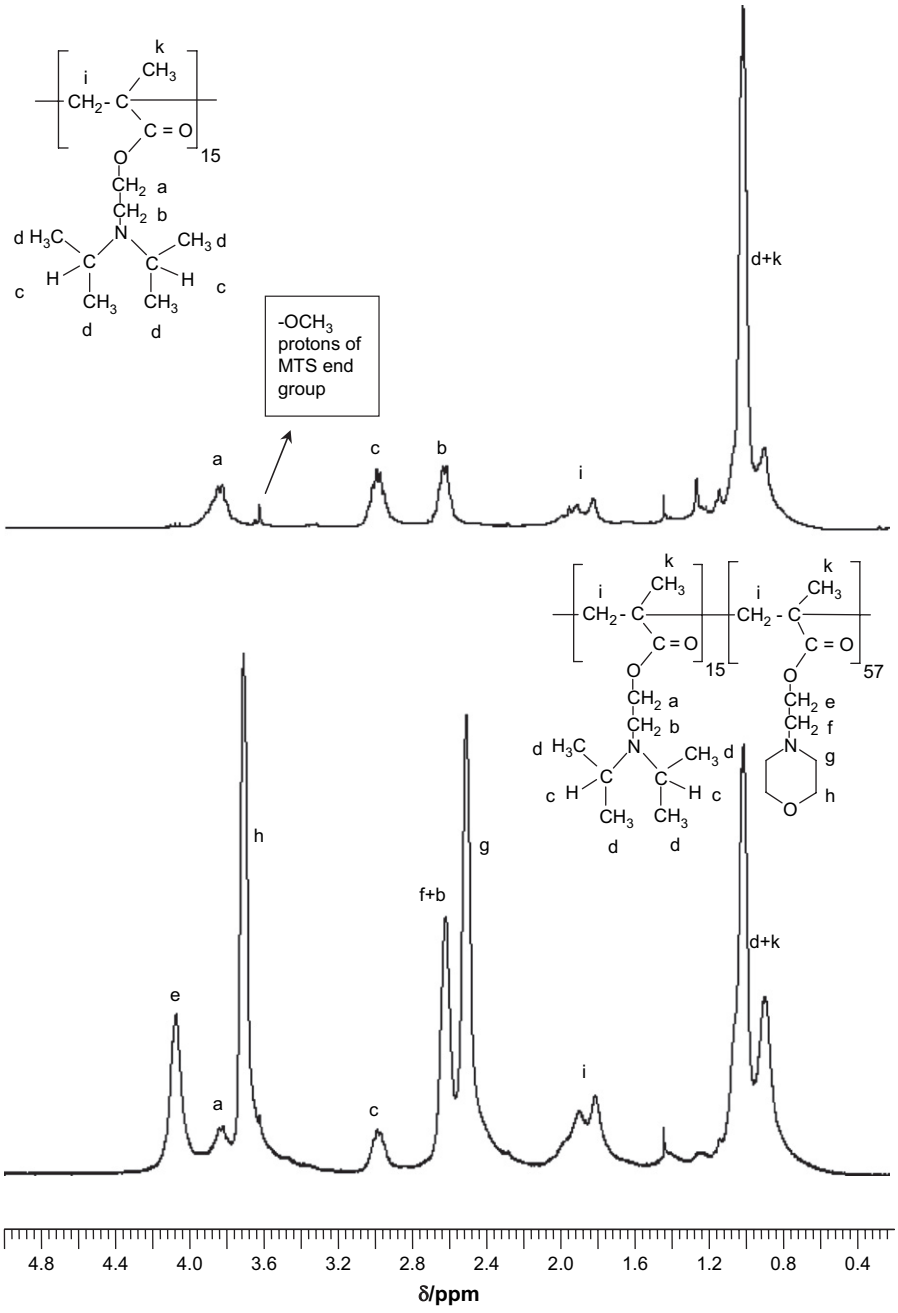

Fig. 4. Proton NMR spectra of a PDPA homopolymer (before addition of MEMA monomers) and a PDPA-*b*-PMEMA diblock copolymer (**V**, 21 mol% DPA) in $CDCl_3$.

and ^{1}H NMR spectroscopy. The number-average molecular weights (M_ns) and polydispersity indexes (M_ws/M_ns) of the copolymers were determined by GPC and are summarized in Table 1. The GPC chromatograms of each step in the synthesis of a PDPA-*b*-PMEMA diblock copolymer (**III**) are given in Fig. 3. As GPC indicated little homopolymer contamination, the PMEMA-rich diblock copolymers (**IV**–**VII**) were precipitated from THF into *cold n*-hexane to remove the little PDPA contaminant. Liquid nitrogen bath was used to cool *n*-hexane to around −50 °C. Typically, copolymer (10 g) was dissolved in minimum amount of THF (15 mL) and then poured into cold *n*-hexane (500 mL). The precipitated block copolymer was washed with cold *n*-hexane twice before drying under vacuum at room temperature for 24 h.

For the synthesis of PDPA-rich diblock copolymer, the monomer sequence was reversed in the polymerization, by polymerizing MEMA monomer first, due to the easy removal of PMEMA contaminants *via* precipitation of the diblock copolymer in methanol. As GPC indicated a little PMEMA homopolymer contamination, the PDPA-rich diblock copolymer (see **I**–**III**, Table 1) was precipitated from THF into methanol to remove the little PMEMA contaminant. Typically, copolymer (5 g) was dissolved in minimum amount of THF (8 mL) and then poured into methanol (250 mL). The precipitated block copolymer was washed with methanol twice before drying under vacuum at room temperature for 24 h.

Typical ^{1}H NMR spectra of both PDPA homopolymer (just before addition of second monomer) and the PDPA-*b*-PMEMA diblock copolymer (**V**, 21 mol% DPA) are shown in Fig. 4, recorded in $CDCl_3$ with the relevant signals labelled. Absolute DP_ns and the block compositions were determined by comparing well-defined peak integrals assigned to the different comonomers [19]. The absolute DP_n of the PDPA homopolymer was estimated to be 15 for PMEMA-rich diblock copolymer (**V**) by comparing the peak integrals of the three methoxy protons at δ 3.6–3.7 due to the terminal MMA residues derived from the MTS initiator with the oxymethylene protons (a) of the PDPA residues at δ 3.8 (see upper spectrum in Fig. 4) [19]. Treating this PDPA block as an "end group", inspection of the lower ^{1}H NMR ($CDCl_3$) spectrum for the diblock copolymer indicated average degrees of polymerization (DP_ns) for the PMEMA block of 57 [by comparing the peak integrals of the CH protons (c) of isopropyl group of DPA residues at δ 3.0 with the peak integrals of

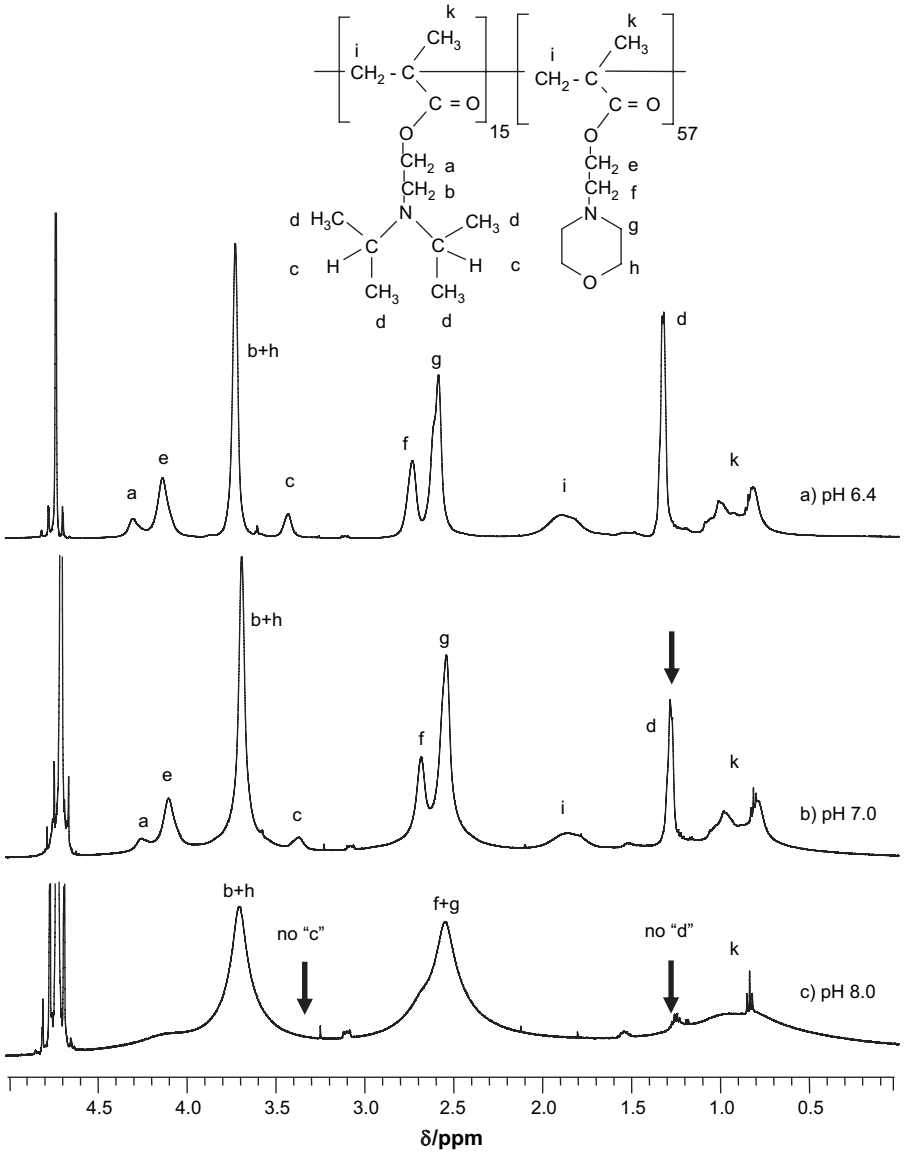

Fig. 5. ^{1}H NMR spectra of a PDPA-*b*-PMEMA diblock copolymer (**V**, 21 mol%) in D_2O: (a) unimers at pH 2.5; (b) unimer-micelle with partially dehydration of PDPA residues at pH 7.0; (c) PDPA-core micelles at pH 8.0. DCl and NaOD were used to adjust the solution pH.

both azomethylene protons (b) of the PDPA residues and six azomethylene protons (g and f) of the PMEMA residues at δ 2.4–2.7]. For the PDPA-rich diblock copolymer (**II**, 84 mol% DPA), it was impossible to determine the absolute DP_ns of the first blocks (PMEMA) due to the overlapping of the peaks of first block PMEMA and MMA protons. But comonomer composition of the PDPA-rich PDPA-*b*-PMEMA diblock copolymer (**II**, 84 mol% DPA) was successfully determined to be 84 mol% and 16 mol%, respectively, by comparing relevant peak integrals of both blocks. In general, good agreement was observed between the theoretical and determined M_ns, DP_ns and comonomer compositions from the NMR/GPC values (see Table 1). All diblock copolymers had narrow polydispersity indexes ($M_w s/M_n s < 1.14$), which is typical of polymers synthesized *via* GTP.

3.2. Aqueous solution behaviour of the diblock copolymer

The PMEMA homopolymer is a weak polybase and it is water-soluble at both neutral and acidic pHs at room temperature but less soluble at pH > 10. It exhibits inverse temperature-solubility behaviour, and its pK_a value is 4.9 as reported in our previous studies [19]. Depending on molecular weight, the cloud points of PMEMA homopolymers range from 34 °C to 54 °C at pH 7. It was also reported that PMEMA homopolymer in its neutral form can also easily be precipitated (salted out) at room temperature from aqueous solution above pH 6 on addition of electrolytes such as Na_2SO_4, K_2CO_3 and so on. On the other hand, PDPA homopolymer dissolves as a cationic polyelectrolyte in acidic solution (pH < 6) due to protonation of its tertiary amine residues. Precipitation from aqueous solution occurs when the solution pH exceeds the pK_a of 6.4 for PDPA homopolymer, because the average degree of protonation drops below a critical value and the chains become hydrophobic. In contrast, PMEMA homopolymer remains water-soluble at room temperature in mildly alkaline media in the absence of electrolyte. In addition, while the PDPA homopolymer is soluble, the PMEMA homopolymer is insoluble in *n*-alkanes.

In view of these observations, we realized that the subtle variation of the hydrophilic/hydrophobic and liophilic/liophobic balance of the PDPA-*b*-PMEMA diblock copolymer provided a unique opportunity to prepare *two* distinct micelle structures from the same diblock copolymer in aqueous solution and in *n*-alkanes; (i) PDPA-core micelles in aqueous solution at neutral pH by the PMEMA block forming hydrated corona and (ii) PMEMA-core micelles in *n*-alkanes by the PDPA block forming the solvated corona (see Fig. 2).

Table 2
A summary of the dynamic light scattering data for the PDPA-*b*-PMEMA diblock copolymers at pH 2.5 and pH 7.5 and the CMC values determined at pH 7.5. All DLS studies were carried out by using 0.5% triblock copolymer solutions at 20 °C

Polymer Code	pH	Radius (nm)	Polydispersity index (μ_2/Γ^2)	Aggregation state	CMC (%)
IV	2.5	1.2	0.19	Unimers	0.030
	7.5	10.0	0.02	PDPA-core micelles	
V	2.5	1.3	0.26	Unimers	0.028
	7.5	11.0	0.06	PDPA-core micelles	
VI	2.5	1.6	0.09	Unimers	0.028
	7.5	16.9	0.08	PDPA-core micelles	
VII	2.5	1.2	0.26	Unimers	0.056
	7.5	15.0	0.16	PDPA-core micelles	

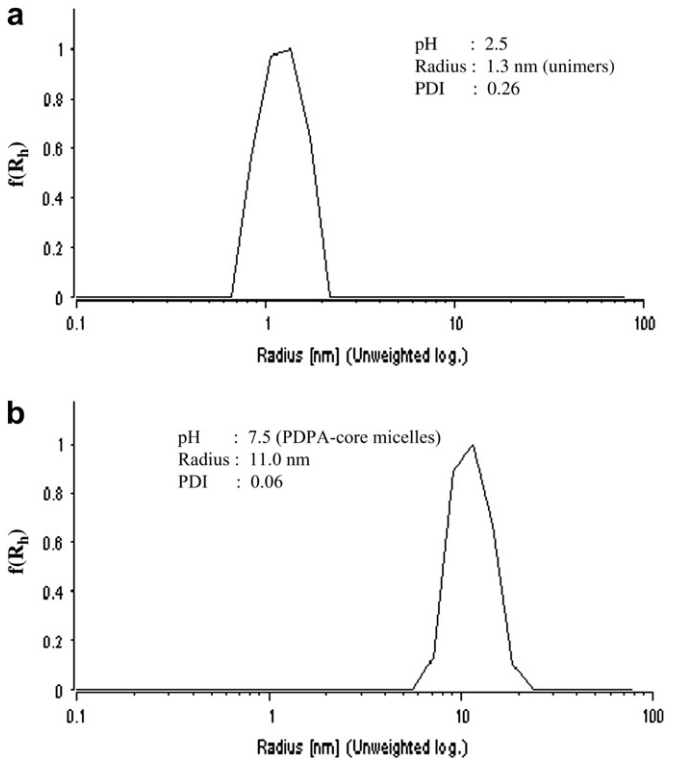

Fig. 6. Hydrodynamic radius distribution for the $PDPA_{15}$-*b*-$PMEMA_{57}$ diblock copolymer (**V**, 0.5%) at 20 °C: (a) unimers at pH 2.5; (b) PDPA-core micellization at pH 7.5.

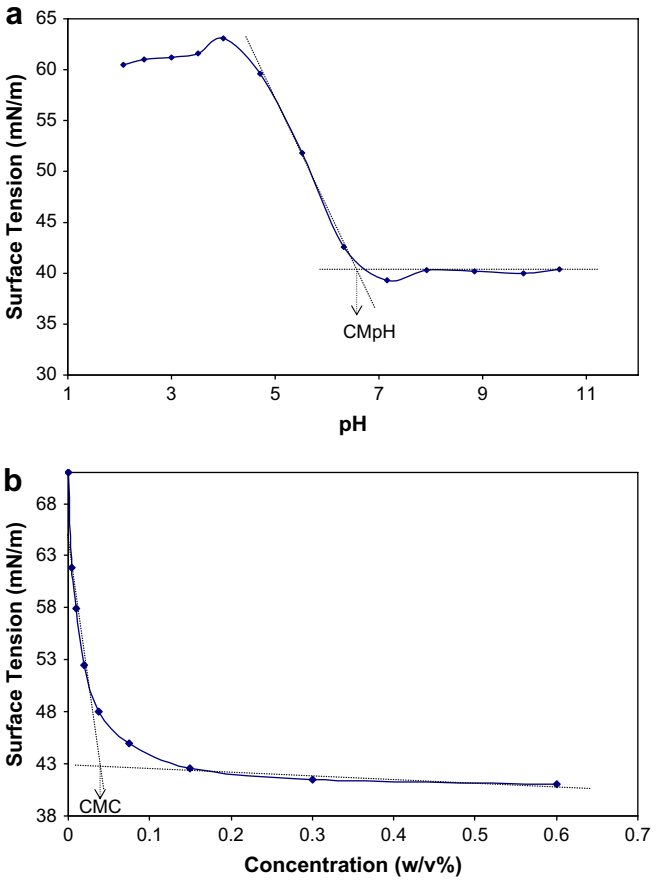

Fig. 7. Variation of surface tension with (a) solution pH for a 0.6 w/v% aqueous solution of the $PDPA_{13}$-*b*-$PMEMA_{55}$ diblock copolymer (**IV**); (b) surface tension curve for the same diblock copolymer as a function of copolymer concentration at pH 7.0.

Table 3
A summary of the dynamic light scattering data on 0.5% solutions of the PDPA-*b*-PMEMA diblock copolymer in various *n*-alkanes with or without the use of cosolvent

Polymer code	Solvent	Cosolvent (THF, vol%)	Radius (nm)	Polydispersity index (μ_2/Γ^2)
I	*n*-Pentane	–	9.0	0.10
	n-Hexane	–	10.0	0.09
II	*n*-Pentane	–	10.8	0.07
	n-Hexane	–	11.1	0.07
	n-Heptane	–	11.2	0.09
III	*n*-Pentane	–	12.2	0.03
	n-Hexane	–	13.0	0.02
VII	*n*-Hexane	–	–	–
	n-Hexane	1.2	14.8	0.07
	n-Hexane	2.5	14.9	0.08
	n-Hexane	5.0	15.2	0.08
	n-Hexane	10.0	15.0	0.09
	n-Hexane	15.0	15.5	0.07

3.2.1. pH-induced micellization with PDPA-core

PDPA-*b*-PMEMA diblock copolymer (**V**, 21 mol% DPA) dissolved molecularly in dilute HCl (or in dilute DCl for ^{1}H NMR studies) at pH 2.5. Careful addition of KOH solution (or KOD for ^{1}H NMR studies) to this acidic solution at 20 °C produced a final pH of 8.0. ^{1}H NMR studies confirmed that PMEMA blocks remain hydrated (note the prominent signals at 2.6 and 3.7 for MEMA residues), whereas the signals due to the PDPA block at 1.3 are suppressed (compare parts "a" and "c" of Fig. 5). This is consistent with the PDPA block forming the nonhydrated micelle cores and PMEMA block forming the hydrated micelle coronas. DLS and ^{1}H NMR studies confirmed this to be the case. A macroscopic precipitation occurs with the further increase on pH (pH > 9, at room temperature) due to less solubility of PMEMA block at higher solution pH [19].

Fig. 6 shows DLS distribution functions of the PDPA-*b*-PMEMA diblock copolymer in aqueous solution (0.5%). DLS studies indicated molecular dissolution at low pH (pH < 6), with micellar self-assembly occurring at around pH 7.5 (see Fig. 6a and b and Table 2).

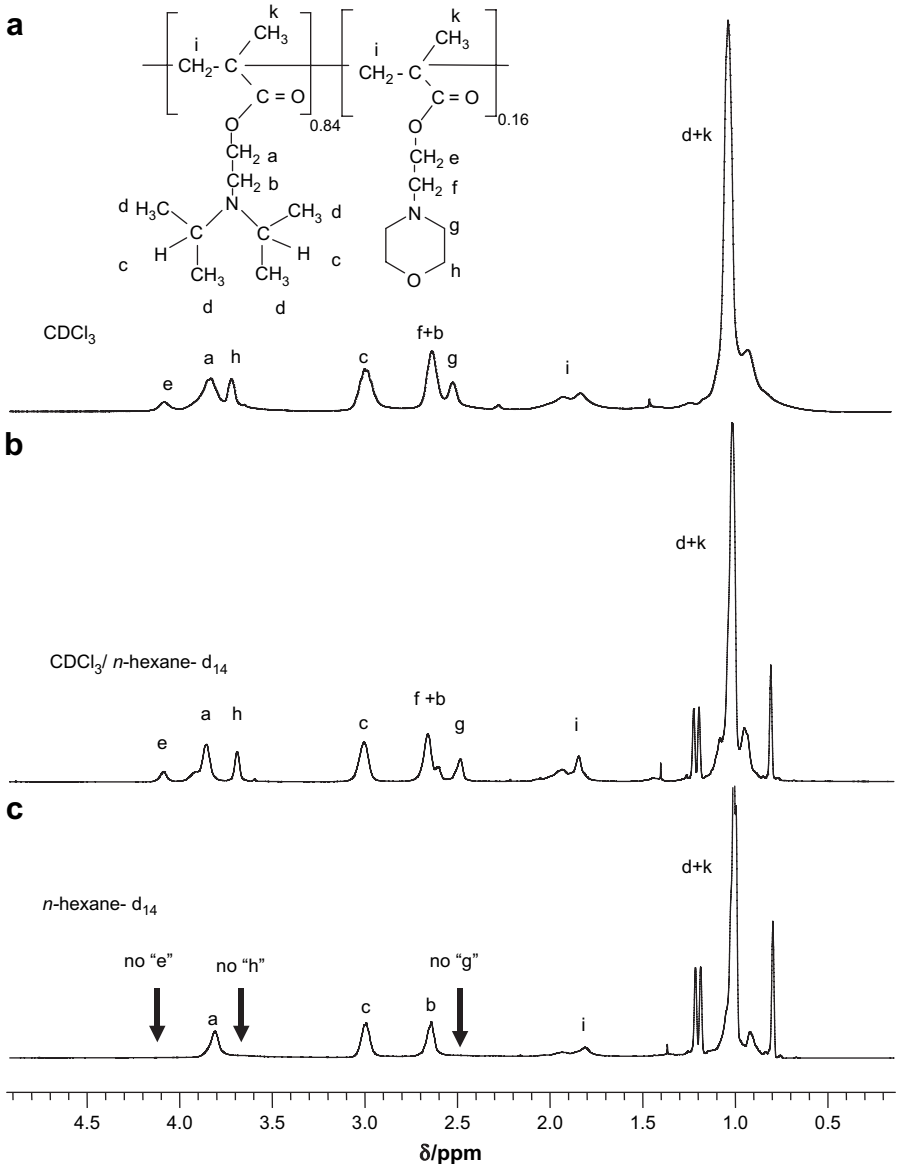

Fig. 8. ^{1}H NMR spectra of a PDPA-*b*-PMEMA diblock copolymer (**II**, 84 mol% DPA): (a) unimers in $CDCl_3$; (b) unimers in *n*-hexane-d_{14}/$CDCl_3$ mixture (30% $CDCl_3$); (c) PMEMA-core micelles in *n*-hexane-d_{14} without the use of cosolvent. Note that there is no signal due to PMEMA protons in the lower spectrum.

It is worth to mention that if the polydispersity index value of the micelles is smaller than 0.05, between 0.05 and 0.10 and bigger than 0.10 the micelles are called as monodisperse, near-monodisperse and polydisperse, respectively. Thus, Fig. 6b indicated near-monodisperse PDPA-core micelle formation at pH 7.5 and 20 °C. The intensity-average radii of the PDPA-core micelles were measured to be 11 nm ($\mu_2/\Gamma^2 = 0.06$) for $PDPA_{15}$-*b*-$PMEMA_{57}$ at pH 7.5 (see Fig. 6, Table 2).

DLS studies indicated micelles with intensity-average micelle radii of between 10.0 nm and 16.9 nm at 20 °C depending on the M_ns of the diblock copolymers having constant comonomer composition (see Table 2). The radii of micelles increase with increasing molecular weight. In addition, the polydispersity index values of the micelles obtained from the diblock copolymer containing around 20 mol% DPA were smaller than 0.09 (near-monodisperse) but the micelles of the 33 mol% DPA containing diblock copolymer (**VII**) had bigger micellar size distribution ($\mu_2/\Gamma^2 = 0.16$, polydisperse). All pH-induced micellizations were completely reversible. Addition of acid led to reprotonation of the PDPA residues, leading to the formation of unimers below pH 6 at 20 °C (see Table 2).

The surface activity of the PDPA-*b*-PMEMA diblock copolymer has pH and concentration dependencies (Fig. 7). As the solution pH is increased, the block copolymer becomes strongly adsorbed at the air–water interface, thus lowering the surface tension of the solution. Above pH 7, the limiting surface tension is approximately 40 mN m^{-1} for the $PDPA_{13}$-*b*-$PMEMA_{55}$ diblock copolymer solution. Presumably, the deprotonated hydrophobic PDPA block becomes adsorbed at the air–water interface, thus lowering the surface tension of the solution. This limiting surface tension is similar to that obtained with small molecule surfactants. The critical micellization pH of the $PDPA_{13}$-*b*-$PMEMA_{55}$ diblock copolymer (**IV**, 19 mol% DPA) is around 6.54 as estimated from the surface tension *vs* solution pH curve (see Fig. 7a).

It is also possible to identify the so-called critical micelle concentration (CMC) by determining the concentration dependence of the surface tension of a block copolymer. Fig. 7b shows the surface tension curve of the $PDPA_{13}$-*b*-$PMEMA_{55}$ diblock copolymer. The CMC for the $PDPA_{13}$-*b*-$PMEMA_{55}$ diblock copolymer is estimated to be 0.03 w/v%. The CMCs of the other two diblock copolymers having similar compositions but higher molecular weights were determined to be 0.028 w/v%. When the DP_n of the hydrophobic PDPA block was doubled (from 18 to 36) by keeping molecular weights of the diblock copolymers constant (see entries **VI** and **VII** in Table 2) the CMC increased from 0.028 w/v% to 0.056 w/v%. These CMCs are similar to those obtained with other tertiary amine methacrylate-based diblock copolymers [19].

3.3. Non-aqueous solution behaviour of the diblock copolymer

PDPA-*b*-PMEMA diblock copolymer is molecularly soluble in many organic solvents such as in THF and in chloroform but forms PMEMA-core micelles in *n*-alkanes. While the PDPA segment of the diblock copolymer is soluble in *n*-alkanes, the PMEMA block is not soluble in such solvents. Thus, a PDPA-*b*-PMEMA diblock copolymer having 20 mol% PMEMA block was expected to give PMEMA-core micelles in *n*-hexane. It is worth to mention that there is no need to use cosolvent to get good micellization with such diblock copolymer (see **I**–**III** in Table 3). Normally in such cases, cosolvent is needed to be used to get near-monodisperse micelles. In our cases, the PDPA-*b*-PMEMA diblock copolymer containing less than 20 mol% PMEMA was directly dissolved in *n*-hexane (1%) and investigated by DLS studies and proton NMR studies.

^{1}H NMR studies indicated desolvation of the PMEMA block of the diblock copolymer in *n*-hexane. The signals due to the PMEMA block at 3.9–4.0 are disappeared (compare spectra "a" in $CDCl_3$ and "b" in *n*-hexane in Fig. 8) and supported DLS studies by PMEMA block becoming liophobic and forming desolvated micelle cores. As can be seen from Figs. 5 and 8, ^{1}H NMR studies on the micellar systems lead to valuable informations of the micellar core–shell structures.

Fig. 9 shows DLS distribution functions on the change of the radii of the micelles by varying *n*-alkanes without use of any cosolvent. It confirmed that the micelle diameters were almost independent on the chain lengths of *n*-alkanes. The average radius and the polydispersity indexes (μ_2/Γ^2) of the $PDPA_{0,84}$-*b*-$PMEMA_{0,16}$ (**II**) micelles in *n*-alkanes were determined to be around 11 nm and 0.07, respectively. As can be seen in Table 3, the micelle radius of the 80:20 PDPA-*b*-PMEMA blocks increase from 10 nm to 13 nm in *n*-hexane with increasing molecular weight from 14,800 g/mol to 26,500 g/mol (see Table 3).

In addition to direct micellization in *n*-alkanes with the diblock copolymer containing less than 20 mol% PMEMA, cosolvent-induced micellization was also observed with the PMEMA-rich PDPA-*b*-PMEMA diblock copolymer. Here the $PDPA_{36}$-*b*-$PMEMA_{74}$ block copolymer which does not form stable colloid dispersion in pure *n*-alkanes (0.05 g) was first dissolved molecularly in THF

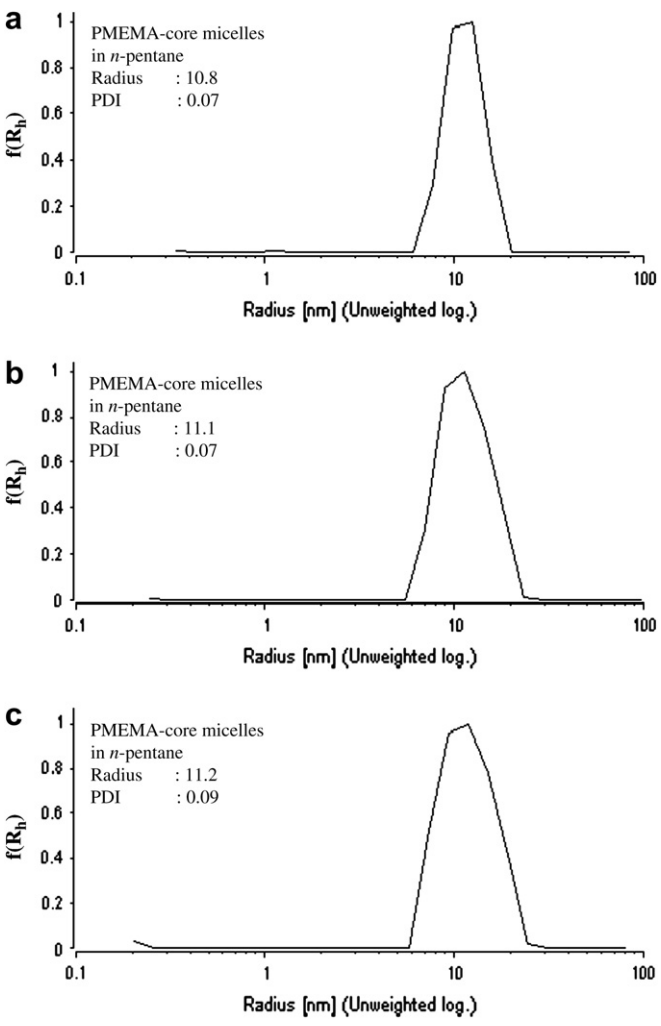

Fig. 9. Hydrodynamic radius distribution for the PDPA-rich PDPA-*b*-PMEMA diblock copolymer micelles (**II**, 0.5%) at 20 °C without any cosolvent: (a) in *n*-pentane; (b) in *n*-hexane; (c) in *n*-heptane.

(1.5 ml) before addition of *n*-hexane (8.5 ml). On addition of *n*-hexane, the PMEMA block of the diblock copolymer (**VII**, 33 mol% DPA) becomes liophobic and micellization occurs with the radius of 15.5 nm and μ_2/I^2 of 0.07 in the presence of 15 vol% cosolvent (see Table 3). The radii of the micelles slightly decreased from 15.5 nm to 14.8 nm with the polydispersity index value of around 0.08 when cosolvent content was decreased from 15 vol% to 1.2 vol% (see Table 3). That might be due to the formation of more compact desolvated-PMEMA-cores.

These novel diblock copolymer micelles might have attraction for potential applications such as in nanosize drug delivery applications since tunable hydrophilicity/hydrophobicity of the A or B block depending on solution pH and the type of organic solvent should allow "triggered release" of both hydrophobic and hydrophilic drugs. Another possible application for such diblock copolymers is their use as novel dispersants in the dispersion polymerization of styrene. The stabilizing effect of the PDPA-*b*-PMEMA diblock copolymer will be reported in detail for the dispersion polymerization of styrene in the near future.

4. Conclusions

In summary, group transfer polymerization was successfully used to prepare a novel water-soluble diblock copolymers of polydispersity index ($<$1.12) based on tertiary amine methacrylates. For the first time, it was demonstrated that a double hydrophilic PDPA-*b*-PMEMA diblock copolymers can form monodisperse PDPA-core micelles in aqueous solution depending on solution pH and near-monodisperse PMEMA-core 'reverse micelles' in *n*-alkanes with or without requiring any cosolvent depending on comonomer ratios.

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