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Polymer 46 (2005) 10699–10708
polymer
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The amphiphilic block copolymers of 2-(dimethylamino)ethyl methacrylate and methyl methacrylate: Synthesis by atom transfer radical polymerization and solution properties

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Received 17 June 2005; received in revised form 8 September 2005; accepted 13 September 2005
Available online 3 October 2005

Abstract

Amphiphilic di- and tri-block copolymers of poly(methyl methacrylate) (PMMA) and poly(2-dimethylamino)ethyl methacrylate (PDMAEMA) have been synthesized by atom transfer radical polymerization (ATRP) at ambient temperature (35 °C) in the environment-friendly solvent, aqueous ethanol (water 16 vol%) using CuCl/*o*-phenanthroline as the catalyst. The PDMAEMA blocks are contaminated with ethyl methacrylate (EMA) residues to the extent of 1–2 mol% of DMAEMA depending on the length of the PDMAEMA block. The EMA forms through the autocatalyzed ethanolysis of the DMAEMA monomer and undergoes random copolymerization with the latter. The rate of ethanolysis is unexpectedly greater in the aqueous ethanol than in neat ethanol, which has been attributed to the higher polarity of the former than of the latter. In contrast to the ethanolysis no hydrolysis of DMAEMA in the aqueous ethanol medium could be detected for 133 h. The block copolymers form micelles in water. Their solubility and CMC in neutral water have been studied. Dynamic light scattering (DLS) studies reveal that for a fixed degree of polymerization (DP) of the PMMA block the hydrodynamic diameter of the micelles in methanolic water (water 95 vol%) increases at a faster rate with the DP of the PDMAEMA block when it is much greater than that of the PMMA block compared to when it is less than or close to that of the latter.

Keywords: Atom transfer radical polymerization; Amphiphilic block copolymer; Block copolymer

1. Introduction

Amphiphilic block copolymers have great application potential e.g. in the stabilization of latex particles [1], emulsions [2], dispersions [3], separations [4] and also as drug and gene delivery vehicles [5–7]. Poly(2-dialkylamino)ethyl methacrylates (PDAAEMA) as the constituents of amphiphilic block copolymers have attracted interest. When the alkyl is methyl the polymer is hydrophilic, whereas when it is ethyl the character of the polymer changes from hydrophobic to hydrophilic as the pH of the medium is lowered to the acidic region [8–10]. Micelles of the A–B–C tri-block copolymer comprising of polyethylene glycol as one end block (block A) and poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) as the other end block (block C) and poly(2-(diethylamino)ethyl methacrylate) (PDEAEMA) as the centre block (block B) have been studied for the stabilization and the controlled release of the hydrophobic drug, dipyridamole [10]. Diblock copolymers with PDMAEMA as the hydrophilic block and poly(alkyl methacrylates) as the hydrophobic blocks have been studied as dispersion polymerization stabilizers [11]. On the other hand, the solution properties of the PMMA–PDMAEMA di-block copolymers and their micelles have been characterized in detail [12,13]. Such polymers were prepared earlier by the classical living anionic or the group transfer polymerization [12–14].

After the advent of atom transfer radical polymerization (ATRP) it has been the method of choice for the synthesis of block copolymers by virtue of its insensitivity towards moisture or other protic compounds, greater tolerance towards functional groups in monomers or initiators as well as impurities [15–18]. Matyjaszewski et al. were the first to report the ATRP synthesis of di-and tri-block copolymers of MMA and DMAEMA at 90 °C in dichlorobenzene using CuBr/4,4′.-di(5-dinonyl)-2,2′.-bipyridine (dNbpy) as the catalyst [19]. Subsequently, Haddleton et al. synthesized di- and tri-block copolymers of *n*-butyl methacrylate (nBMA) and DMAEMA in toluene at 90 °C using

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doi:10.1016/j.polymer.2005.09.045

CuBr/N(*n*-propyl)2-pyridylmethanimine as the catalyst and studied some aspects of their aggregation behavior in aqueous solution [20].

On the other hand, in recent years aqueous alcohols (methanol, ethanol, isopropanol) have attracted interest as the medium of polymerization [8–10,21–29]. This is because the polymerization can be carried out at ambient temperature at reasonably fast rates and the solvents are environment-friendly. However, methanol is reported to be an unsuitable medium for the ATRP of DMAEMA and other *t*-amine methacrylates such as DEAEMA and 2-(diisopropylamino)ethyl methacrylate (DiPAEMA) inasmuch as these monomers undergo transesterification reaction with methanol at rates which are comparable with the rates of polymerization leading to the formation of statistical copolymers with MMA [24]. On the other hand, transesterification is insignificant in *i*-propanol due to steric reasons [24]. Matyjaszewski et al. used aqueous *i*-propanol (10% water by volume) as the medium for the ATR block as well as random and gradient copolymerization of nBMA, DMAEMA and DEAEMA at 25 °C [9].

Recently, we reported the ambient temperature ATRP of MMA in the environment-friendly solvent aqueous ethanol in which PMMA is soluble in the composition range, $6 \leq \text{water} \leq 30$ volume percent [29]. PDAAEMA and many other hydrophilic polymers are also soluble in aqueous ethanol. The method, therefore, presents an opportunity for the convenient synthesis of amphiphilic block copolymers with PMMA as the hydrophobic block in this environment-friendly solvent. In this paper we present the ATRP synthesis of di- and tri-block copolymers of DMAEMA and MMA at ambient temperature in aqueous ethanol. The block copolymers have been characterized which included a study of the transesterification of DMAEMA with ethanol and aqueous ethanol. The micellar dimensions of the block copolymers are also reported.

2. Experimental section

2.1. Materials

MMA (BDH) was washed with 5% NaOH solution followed by distilled water, dried over $CaCl_2$ and distilled under reduced pressure. It was stored under nitrogen atmosphere at −15 °C. DMAEMA (98%, Aldrich) was distilled under vacuum. CuBr (98%, Aldrich) and CuCl (98%, BDH) were purified by washing with corresponding acids (10% HCl or HBr in water) followed by methanol and diethyl ether in a Schlenk tube under a nitrogen atmosphere. Absolute ethanol (Bengal Chemical and Pharmaceutical works, India) was refluxed for 2 h with Mg wire and distilled. Commercial distilled water was redistilled over alkaline permanganate. *o*-Phenanthroline (*o*-phen, 99.5%, E Merck), and ethyl 2-bromoisobutyrate (EBiB, 97%, Aldrich) were used as received. The difunctional initiator, 1,2-bis(bromoisobutyryloxy) ethane (BiBE), was synthesized using a literature procedure [30].

2.2. The molecular weights (MW) and their polydispersity indices (PDI)

These were measured by GPC at room temperature using a Waters model 510 HPLC pump, a Waters series R-400 differential refractometer and Waters Ultrastyragel columns of 10,000, 1000, 500 Å pore size which were preceded by a prefilter. HPLC grade THF (Spectrochem, India) mixed with triethyamine (5 vol%) was used as the eluent at a flow rate of 1 ml/min. Before injection into the GPC system the polymer solutions were passed through a silica gel column using THF as the eluent to free them from Cu salts. They were then filtered through a prefilter–filter combination system compatible with organic solvents. Waters poly (methyl methacrylate) standards were used for calibration.

2.3. Homo polymerization of DMAEMA

A typical procedure for the ATRP synthesis of PDMAEMA is as follows. In a nitrogen purged reaction vessel (15 ml) provided with a B-19 standard joint were taken CuBr (33 mg, 0.23 mmol) and *o*-phen (92 mg, 0.46 mmol). Deoxygenated (nitrogen purged) ethanol (4 ml), water (1 ml) and DMAEMA (4.66 g, 29.7 mmol) were next added into the vessel under nitrogen. The vessel was then closed with a rubber septum, which was secured by Cu wire. The admixture was sonicated for 2 min. A deep brown solution was obtained. The vessel was then placed in a thermostated water bath maintained at 35 °C. EBiB (0.035 ml, 0.23 mmol) was next introduced into the vessel using a gas-tight syringe which was purged with nitrogen. The polymerization was continued for 4 h. The polymerization mixture was then diluted with acetone (3 ml) and poured into excess petroleum ether. The polymer was purified by passing its solution through a silica gel column using THF as the eluent. The polymer so purified was isolated and dried in a vacuum oven at 45 °C for 48 h and weighed. Conversion was 98%. The M_n and PDI of the polymer were 19, 700 and 1.28, respectively.

For kinetic studies, aliquots (1.5 ml) were withdrawn from time to time from the reaction vessel using gas tight syringes and poured into petroleum ether. The polymer was isolated and dried as above.

2.4. Homo polymerization of MMA

It is similar to that described above and published earlier [29].

2.5. Synthesis of PMMA-b-PDMAEMA di-block copolymer

A representative example is as follows. A monofunctional PMMA macroinitiator was prepared using the EBiB initiator and the CuCl/*o*-phen catalyst with the following recipe: MMA (4.7 g, 47 mmol), EtOH (4.2 ml), H_2O (0.8 ml), CuCl (58.16 mg, 0.587 mmol), *o*-phen (232.45 mg, 1.174 mmol), EBiB (0.088 ml, 0.587 mmol). The polymer was purified as described above. The polymer (0.467 g, 0.093 mmol, $M_n = 5200$ and PDI = 1.35) was dissolved in 5 ml degassed aqueous ethanol (16% v/v water) in a reaction vessel. DMAEMA (5 ml, 29.7 mmol) previously purged with nitrogen was then added into the vessel under nitrogen atmosphere followed by *o*-phen (0.037 g, 0.186 mmol) and CuCl (9.2 mg, 0.093 mmol). The vessel was then closed with a rubber septum, which was secured with Cu wire. The reaction mixture was stirred at 35 °C for 14 h. The polymerized mass was diluted with acetone (3 ml) and the polymer was precipitated into petroleum ether. The polymer was purified by passing its solution through a silica gel column using THF as eluent. The conversion was 80%. The M_n and PDI values of the block copolymer were 45,200 and 1.19, respectively.

2.6. Synthesis of PDMAEMA-b-PMMA-b-PDMAEMA tri-block copolymer

A representative example for the synthesis is as follows. First, a difunctional Br–PMMA–Br was prepared at 35 °C using CuBr/*o*-phen as the catalyst and 1,2-bis(bromoisobutyryloxy) ethane as the initiator with the following recipe : MMA (4.7 g, 47 mmol), EtOH (4.2 ml), H_2O (0.8 ml), CuBr (134.9 mg, 0.94 mmol), *o*-phen (372.3 mg, 1.88 mmol) and 1,2-bis(bromoisobutyryloxy) ethane (340 mg, 0.94 mmol). The polymer was purified as described above. After 1 h the conversion reached 70% and the M_n and PDI values were 5000 and 1.33, respectively. In the next step the purified Br–PMMA–Br macroinitiator was used to polymerize DMAEMA. The recipe was as follows: DMAEMA (4.66 gm, 29.7 mmol), EtOH (4.2 ml), H_2O (0.8 ml), CuCl (9.2 mg, 0.093 mmol), *o*-phen (36.9 mg, 0.186 mmol) and Br–PMMA–Br (466 mg, 0.093 mmol) ($M_n = 5000$ and PDI = 1.33). After 7.5 h the conversion was 80%. The polymer was purified by passing its solution through a silica gel column using THF as eluent. The M_n and PDI values were 45,000 and 1.25, respectively. The corresponding synthesis using a Cl ended difunctional PMMA macroinitiator was done following essentially the same procedure. The Cl–PMMA–Cl macroinitiator was prepared using the same recipe as that used for Br–PMMA–Br given here except for replacing CuBr with CuCl. Such combination of bromide initiator and chloride (CuCl) catalyst gives Cl ended polymer [31,32].

2.7. Nuclear magnetic resonance spectroscopy

All NMR spectra were recorded using a Bruker AC-P 300 MHz instrument in $CDCl_3$, D_2O or CD_3OH used as solvents.

2.8. Surface tension

The surface tension (γ) measurements were carried out using a du Nouy tensiometer Krüss K 8, equipped with a platinum Wilhelmy plate at 37 °C. The glassware was dipped in a sulfochromic acid solution for at least 6 h, thoroughly rinsed with distilled water, and dried in an oven at 50 °C. The platinum plate was cleaned with water and chloroform and flamed before each measurement. The cleanness of the glassware was checked by measuring the surface tension of double distilled water which was measured to be 70.6 mN/m. All measurements were carried out at 37 °C. The solutions were stirred with a small bar magnet for 30 min before each measurement. Solution temperatures were controlled by means of a thermostated water bath. Each measurement was repeated at least five times and accepted whenever the values were steady within 0.02 mN/m.

2.9. Dynamic light scattering (DLS)

Solutions for light scattering measurements were prepared by the dissolution of the block copolymers in methanol, which was filtered through a 0.45 μm membrane filter. The solutions were diluted with double distilled water which was similarly filtered to make the solvent composition, water:methanol 95:5 (v/v). The polymer concentrations were 1 g/l. All the solutions were stored at room temperature for 2 days and filtered again before analysis. The measurements were carried out at the Indian Institute of Technology, Kharagpur, India, using a Photal (Otsuka Electronics) DLS-7000 instrument at a scattered angle of 90°. The incident light was the 488 nm line of a Photal argon laser GLS 3110. All the measurements were done at 25 °C. The viscosity of the water–methanol medium was obtained from the literature [33].

2.10. Transmission electron microscopy (TEM)

It was done using a JEOL JEM 2010 TEM instrument, operating at 200 kV. The block copolymer was dissolved in a mixture of 5% MeOH and 95% water (v/v). A droplet of the solution containing the polymer (1 mg/ml) was deposited onto carbon coated 300 mesh copper grids. The excess of liquid was removed by placing the grid onto filter paper. The grid was dried in air.

3. Results and discussion

The ATRP of MMA in aqueous ethanol at 35 °C using CuBr/*o*-phenanthroline as the catalyst and EBiB as the initiator was discussed by us in an earlier work [29]. Before the syntheses of the present block copolymers were undertaken, the ATRP of DMAEMA in aqueous ethanol was investigated. The solvent composition of ethanol:water = 4:1 (v/v) was about the same as that was used in the ATRP of MMA [29]. Fig. 1 shows the first order kinetic plots for DMAEMA disappearance using EBiB as the initiator and CuBr/*o*-phen or CuCl/*o*-phen as the catalyst. The plots are linear which is required of a living polymerization. The CuBr based catalyst gives a much faster rate than the CuCl based one. The same was observed in the ATRP of MMA and explained [29,32]. Fig. 2 shows that the molecular weights reasonably agree with theory for both the catalysts. However, with CuCl the PDI is smaller which is opposite to that observed in the ATRP of MMA in ethanol–water media [29]. This difference in behavior for the two methacrylates, MMA and DMAEMA, may arise from the ability of the latter to take part in complexing Cu ions and thus

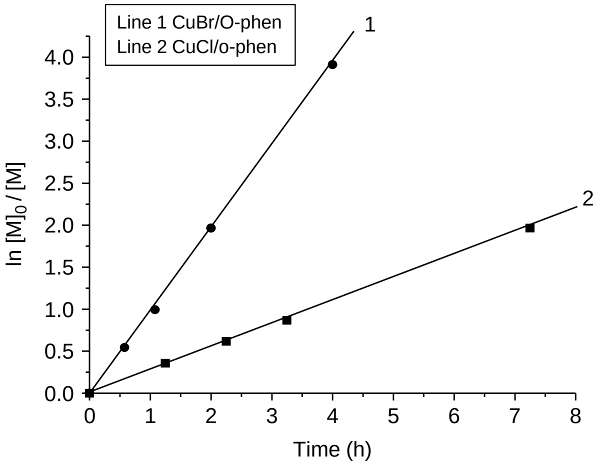


Fig. 1. Kinetic plots for monomer disappearance in the ATRP of 2-(dimethylamino)ethyl methacrylate in ethanol–water (16 vol% water) using CuBr/*o*-phen and CuCl/*o*-phen catalysts at 35 °C. [DMAEMA] = 2.97 mol/dm^3, [CuCl] = [CuBr] = 1/2[*o*-Phen] = [EBiB] = 0.023 mol/dm^3.

influence the deactivation rate. For the synthesis of block copolymers, therefore, the PMMA part was prepared using the CuBr catalyst and the PDMAEMA part using the CuCl catalyst.

The difunctional Br–PMMA–Br was used as the macroinitiator for the polymerization of DMAEMA using the CuCl catalyst to produce the tri-block copolymer with PMMA as the centre block. Such a combination of halide type between the initiator and the catalyst also provides efficient initiation [32]. Fig. 3 shows the first order kinetic plot for monomer disappearance in block copolymerization. The plot is linear indicating a constant concentration of growing polymer radicals. Fig. 4 shows the evolution of the GPC traces with time during the synthesis of the tri-block copolymer using Br–PMMA–Br as the macroinitiator and CuCl/*o*-phen as the catalyst. The GPC traces are unimodal and they are laterally shifted with time towards higher molecular weight. These results indicate that the initiation is fast and quantitative. Use of the Cl–PMMA–Cl macroinitiator and CuCl/*o*-phen catalyst also gave rise to similar results. Other combinations such as the bromide macroinitiator and bromide catalyst or chloride macroinitiator and bromide catalyst gave block copolymers with broad MWD (PDI ~ 1.6) with tailing in the lower molecular weight region. This result for the all bromide system is unexpected in view of the lower PDI ~ 1.3 (Fig. 2) of PDMAEMA which forms using the monofunctional initiator EBiB and CuBr catalyst. However, although the PDI for the latter system is rather low, the chromatogram is skewed towards the low molecular weight side with a small tail (Fig. 5). The result is similar for PMMA similarly prepared (Fig. 5). This may be attributed to slow rate of initiation of polymerization by the EBiB/CuBr system [32]. The shape of the chromatogram remains the same for Br–PMMA–Br prepared with the difunctional bromide initiator BiBE (Fig. 4, the macroinitiator). But the tail becomes long for Br-PDMAEMA-Br (Fig. 5). A long tail is also found in the chromatogram of the tri-block copolymer prepared using the Br–PMMA–Br macroinitiator which is also shown in Fig. 5. The tail, therefore, is typical of PDMAEMA prepared with the difunctional bromide initiators (both low molecular weight and macro). The reason remains unclear.

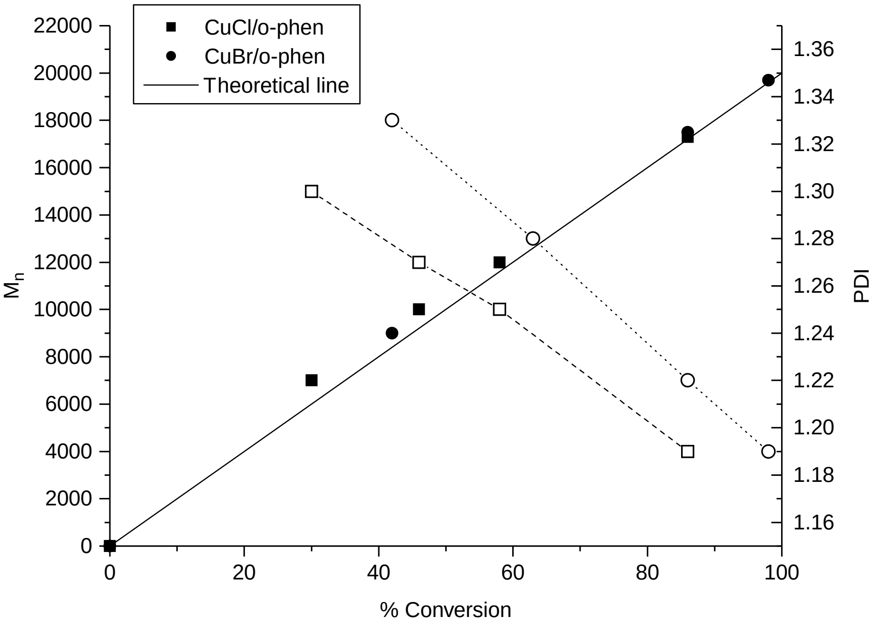


Fig. 2. M_n and PDI vs. % conversion for the ATRP of 2-(dimethylamino)ethyl methacrylate in ethanol–water (16 vol% water) using CuBr/*o*-phen and CuCl/*o*-phen catalysts at 35 °C. [DMAEMA] = 2.97 mol/dm^3, [CuCl] = [CuBr] = 1/2[*o*-Phen] = [EBiB] = 0.023 mol/dm^3. Filled and open symbols represent M_n and PDI, respectively.

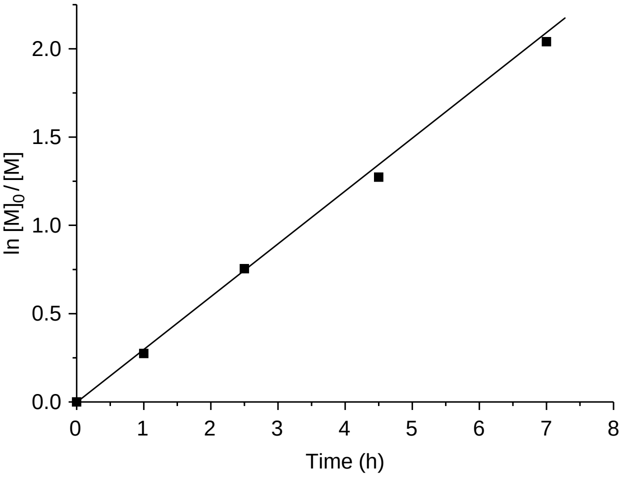


Fig. 3. Kinetic plot for monomer disappearance in the tri-block copolymerization of 2-(dimethylamino)ethyl methacrylate in ethanol–water (16 vol% water) using CuCl/*o*-Phen as the catalyst and Br-polymethyl methacrylate-Br ($M_n=5000$, PDI = 1.33) as the initiator at 35 °C. [DMAEMA] = 2.97 mol/dm^3, [CuCl] = 1/2[*o*-Phen] = [Br–PMMA–Br] = 0.013 mol/dm^3.

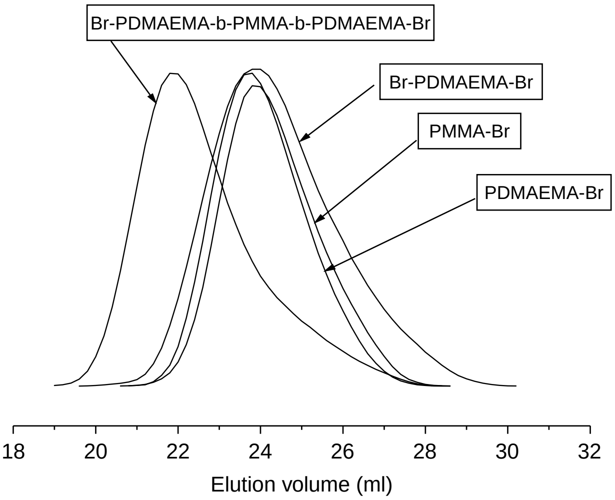


Fig. 5. GPC traces of polymers prepared using CuBr catalyst and bromide initiators. The conversion is ~65% in all cases.

The compositions of the block copolymers were determined from the proton NMR spectra of the copolymers in $CDCl_3$ (Fig. 6) making use of the intensities of the N–CH_3 and O–CH_3 resonances, respectively for the DMAEMA and MMA residues in the copolymers. The molecular weights of the PMMA blocks were determined using GPC and PMMA calibration. Both these informations were used to determine the blockwise M_ns of the copolymers. The results are given in Table 1. The PDI decreases with the increase in the block length. This is in conformity with the theoretical prediction of higher polydispersities for shorter chains [17].

The extent of transesterification of the PDMAEMA blocks was also studied using NMR spectroscopy. The transesterification of the monomer would have produced ethyl methacrylate (EMA) and consequently the statistical copolymer of DMAEMA and EMA. In the proton NMR spectrum the methyl protons of the ester function of the PEMA appears at 1.25 ∂. Unfortunately, this resonance overlaps with those of the isotactic alpha CH_3 resonances in PDMAEMA and PMMA blocks (Fig. 6). However, the contributions of the latter two to its intensity were estimated from the mole fraction of the isotactic content of pure PMMA (0.054) and PDMAEMA (0.075) multiplied, respectively, with the intensities of the OCH_3 resonance and 1.5 times the NCH_2 resonance of the block copolymer. The above values of the isotactic fractions were arrived at from the NMR spectra of PMMA and PDMAEMA prepared in ethanol–water and acetone (to avoid ethanolysis of DMAEMA), respectively using the same catalyst as is used here. After due correction the percentage of EMA residues in the PDMAEMA blocks was calculated and the values are given in Table 1 (last column). EMA incorporation varied between 1 and 2.3 mol% of the DMAEMA units. In general, the longer the length of the PDMAEMA block the greater is the EMA incorporation, as would be expected, since polymerization was carried out for longer time and also higher DMAEMA monomer concentration (and hence more alcoholysis) to achieve longer PDMAEMA blocks.

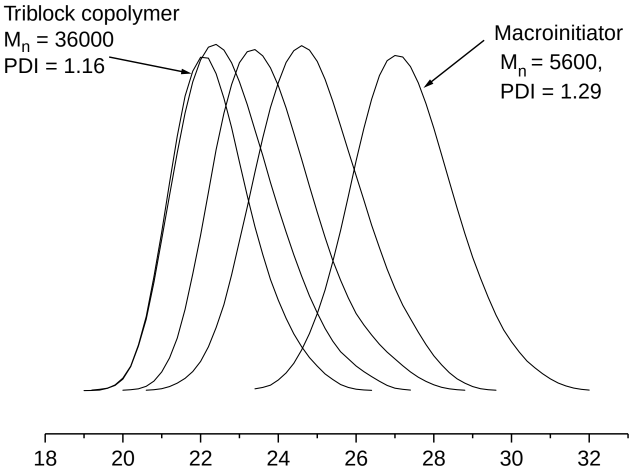
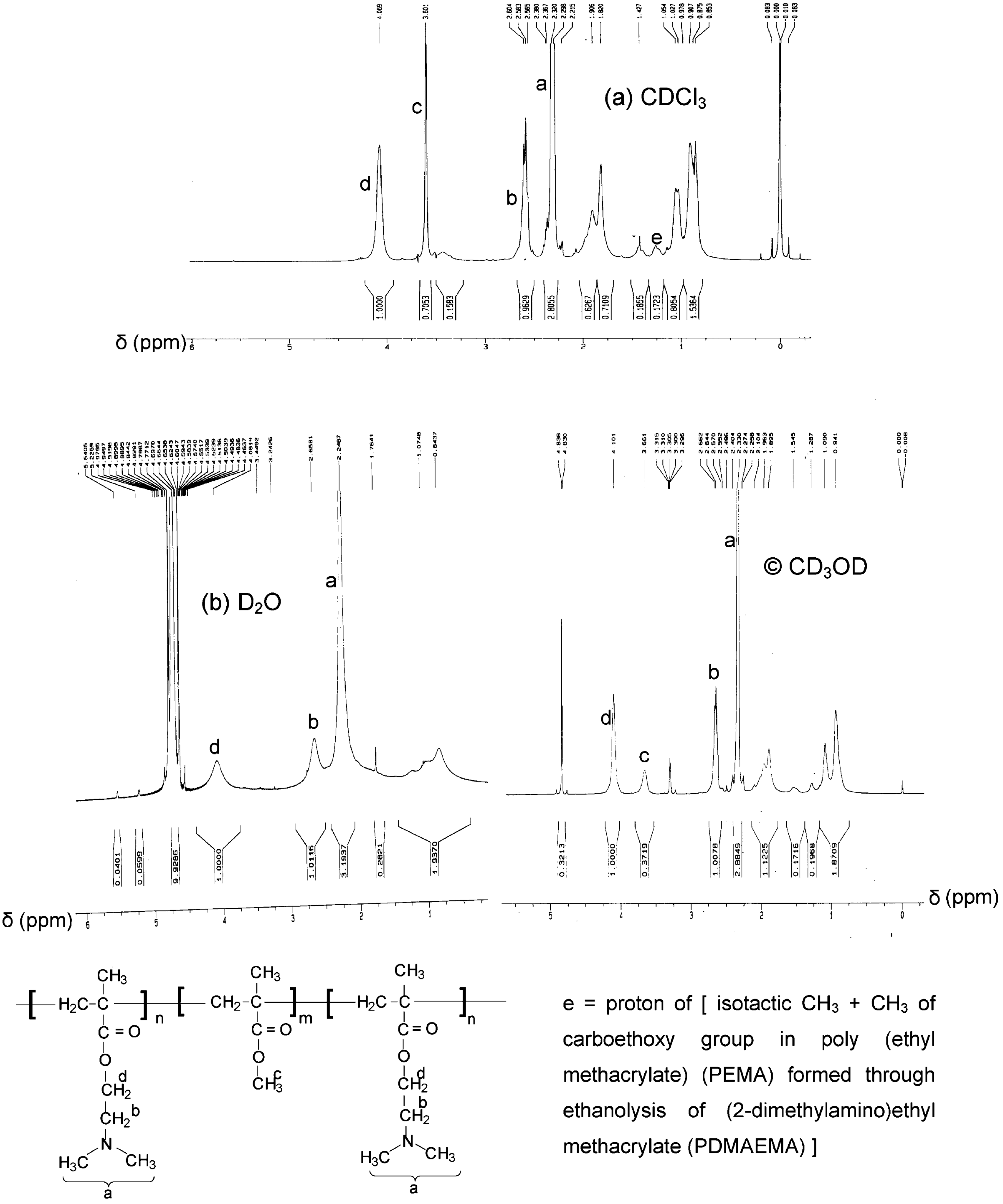


Fig. 4. Evolution of GPC traces with time in the tri-block formation using the Br–PMMA–Br macroinitiator and CuCl/*o*-Phen as the catalyst.

Boris-Azeau and Armes showed that the ATRP of DMAEMA in methanol (50 w/w%) at ambient temperature results in the incorporation of 7 mol% methyl methacrylate (MMA) units in the polymer. When the medium composition was progressively changed from methanol to water the extent of MMA incorporation decreased progressively to zero [24]. This was attributed to increasingly faster polymerization relative to transesterification with increasing water concentration. In contrast to the monomer the polymer does not undergo the transesterification reaction [24]. Transesterification of DMAEMA with ethanol was, therefore, studied here using NMR spectroscopy. Fig. 7 shows the NMR spectra of



e = proton of [isotactic CH_3 + CH_3 of carboethoxy group in poly (ethyl methacrylate) (PEMA) formed through ethanolysis of (2-dimethylamino)ethyl methacrylate (PDMAEMA)]

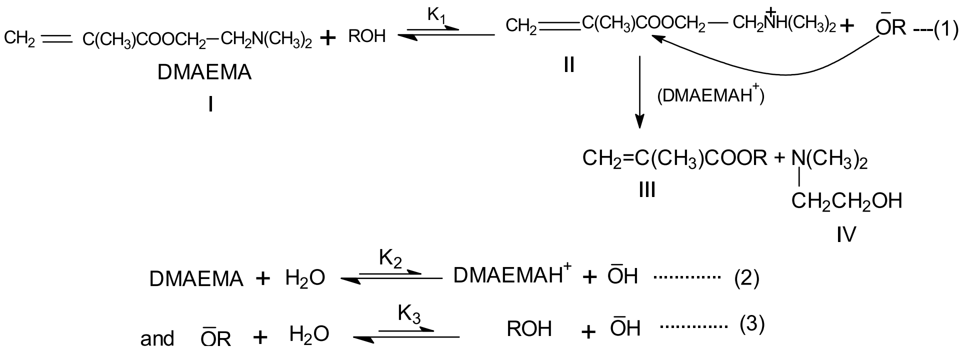
Fig. 6. NMR spectra of the (a) PDMAEMA-*b*-PMMA-*b*-PDMAEMA (15,000)-(15,000)-(15,000) tri-block copolymer in $CDCl_3$, (b) of the PDMAEMA-*b*-PMMA-*b*-PDMAEMA (17,000)-(5000)-(17,000) copolymer in D_2O and (c) of the PDMAEMA-*b*-PMMA-*b*-PDMAEMA (17,000)-(8800)-(17,000) copolymer in CD_3OD.

the monomer after keeping it mixed with ethanol–water (water 16 vol%) in 1:1 v/v proportion for 133 h at 35 °C. The triplet at $\partial = 1.31$ and a quartet (partially eclipsed) at $\partial = 4.21$ and the resonances $\partial = 5.55$ and 6.1 were confirmed to be due to the ester methyl, methylene and vinyl hydrogen resonances in EMA that forms on the ethanolysis of DMAEMA. The triplet at $\partial = 2.50$ is attributable to the N–CH_2 resonance of the other product, 2-(dimethylamino)ethanol. The rate of ethanolysis is faster in ethanol–water than in water as would be found in the kinetic plots in Fig. 8. Bories-Azeau and Armes explained the alcoholysis of DMAEMA to be self-catalysed as follows [24] (Scheme 1, reaction 1).

Table 1
Designation of di- and tri-block copolymers and their molecular weights by NMR, PDI and percent of ethanolysis

Block copolymer composition[a]	DMAEMA in copolymer mol% (NMR)	M_n[b] of PMMA block	PMMA block PDI	M_n of block copolymer[c]	Block copolymer PDI	mol% ethanolysis of PDMAEMA block
D_{57} M_{52}	58	5200	1.35	9000–5200	1.26	1
D_{89} M_{52}	62	5200	1.35	14,000–5200	1.25	1.9
$D_{223}M_{52}$	75	5200	1.35	35,000–5200	1.14	2.3
D_{23} M_{50} D_{23}	56	5000	1.33	3600–5000–3600	1.23	1.1
D_{33} M_{50} D_{33}	68	5000	1.33	5200–5000–5200	1.22	1.1
D_{48} M_{50} D_{48}	72	5000	1.33	7500–5000–7500	1.21	1.9
D_{79} M_{50} D_{79}	72	5000	1.33	12,400–5000–12,400	1.20	2.1
D_{108} M_{50} D_{108}	86	5000	1.33	17,000–5000–17,000	1.19	2.3

[a] D and M refer to DMAEMA and MMA, respectively. The subscripts denote the degrees of polymerization calculated using data in columns 2 and 3.
[b] Determined by GPC.
[c] Calculated using the data in columns 2 and 3.



Scheme 1.

However, when water is also present two more equilibria (2) and (3) operate. K_1 and K_2 are small but $K_2 \gg K_1$ and $K_3 = K_2/K_1 \gg 1$. Due to the coexistence of all the three equilibria (1)–(3) the concentration of the protonated monomer (II) will be greater and that of RO^- smaller than what would have been obtained in the absence of equilibria (2) and (3), i.e. if water were not present. However, the rate of the alcoholysis should have remained constant since the product of the concentrations of the two species in the right hand side of Eq. (1) should remain constant in order to held K_1 constant. The rate increase could, therefore, be due to the higher polarity of the ethanol–water medium than pure ethanol. On the other hand, it would be expected that the presence of water should bring about the hydrolysis of DMAEMA. In fact, the literature reports that DMAEMA hydrolyses at the rate of $t_{0.5} = 17$ h at pH 7.4 and 37 °C [34]. Occurrence of hydrolysis should result in the appearance of additional signals in the vinyl hydrogen region ($\partial = 5.45$ and 6.01) due to the hydrolysis product methacrylic acid (Fig. 7(b)). The absence of these signals in the spectra taken after 133 h of reaction (Fig. 7(a)) testifies the absence of the hydrolysis reaction. This could be due to the low concentration (16 vol%) of water and also the lower polarity of the ethanol–water medium than pure water which renders the rate of hydrolysis insignificant.

The earlier literature reported that the di-block copolymers become freely soluble in water when the PDMAEMA content is 60–67 mol% or more [12,13]. We found that the solubility in water depends greatly on the PMMA block length, as would be expected. Thus, with the PMMA block at $M_n = 8800$ the block copolymer could not be dissolved in water (pH = 7) even when the PDMAEMA content is 80 mol%. However, with a nominal $M_n = 5000$ for the PMMA block the block copolymer goes into solution in water (pH = 7) when the PDMAEMA content is 68 mol% or above. All the copolymers are, of course, freely soluble in methanol or ethanol or in their mixtures with water, acidic water (pH < 3) at one hand and the apolar solvent benzene at the other as have been reported in previous studies with the di-block copolymer [12,13].

The block copolymers in dilute solution in water exhibit surface activity as is evident from Fig. 9 which shows the decrease of surface tension of water by both the di- and the tri-block copolymers having a nearly equal mole ratio of the hydrophobic (PMMA) to hydrophilic (PDMAEMA) segments. Vangeyte et al. found a remarkable beneficial effect of stirring on the direct dissolution of their poly(ethylene oxide)-*b*-poly(-caprolactone) copolymers in water [35]. Without stirring it took a long time to reach the equilibrium surface tension. The solutions under study here were all prepared

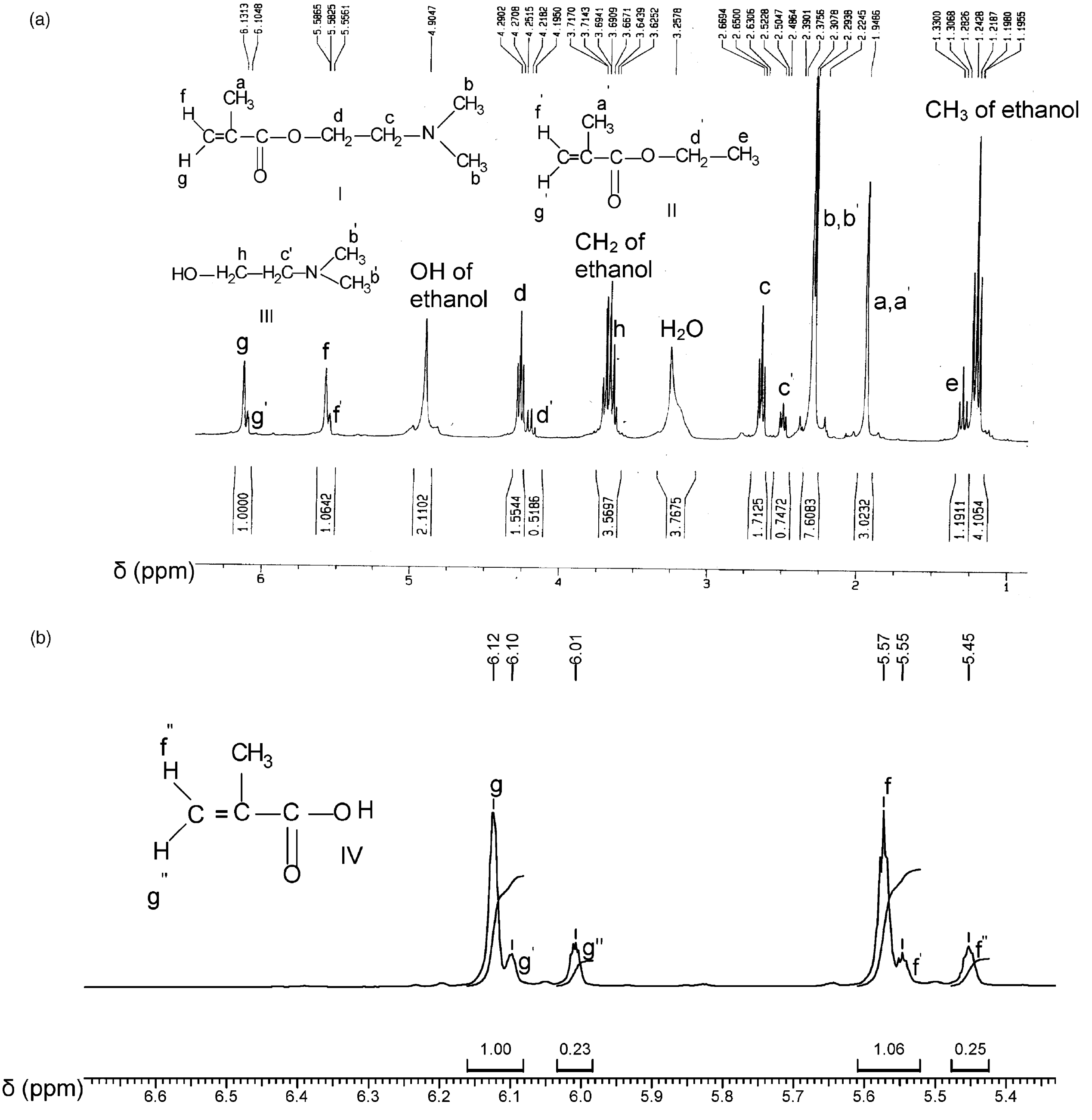


Fig. 7. NMR spectrum of (a) the reaction mixture of DMAEMA (50 vol%) in ethanol–water (16 vol% water) at 35 °C after 133 h and (b) vinyl proton resonance portion of a synthetic mixture of DMAEMA, ethyl methacrylate and methacrylic acid (8:1:1 v/v), respectively.

directly in water and with stirring. The surface tension reaches a constant value at a concentration (CMC) of about 0.35 and 0.55 g/L, respectively, for the PDMAEMA(17,000)-*b*-PMMA(5000)-*b*-PDMAEMA(17,000) and PMMA(5200)-*b*-PDMAEMA(35,000) tri- and di-block copolymers used in the study. The higher molecular weight of the hydrophilic PDMAEMA in the di-block copolymer presumably makes it less surface active. The CMC values are of the same order as that reported by Baines et al., e.g. CMC = 0.5 g/L at 22 °C for the di-block PMMA(1800)-*b*-PDMAEMA(9300) [12]. Fig. 9 also includes the results of the decrease of surface tension effected by the tri-block copolymer in a buffer solution (0.1 M phosphate) of pH 7.5. It is evident that the CMC is reduced to 0.15 g/L from the value of 0.35 g/L in water. This is attributable to the salting out effect of salts present in the buffer solutions on these amphiphilic block copolymers [12]. The figure also reveals that the transition to the micellar phase is much broader in comparison to low molecular weight surfactants. This point has been discussed by earlier workers and attributed to the polydispersity of the copolymer [36] and/or the effect of molecular rearrangement occurring before micellization [37].

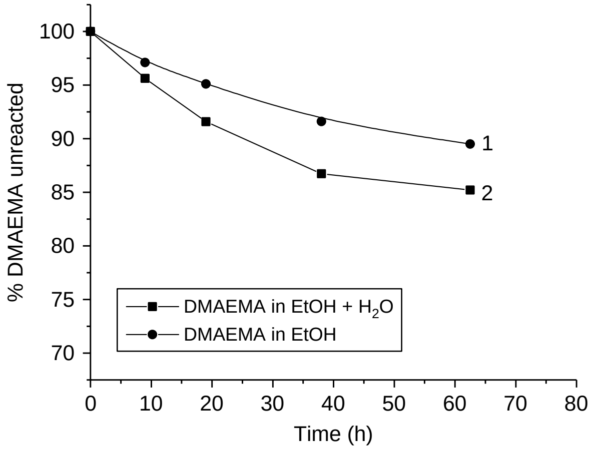


Fig. 8. Kinetic plots for the ethanolysis of DMAEMA monomer in ethanol–water (16 vol%) and in pure ethanol medium at 35 °C.

Also, the earlier studies indicated a core shell structure of the micelles from the analysis of the NMR spectra of the polymers in D_2O which is a selective solvent for the PDMAEMA block vis-à-vis that in $CDCl_3$ which is a non-selective solvent, i.e. solvent for both the blocks [12]. As is evident from Fig. 6 the easily distinguishable carbomethoxy proton in PMMA is not seen in the spectra obtained in D_2O but seen in $CDCl_3$. This suggests that PMMA is buried and the protons are not accessible to NMR in water. Methanol also works as a non-selective solvent at least up to the $M_n=8800$ of the PMMA block as is evident from the spectrum c in Fig. 6. PMMA is reported to be soluble in methanol up to the molecular weight of 20,000 [38].

The size of the micelles was determined using DLS. When the polymers were directly dissolved in water the size of the micelles varied erratically as the M_n of the blocks was varied systematically as shown in Table 2. However, when the polymers were dissolved first in methanol and diluted with the gradual addition of water to a 95% concentration (by volume) of the latter following the procedure of Baines et al. [13] a systematic variation in micelle size was achieved with block lengths. Such phenomenon has been attributed to the non-equilibrium structures of the micelles in the selective solvent which occurs when the hydrophobic block is glassy [39]. For the tri-block copolymer in aqueous methanol the micelle diameter increases from 10 to 22.8 nm as the M_n of the shell polymer is increased from 3600 to 17,000 while keeping the M_n of the core polymer (centre block) fixed at 5000. Similarly, for the di-block copolymer an increase of the M_n of the shell polymer from 9000 to 35,000 increased the diameter from 11.5 to 35.2 nm. The polydispersity in particle diameters (D_w/D_n) is rather high ca. 1.4–1.5. This is attributed to the molecular weight polydispersity of the PMMA and the PDMAEMA blocks in the copolymers. A log–log plot of the diameter of the particles vs. the DP (degree of polymerization) of the PDMAEMA blocks is shown in Fig. 10. It turns out that for both types of block copolymers (di- or tri-) D_n increases at a faster rate with DP of the hydrophilic block when the latter is much greater than that of the hydrophobic block (the so called hairy micelles) in comparison to the reverse case

Table 2
Size of di- and tri-block copolymer micelles as measured by DLS

Polymer designation	Hydrodynamic diameter (DLS) (nm)		D_w/D_n
	MeOH:water (5:95)	Water	
D_{57} M_{52}	11.5	–	1.47
D_{89} M_{52}	13	–	1.54
$D_{223}M_{52}$	35.2	–	1.46
D_{23} M_{50} D_{23}	10	–	1.45
D_{33} M_{50} D_{33}	11	59.4	1.51
D_{48} M_{50} D_{48}	12.5	–	1.43
D_{79} M_{50} D_{79}	13.7	11.7	1.52
D_{108} M_{50} D_{108}	22.8	36	1.45

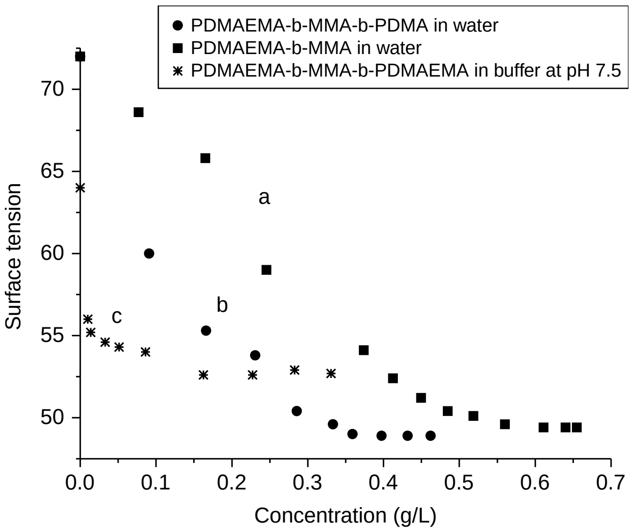


Fig. 9. Surface tension vs. concentration (g/L) of (a) di-block copolymer PMMA(5200)-*b*-PDMAEMA(35,000), (b) the tri-block copolymer ($M_n=17$, 000-5000-17,000) in water and (c) of the latter in 1 (M) phosphate buffer solution at 37 °C.

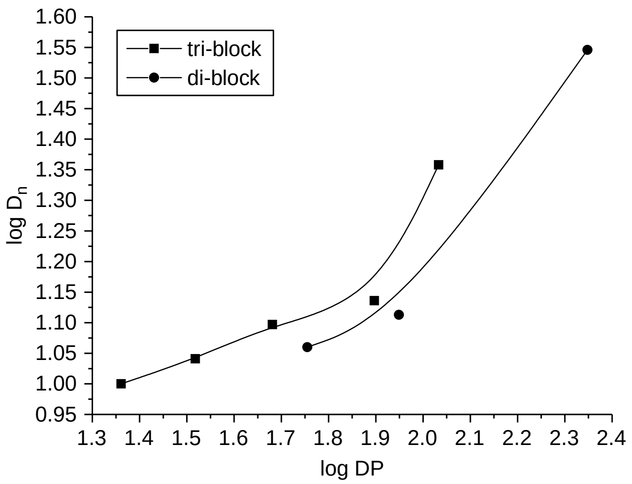


Fig. 10. log–log plot of the diameter (D_n) of the micelles vs. the DP of the hydrophilic PDMAEMA block in water:methanol (95:5 v/v) for a nominal DP=5000 for the PMMA block.

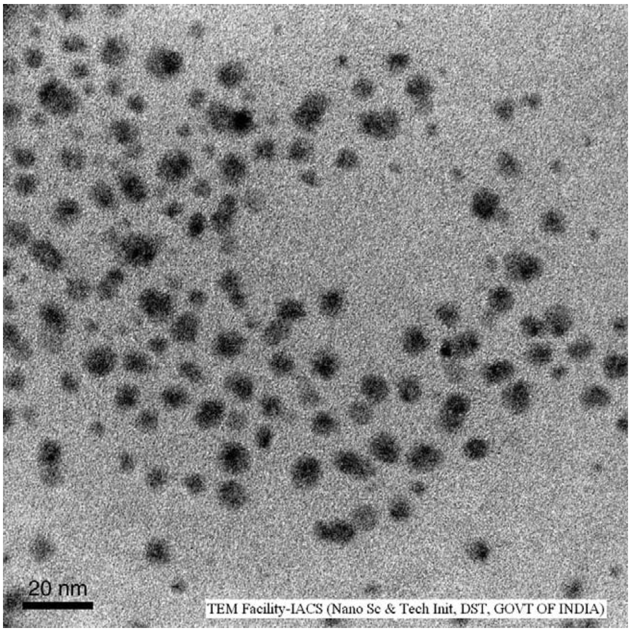


Fig. 11. A representative TEM picture of the micelles from the tri-block copolymer PDMAEMA(3600)-*b*-PMMA(5000)-*b*-PDMAEMA(3600) copolymer prepared in water:methanol (95:5 v/v).

(the so called crew-cut micelles). The micelles of the di-block copolymers are somewhat smaller than those of the tri-block copolymers.

The TEM picture of the micelles is shown in Fig. 11. It reveals their polydisperse nature.

4. Conclusion

This study thus shows that the di- and tri-block copolymers of DMAEMA and MMA can be prepared by ATRP at ambient temperature in the environment-friendly solvent aqueous ethanol (16 vol% water). The PDMAEMA blocks are, however, contaminated by ethyl methacrylate residues to the extent of 1–2 mol% of DMAEMA (higher value for longer PDMAEMA block produced by using higher DMAEMA concentration and longer time of polymerization) due to ethanolysis of the latter and subsequent copolymer formation. The size of the micelles in water:methanol mixture (95:5 v/v) increases at a rapid rate with DP of the hydrophilic PDMAEMA block when the latter is much greater than the DP of the hydrophobic block.

Acknowledgements

Thanks are due to the Department of Science and Technology and the Council of Scientific and Industrial Research, Government of India for financial support.

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