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ORIGINAL CONTRIBUTION

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Micellization and applications of narrow-distribution poly[2-(dimethylamino)ethyl methacrylate]

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Abstract Oxyanion-initiated polymerization of 2-(dimethylamino)ethyl methacrylate (DMAEMA), initiated by potassium benzyl alcoholate (BzOK), produced a number of well-defined, water-soluble benzyloxy end-capped homopolymers of various molecular weights. The structure of these homopolymers was confirmed by FTIR and ^{1}H NMR. The molecular weights of the polymers were estimated by comparing the ^{1}H NMR peak integrals for phenyl protons of the benzyloxy group with those of the dimethylamino protons of the monomeric unit. GPC analysis showed that these homopolymers possess a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$) in the range of 1.15–1.28. Under acidic or neutral conditions, the polymers exhibit the behavior of polymeric surfactants bearing protonized tertiary amines in their pendants, with critical micelle concentration (CMC) between 0.5 to 1 g/L and surface tension dropping below 40 mN/m. It was also found that the lower critical solution temperature (LCST) of the polymeric surfactants (as determined by UV-visible spectroscopy) varied with properties such as molecular weight, concentration, and pH in aqueous media. The polymeric surfactants showed excellent pH-response and emulsifier properties when used in the emulsion polymerization of styrene.

Keywords Polymeric surfactant · PDMAEMA · Micellization · Emulsion polymerization

Introduction

Poly[2-(methylamino)ethyl methacrylate] (PDMAEMA) and 2-(methylamino)ethyl methacrylate-based copolymers are among the most academically and industrially important water-soluble or amphiphilic (co)polymers [1, 2, 3, 4]. PDMAEMA can form a cationic polyelectrolyte under acidic/neutral conditions, or transform into ampholytes via straightforward quaternization [5, 6]. There have been many reports about block copolymers containing PDMAEMA, which have many potential application areas, including flocculation for water and waste water treatment, adhesives, and emulsion and dispersion stabilizers [1, 7]. In addition, PDMAEMA properties show good pH/temperature response in aqueous solution, which is useful for the design of drug-delivery systems and for modification of biomedical polymer surfaces [8, 9, 10].

Since Nagasaki et al [11] reported the homopolymerization of 2-(diethylamino)ethyl methacrylate via oxyanionic polymerization, this new polymer chemistry has been used to make novel, well-defined amphiphilic block copolymers [12, 13, 14, 15, 16]. Báñez et al synthesized amine methacrylate-based homopolymers and block copolymers by oxyanion-initiated polymerization [4]. Their results indicated that the oxyanionic polymerization appeared to have reasonable "living" character. DMAEMA homopolymer was synthesized in other controlled process, such as living anionic polymerization [1, 17, 18] or group transfer polymerization (GTP) [2, 3, 19, 20, 21].

However, it is also necessary to study the PDMAEMA homopolymer, particularly in regard to the variation of micelle formation and LCST with the molecular weight of the polymer. Also, little has been reported about effect of these homopolymers as a stabilizer for the emulsion polymerization of styrene.

In the present work, we used oxyanion-initiated polymerization to prepare a number of benzyloxy end-capped PDMAEMA homopolymers with different molecular weights and a narrow molecular weight distribution. In a range of pH conditions, a solution of the polymers exhibited phase-separation, and the solution turned cloudy when the temperature was raised above the LCST. The influence of the degrees of polymerization (*DP*) and pH conditions on both micellization and pH/temperature sensitivity were studied in detail. Using the homopolymer as emulsifier in the emulsion polymerization of styrene, we obtained near-monodispersed polystyrene microspheres after varying the recipe for emulsion polymerization.

Experimental

Materials

Potassium hydride (KH), from Aldrich was washed by dry THF before use. Benzyl alcohol (from Yixing Chemical Reagent Co., China) was distilled under pressure and dried by CaH_2 more than 12 h before use. DMAEMA monomer (Jiangsu Xinyu Chemical Reagent Co., China) was passed through an activated basic alumina column and distilled immediately *in vacuo* before use. THF (Shanghai Chemical Reagent Co., China) was dried with sodium wire for 3 days and subsequently refluxed in the presence of sodium wire for 3 days before use. Commercially available styrene (Shanghai Chemical Reagent Co., China) was cleaned and distilled under reduced pressure before use. 2,2'-Azobis- (2-methylpropionamidine) dihydrochloride (V50, Aldrich) was of reagent grade and used as received. Deionized water was used throughout this work.

Preparation of benzyloxy-capped DMAEMA polymers by oxyanionic polymerization

The polymerization was carried out in a similar way to that reported in previous literature [4, 14, 15]. To summarize, benzyl alcohol (BzOH) was first reacted with KH in a flask to form potassium benzyl alcoholate (BzOK), to be used as an initiator. Subsequently, DMAEMA monomer was injected into the above flask and initiated to produce a polymer.

A more detailed description of our technique is as follows. Into a preweighed flask with a magnetic bar, dry THF (25 mL) and washed KH (0.05 g, 2.08×10^{-3} mmol) were added. Benzyl alcohol equivalent to the molar amount of KH was first reduced by THF and then added via a syringe to the flask. The reaction solution was stirred at 0 °C for 0.5 h to yield the BzOK. A stoichiometric amount of DMAEMA monomer was then added to the flask by a syringe. The polymerization proceeded at 30 °C for 1 h before being quenched with methanol. This reaction scheme for benzyloxy-capped poly(DMAEMA) (BzO-PDMAEMA) is shown in Fig. 1.

The solvent was then removed with a rotary vacuum distillatory. The polymer was purified by repeated precipitation into cold n-hexane (to remove the unreacted monomer). Finally, the samples were dried in a vacuum oven at 40 °C for 3 days.

Characterization of BzO-PDMAEMA

Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra were recorded on a Nicolet Magna 550 FT-IR spectrometer, and the samples were prepared by the casting of the sample solution onto a piece of KBr slice.

NMR spectroscopy

The composition of benzyloxy-capped poly(DMAEMA) was evaluated via 400-MHz ^1H nuclear magnetic resonance spectroscopy (INVOA-400). Samples were run in $CDCl_3$ at ambient temperature. The molar content of DMAEMA monomeric units was obtained by comparing their integrated signals (six dimethylamino protons) with that of the five phenyl protons.

GPC measurements

GPC studies were carried out using a Shimadzu-1C-10A instrument. THF and triethylamine was used as the eluent at a flow rate of 1 mL·min^{-1}. Standard polystyrene was used for the calibration.

Surface tension measurement

Surface tension measurements were carried out with a JZHY-180 surface tensiometer (Chengde Experimental Instrument Co., China). Aqueous stock polymer solutions of various pH were prepared by dissolving the pure polymer in a known amount of deionized water, and adjusting the solutions to pH 3.0, 5.0 and 7.0, respectively, using a hydrochloric acid diluent. A series of aqueous polymer solutions with different concentrations were prepared by the dilution of the stock solution, maintaining the same pH with hydrochloric acid. All measurements were carried out at 20 °C, and the obtained values were checked periodically via measurement of the surface tension of dionized water.

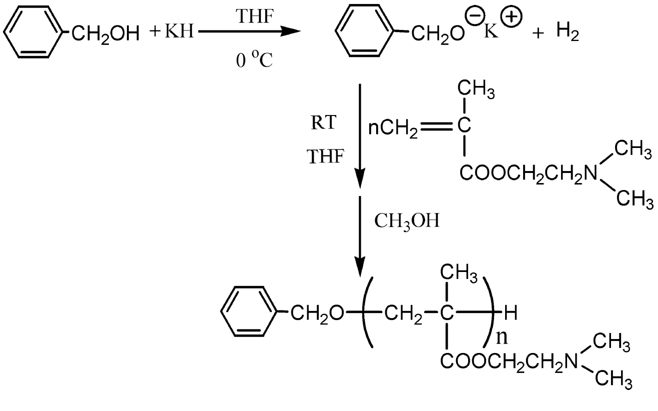

Fig. 1 Reaction scheme for the synthesis of benzyloxy end-capped poly(DMAEMA)

Table 1 Recipe used for emulsion polymerization with selected benzyl-capped DMAEMA polymer used as an emulsifier

Ingredients	Quantities (g)
Styrene	1.0
Polymeric surfactant	0.01–0.20
V50	0.02
H_2O	50.0

LCST measurement

Turbidimetric measurements of the polymer aqueous solutions at various temperatures were conducted with a Perkin-Elmer Lambda 17 UV-visible spectrophotometer at 500 nm. The quartz cell was thermostated with a circulating water jacket equipped with a temperature controller. The polymer solutions of various concentrations were heated slowly from a starting temperature of 10 °C at a heating rate of 0.5 °C/min. The LCST was defined as the onset temperature of the cloud point curves [14].

Preparation of polystyrene latexes

Polystyrene latexes bearing cationic groups were prepared by the emulsion polymerization of styrene, using benzyloxy-capped poly(DMAEMA) as emulsifier at selected pH. V50 was used as initiator. The typical recipe for emulsion polymerization is given in Table 1.

Determination of polystyrene particle size and size distribution

The particle size and size distribution of polystyrene latexes were measured by a dynamic light scattering (DLS) spectrometer (Malvern Autosizer 4700) at 25 °C. The cumulant method was chosen for measuring the *z*-average hydrodynamic diameter (D_z) and polydispersity. The morphology of polystyrene particles was observed by transmission electron microscopy (TEM), using a Hitachi H-600.

Results and discussion

Synthesis and characterization of BzO-PDMAEMA

Benzyloxy end-capped DMAEMA polymer was synthesized by oxyanion-initiated polymerization, as described in the previous section. According to the report by Báñez *et al.* [4], the number-average molecular weight increased linearly with conversion and the polydispersity remained low throughout the polymerization. From the FTIR spectrum of the polymer, we found that the strong wide band of hydroxyl groups at 3500 cm^{-1} was not observed, as shown in Fig. 2, indicating that the hydroxyl groups of BzOH quantitatively converted into alcoholate salts during preparation of the BzOK initiator. The strong carbonyl band at 1734 cm^{-1} is attributed to the ester group (C = O) of poly(DMAEMA).

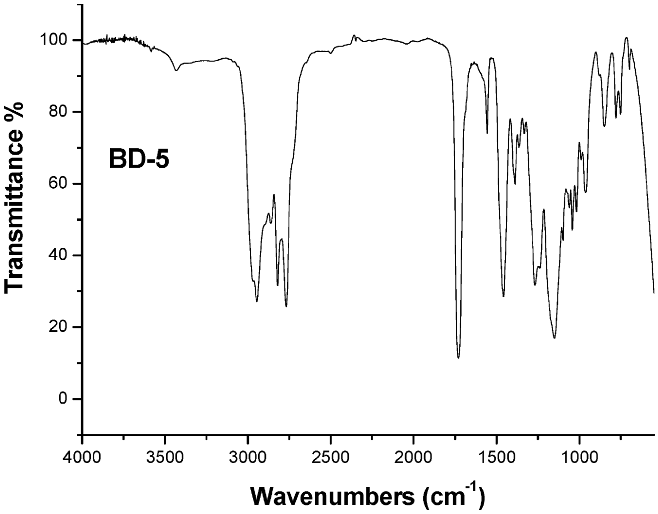

Fig. 2 FTIR spectrum of benzyloxy end-capped poly(DMAEMA) (Sample BD-5)

^{1}H NMR was used to investigate the composition of the polymer. The benzyloxy group was considered the labeled compound in the ^{1}H NMR analysis. The ^{1}H NMR signals from the six dimethylamino protons of poly(DMAEMA) are clearly visible at $\delta =$ 2.2–2.3 ppm, as shown in Fig. 3. By comparing these with the peak integrals obtained for the signals of five phenyl protons at $\delta = 7.2$–7.4 ppm, which were used as a label, the molecular weight ($\bar{M}_n$) of the DMAEMA polymer was calculated. The molecular weights were slightly higher than those expected from the ratio of monomer to initiator because of the initiation efficiency.

GPC measurement established the molecular weight distribution of these polymers. The $\bar{M}_w/\bar{M}_n$ values of the polymers were in the range of 1.15–1.28, suggesting that the polymers were almost narrow-distribution polymers. Table 2 summarizes the compositions, molecular weights, molecular weight distribution and other physical properties of the polymers.

Micellization of BzO-PDMAEMA

Surface tension measurements of the aqueous solutions of selected polymers were carried out in order to examine the surface activities of the BzO-PDMAEMA at pH = 7 and 20 °C. Fig. 4a, b and c show the surface tensions of the polymer solutions as a function of the logarithm of polymer concentrations for samples BD-1, BD-2 and BD-5, respectively. The pH values of these aqueous solutions were 7.0.

In all cases, surface tension decreased with increasing polymer concentration, indicating that micelle formation in the aqueous solution occurs. For the three samples, the breakpoints of the decreasing surface tension indicated the critical micelle concentrations (CMC) of these polymers ranged between 0.5~1 g/L. The lowest surface tensions achieved were 35.6 mN m^{-1} (for BD-1), 38.4 mN m^{-1} (for BD-2) and 40.0 mN m^{-1} (for BD-5), respectively. As expected, the relationship between concentration and CMC for BzO-PDMAEMA in neu-

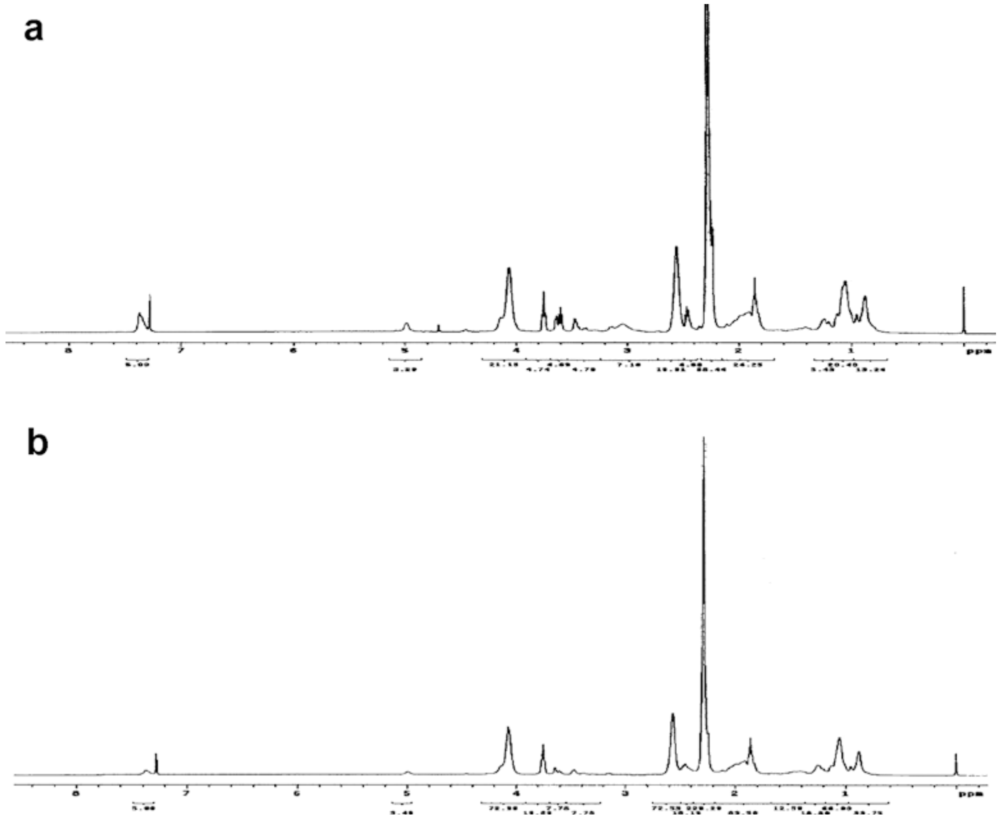

Fig. 3 ^{1}H NMR spectra of **a** BD-1 and **b** BD-2 in $CDCl_3$

Table 2 Experimental data for benzyloxy end-capped poly (DMAEMA). Note that the aqueous solutions for the LCST measurements was maintained at pH 8.5–9.0, the molecular weight ($\bar{M}_n$) was determined by ^{1}H NMR spectroscopy in $CDCl_3$, and the molecular weight distribution ($\bar{M}_w/\bar{M}_n$) was determined by GPC in THF.

Sample No.	$\bar{M}_n$		$\bar{M}_w/\bar{M}_n$	LCST (°C)	CMC (g/L)
	Theoretical	Actual			
BD-1	1680	1950	1.15	14	0.803
BD-2	3250	4720	1.21	30	0.625
BD-5	4820	6110	1.21	33	0.527
BD-4	6390	7660	1.28	39	0.513

tral aqueous solution exhibited significant surface-active behavior with increasing polymer concentration. From Fig. 4 and Table 2, it can be seen that CMC values of these polymers depend on their molecular weights. Polymers with higher molecular weights, for example BD-5, resulted in a lower CMC than those of BzO-PDMAEMAs with lower molecular weights.

So, these results suggest that the polymers in aqueous solutions formed micelles for a wide range of molecular weight. It can be postulated that both the benzyloxy groups and the carbon chain of poly(DMAEMA) aggregated as the core and the amphiphilic pendent dimethylamino groups of poly(DMAEMA) as a corona in water.

When pH values of the polymer aqueous solutions were adjusted to lower than 7.0, no obvious breakpoint (unlike the case of pH = 7.0) was observed because partial dimethylamino groups of these DMAEMA polymers were protonized in acidic media and tended to strong hydrophilicity. The plots of surface tension with concentration for these polymers are shown in Fig. 5.

Aqueous solution properties of BzO-PDMAEMA

The effect of molecular weight of BzO-PDMAEMA on LCST under basic conditions (pH values at 8.5–9.0) are shown in Table 2. Lowe et al reported that the cloud-point temperature for a 1.0% m/v aqueous solution of DMAEMA homopolymer is in the range 32–46 °C [20]. In our experiment, we found that the LCST of BzO-PDMAEMA distinctly increased with the increase of polymerization degree of the poly(DMAEMA) moiety. For BD-1 ($\bar{M}_n = 1950$), the LCST was only 14 °C, but the value increased when the molecular weight increased: for example, the LCST of BD-4 ($\bar{M}_n = 7660$) was 39 °C. This phenomenon resulted from the presence of the hydrophobic benzyloxy groups and the length of DMAEMA polymer carbon chains, which displayed a great influence on LCST, especially for those of BzO-PDMAEMA polymers with both lower molecular weight and smaller molar ratio of hydrophilic groups. On the other hand, the relatively long poly(DMAEMA) chains promoted intra/interchain hydrophilic interac-

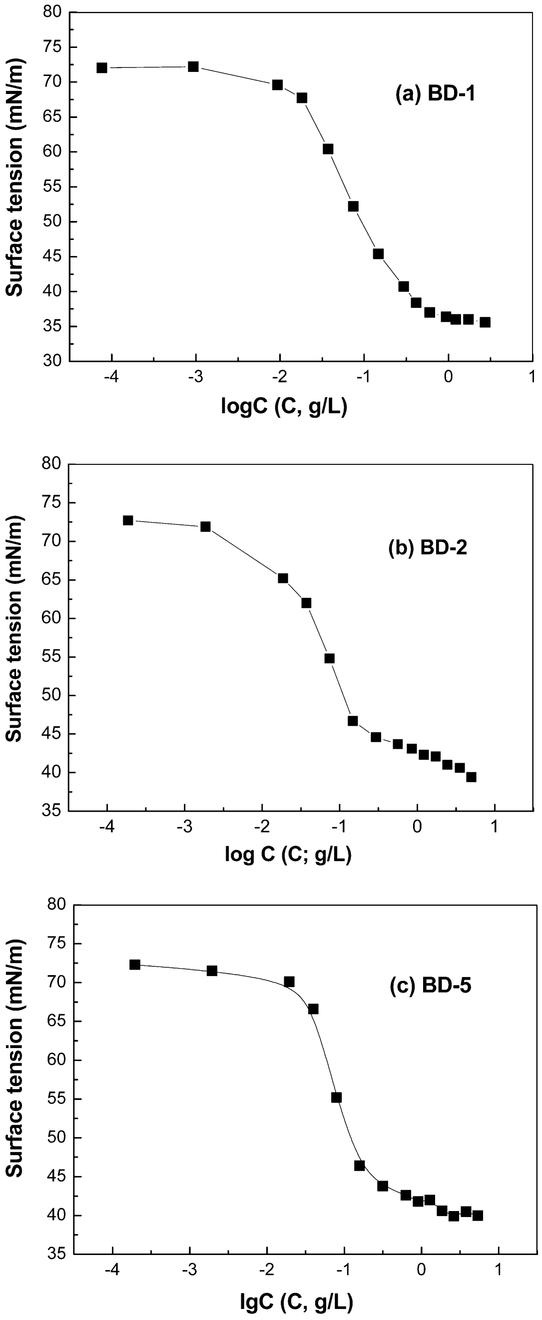

Fig. 4 Surface tension of benzyloxy end-capped polymer solutions as a function of polymer concentration for **a** BD-1, **b** BD-2 and **c** BD-5, measured at pH = 7 and 20 °C

tion. This result is consistent with the report by Báñez et al for block DMAEMA copolymers [14].

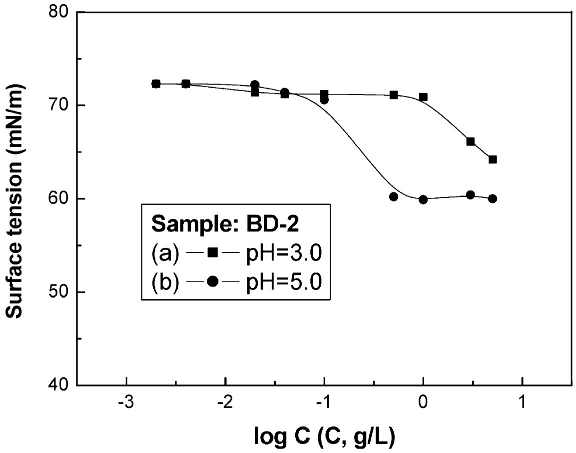

Fig. 5 Surface tension of benzyloxy end-capped polymer solutions as a function of polymer concentration for BD-2, measured at **a** pH = 3.0 and **b** pH = 5.0. All of the measurements were carried out at 20 °C

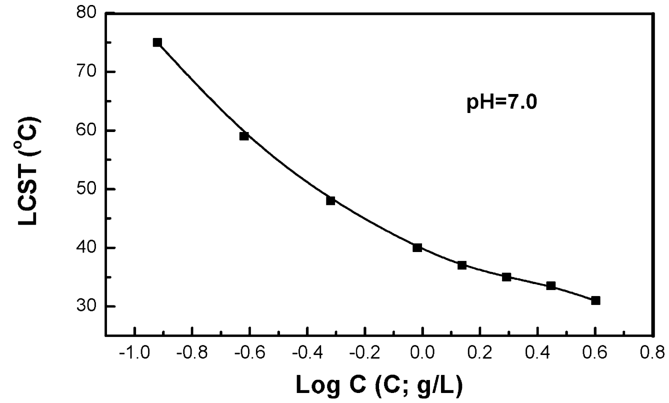

Fig. 6 Effect of concentration of Sample BD-2 on the LCST, measured at pH = 7.0

The effect of polymer concentration on the LCST was investigated by UV-visible spectrophotometer at 500 nm. A series of aqueous solutions of polymer BD-2 with different concentrations were prepared by diluting a stock solution of BD-2. In all cases, the pH values of the solutions were maintained at 7.0. We heated the solution in a water bath at the rate of 0.5 °C/min and recorded the temperature when the solution came into turbidity. Fig. 6 shows the variation of LCST with logarithmic concentration of BD-2. As expected, the LCST changes most rapidly in the range of lower concentration (from 0.01 to 0.5 g/L). The lower the concentration of the polymer, the higher the LCST. Since the appearance of LCST depended on the aggregation of the hydrophobic portions of the polymers at a particular temperature, it is thought that the interactions between the polymers were not close in the dilute solution. However, the LCST varied slowly when the concentration was more than 1.0 g/L. Interestingly, the critical concentration in Fig. 6 corresponded with the CMC measured by the surface tension method in Fig. 4b. The cloud point of the polymer in acidic media was not easily observed with the same method, even though the concentration of polymer was much higher than CMC and the heating temperature near 100 °C. This result can be attributed to the

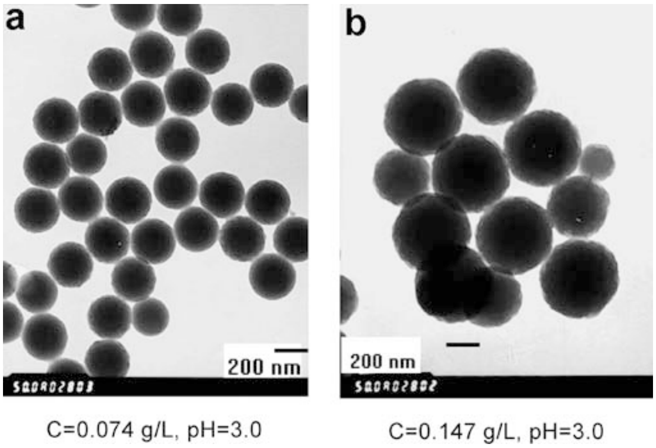

Fig. 7 TEM micrographs of polystyrene latex stabilized by benzyloxy end-capped PDMAEMA with **a** BD-2 and **b** BD-1. The emulsion polymerization of styrene was carried out at pH = 3 and 70 °C.

protonation of the dimethamino groups of the DMAEMA polymer.

Emulsion polymerization

To study the influence of the benzyloxy end-capped PDMAEMA on the formation of the latex during free-radical emulsion polymerization, we utilized the narrow-distribution polymer as a polymeric surfactant in the emulsion polymerization of styrene without any other small-molecular weight surfactant. V50 was used as an excellent radical initiator in the system, yielding two positively charged radicals in acidic or neutral aqueous media [22]. Fig. 7a and b shows the TEM micrographs of polystyrene particles stabilized by BD-2 and BD-1, respectively. It is clear that the near-monodispersed latex particles were obtained in acidic conditions (see Fig. 7a) although the concentration of polymer did not reach the CMC. This result can be explained by postulating that the molecules of the polymer formed cationic polyelectrolytes in acidic media, which acted as a protecting layer on the surface of the polystyrene particles.

The polystyrene particle in Fig. 7b was stabilized by BD-1 at pH = 3. The rough surface layer can be considered the hydrophilic protonized poly(DMAEMA). The particle size (D_z) obtained from the measurement of dynamic light scattering (DLS) was 240 nm for the sample in Fig. 7a, and 380 nm for the sample in Fig. 7b, respectively. The polydispersity of the samples was lower than 1.0. It is clear that increasing the hydrophilic chain favors the production of smaller latex particles. The average diameter measured by TEM was smaller than that of particles measured by DLS due to the shrinkage of poly(DMAEMA) in the electron beam. This observation is in good agreement with results obtained by other researchers [23, 24]. It demonstrates the existence of the hydrophilic PDMAEMA layer on the polystyrene surface. We suggest that the hydrophobic benzyloxy group was absorbed or anchored into the polystyrene microsphere and the PDMAEMA moiety extended into the water, because the latter have cationic long chains in acidic conditions.

Conclusions

Well-defined benzyloxy end-capped poly(DMAEMA) polymers with different molecular weights were synthesized via oxyanion-initiated polymerization. Their molecular weight distribution was in the range of 1.15–1.28. The effects of the molecular weight of the PDMAEMA portion on the aqueous behavior and micellization of polymers in water were investigated in detail. Under constant pH (7), the polymer with higher molecular weight exhibited lower CMC than that of samples with lower molecular weight. However, the variation of CMC for the polymers in a limited concentration declined a little in acidic media. The LCST of the polymers increased from 14 °C to 39 °C when increasing molecular weight ($\bar{M}_n$) from 1950 to 7660. LCST can be observed only in basic or neutral media, indicating that poly(DMAEMA) would tend to strong hydrophilicity. Protonation of the amine moiety produces water-soluble cationic polymers, which in combination with the hydrophobic benzyloxy group results in highly efficient stabilizers for the emulsion polymerization of styrene.

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