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SYNTHESIS AND CHARACTERIZATION OF AMPHIPHILIC DIBLOCK COPOLYMER BY REVERSE IODINE TRANSFER POLYMERIZATION (RITP)

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Abstract: Iodine transfer radical homo- and diblock copolymerization of N-[3-(dimethylamino)propyl] methacrylamide (DMAPMA) with methyl methacrylate (MMA) were carried out in the presence of iodine I_2 and 2,2′-azobis(isobutyronitrile) (AIBN) as chain transfer agent and initiator, respectively. Using reverse iodine transfer polymerization (RITP) method based on the *in situ* generation of transfer agents using molecular iodine I_2. The homopolymer and copolymer were characterized by FT-IR and ^{1}H NMR. The self-assembly behaviours of diblock copolymer in water are studied by viscosity and tensiometry techniques. The water-soluble fraction of P(DMAPMA-b-MMA) block copolymer formed micelles which were investigated at 25°C in water at 0.2 mg.mL^{-1} concentration using a tensiometry device. Dynamic light scattering technique (DLS) was performed over a wide range of concentration to determine hydrodynamic size of the aggregates.

Keywords: Amphiphilic diblock copolymer, Reverse iodine transfer polymerization (RITP), Self-organization.

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Introduction

Amphiphilic block copolymers have been arousing a strong interest amongst researchers for several decades. They are composed of at least one hydrophobic block and one hydrophilic block[1-3] and are usually called polymeric surfactants or “macrosurfactants”. In comparison to classical surfactants, amphiphilic diblock copolymers have reduced mobility and slower diffusion rates.[4]

Moreover, macrosurfactants have much lower critical micelle concentration (CMC) than their low molecular mass counterparts[5-7] typically, the CMCs of macrosurfactants have been reported in the concentration range from 10^{-9} to 10^{-4} mol.L^{-1}.[4, 8-10]

Amphiphilic block copolymers have a wide field of application, such as rheology modifiers, emulsifiers,[11-13] latex stabilizers,[14,15] demulsifiers,[5] and as enhancers of efficacy in microemulsions[16-19] or as flocculants.[11]
Amphiphilic block copolymers are also used as solubilizing agents for hydrophobic dyes[20-22] for liquid crystals[23] and for metal salts[24] as well as for the transport of oxygen in water.[25] In addition, they have been studied as controlled drug delivery systems[26-28] and used to form micelles of compounds in aqueous solutions, as nanocarriers for encapsulating nanoparticles.[29]

The most important and effective synthetic strategies leading to the preparation of amphiphilic block copolymers involve various controlled radical polymerization methods. Hence, resorting to these methods which include atom transfer radical polymerization (ATRP),[30,31] nitroxide-mediated polymerization (NMP),[32] reversible addition-fragmentation chain transfer (RAFT),[33] and iodine transfer polymerization (ITP),[34] diblock and gradient copolymers with new properties were successfully devised.

A new controlled radical polymerization method developed by Lacroix-Desmazes *et al.*[35] known as reverse iodine transfer polymerization (RITP) was applied. Already, RITP was proved to be successful for the polymerization of a wide range of monomers like styrene,[36,37] methyl acrylate,[38] methylmethacrylate,[39] butyl α-fluoroacrylate[40] and vinylidene chloride.[41] The potential of RITP lies in the *in situ* generation of alkyl iodides as transfer agents by using molecular iodine (I_2). The initiator decomposes to form radicals that react with molecular iodine resulting to *in situ* transfer agents. After consumption of all free iodine, a degenerative chain transfer mechanism governs the polymerization.[42]

We report here, the RITP method to synthesis diblock copolymer of poly(methyl methacrylate) (PMMA) as hydrophobic segments and poly(N-[3-(dimethylamino)propyl] methacrylamide]) (PDMAPMA) as hydrophilic segment.

Furthermore, we describe these new amphiphilic structure and the physico-chemical properties related to their behaviour in the aqueous medium, based on viscometry, surface tension measurements and dynamic light scattering.

Experimental Section:

Materials

Commercial N-[3-dimethylamino)propyl] methacrylamide (DMAPMA, Aldrich) was distilled under reduced pressure (80-85°C-0.2 mmHg) in order to remove the stabilizer. Methyl Methacrylate (MMA, Merck-Schuchart), 2,2-Azobis (2-methylpropionitrile) (AIBN, AcrosOrganics) was recrystallized from methanol, Iodine (I_2, Aldrich, 99.8%) was used as received.

Measurements

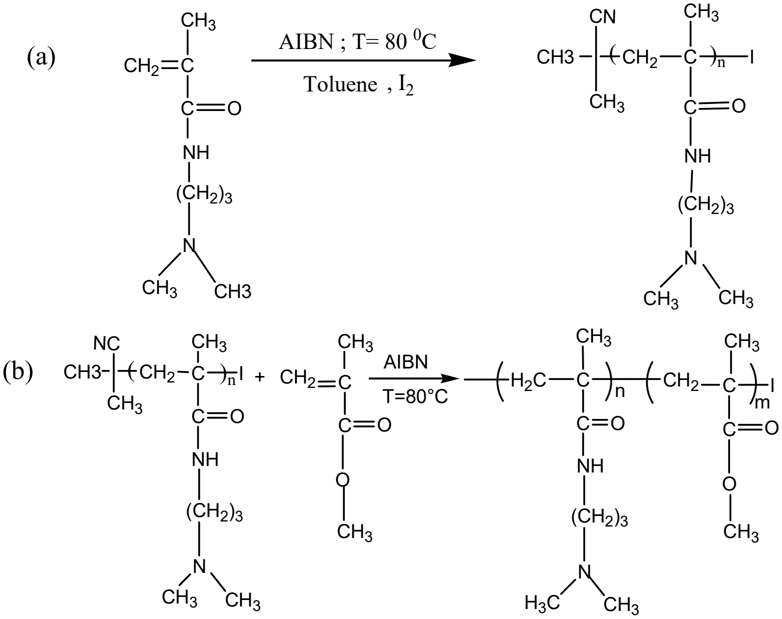
- The FTIR spectra of the homopolymer and copolymer were recorded on Schimadzu FTIR-8300 spectrometer.
- The ^{1}H NMR and ^{13}C NMR were recorded on the 300 MHz Brücker "avance" in $CDCl_3$ as solvent.
- Surface tension (γ): The measurements were done by the plate method with Gibertini TDS digital tensiometer at 25°C.
- Viscosities of polymer solutions were measured by use of capillary viscometer standard Ubbelohde in water bath maintained at 25°C±0.1.
- Dynamic light scattering: The sizes of the copolymer particles formed in aqueous solutions at 25°C were determined using a NanoZetasizer, Nano ZS Malvern device.

Synthesis of macrotransfer agent

In a single-neck flask, 2 mL of toluene were added to a mixture of 2 g of DMAPMA, iodine I_2 (0.017 mg) and (0.02 mg) of AIBN. The flask was closed under argon atmosphere, and immersed in a preheated oil bath at 80°C; in absence of light; under magnetic stirring for 24 h. The visual observation of the reaction mixture indicates that the solution is brown at the beginning of the polymerization (due to the presence of iodine), whereas the final solution is uncolored. After the reaction was stopped by cooling the flask, the polymer was dissolved in chloroform and precipitated in a large excess of heptane. The polymer recovered by filtration was then dried under vacuum at 60°C overnight, and then analyzed by FTIR and NMR spectroscopy to determinate its molecular structure.

Synthesis of block copolymerization

The block copolymer was synthesized by dissolving 1g of ω-iodo-PDMAPMA in toluene solution containing MMA monomer (0.16 g, 1.59 mmol) and AIBN (4.1 mg, 2.49 10^{-2} mmol) at 80 °C. The mixture was put into a flask and then flushed with argon for 10 minutes. The flask is then immersed in an oil bath at 80 °C, in absence of light and under magnetic stirring for 24 h. The copolymer was dissolved in the smallest amount of chloroform and precipitated in an excess of heptane. The diblock copolymer was recovered by filtration, carefully dried in vacuum at 60°C overnight.



Scheme 1. Synthetic routes of (a) homopolymer and (b) diblock copolymer.

Results and discussion

Synthesis and characterisation

RITP is an excellent method for obtaining block copolymers using simple experiment procedure, especially for preparation of amphiphilic block copolymers. The synthesis of the materials via RITP is thoroughly described in literature.[42]

Amphiphilic diblock copolymer was synthesized from DMAPMA and MMA, using AIBN as an initiator and I_2 as a control agent via two-step strategy: The polymerization of the first monomer leading to a first sequence as a macrotransfer agent was followed by the introduction of the second monomer using AIBN to carry out its polymerization. This led to a diblock copolymer. The synthetic routes of homopolymer and diblock copolymer are shown in Scheme 1.

Synthesis of homopolymers and block copolymers

We investigated the synthesis of homopolymer of PDMAPMA by RITP. Table 1 reports the most successful results obtained by varying the experimental conditions. We have carried out the polymerization at different temperatures and different molar ratio of AIBN to iodine. It has been observed that high conversion could be obtained at 80°C with a molar ratio [AIBN]/[I2] = 1.8.

Table 1. Synthesis of homopolymers by RITP after 24 h.

Polymer	T(°C)	[AIBN]/[I_2]	Conv(%)
$PDMAPMA_1$	50	1.8	60
$PDMAPMA_2$	70	1.8	96
$PDMAPMA_3$	80	1.8	98
$PDMAPMA_4$	80	1	92
$PDMAPMA_5$	80	1.5	93

Figure 1 shows a plot of $\ln([M]_0/[M])$ as a function of time, $[M]_0$ and $[M]$ respectively standing for the original and current monomer concentrations in the bulk. The plot is nearly a straight line demonstrates that polymerization of PDMAPMA can be controlled in the presence of iodine. The linear relationship between ln([M]$_0$/[M]) and time indicates that radical concentration is constant throughout the reaction and polymerization rate is also proportional to the first order of the monomer concentration.

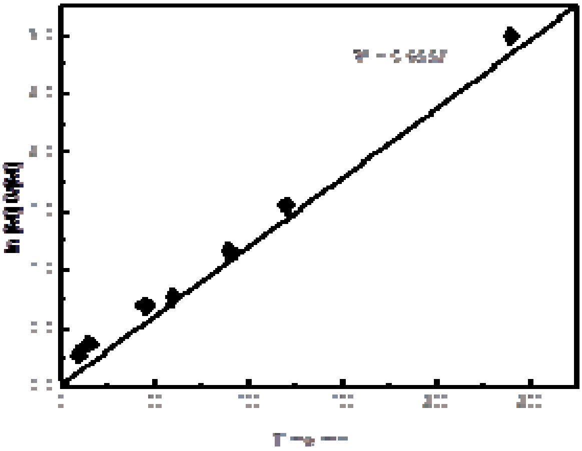


Figure 1. Plot of ln([M]$_0$/[M]) versus time for PDMAPMA homopolymer at 80°C in toluene with [AIBN]/[I$_2$] = 1.8.

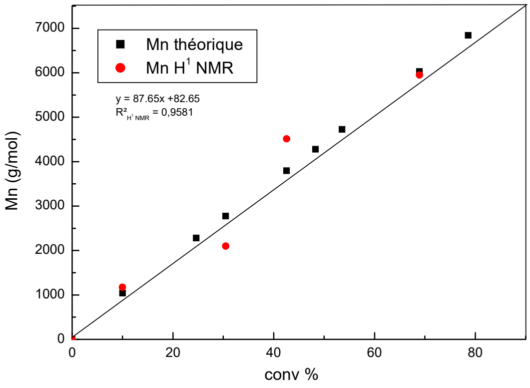


Figure 2. Evolution of molecular weight (M$_n$) versus monomer conversion.

Figure 2 shows the variation of Mn with monomer conversion during the RITP reaction of PDMAPMA at 80 °C in toluene with molar ratio [AIBN] / [I$_2$] = 1.8. M$_{n,th}$ = (mass of monomer) x (monomer conversion) / (2 x nI$_2$) + MA-I, where nI$_2$ is the number of moles of iodine and $M_{A\text{-}I}$ is the molecular weight of the chain-ends, knowing that $M_{A\text{-}I} = 195$ g.mol^{-1}).[42]

The observed linear dependence is a strong indication that the polymerization of PDMAPMA using iodine is indeed a controlled radical polymerization process.

The diblock copolymer was obtained by ITP polymerization of MMA from PDMAPMA-I macrotransfer agent. Direct synthesis of P(DMAPMA-*b*-MMA) block copolymer has been performed starting from a mixture of PDMAPMA-I dissolved in a toluene solution containing MMA monomer as hydrophobic segment and AIBN at 80°C. Homopolymer and diblock copolymer were characterized by spectroscopic methods IR and RMN analysis.

Characterization of homopolymer and amphiphilic diblock copolymer:

Fourier transform infrared spectroscopy: Curves (a) and (b) in Figure 3 present the FT-IR spectra of homopolymer PDMAPMA-I Compared with diblock copolymer P(DMAPMA-*b*-MMA). In PDMAPMA-I spectrum, the typical peak appearing at 3200-3500 cm^{-1} (corresponding to N-H stretching vibration). The typical peak appearing at 1647 cm^{-1} (corresponding to amide groups), the bands at 2925 and 2854 cm^{-1} were the characteristic band of the $-(CH_2)_n-CH_3$.

In P(DMAPMA-*b*-MMA) spectrum, the typical peaks of both PDMAPMA segments are all detected and a new typical peak appearing at 1729 cm^{-1} (Corresponding to C=O stretching band of the PMMA segments).

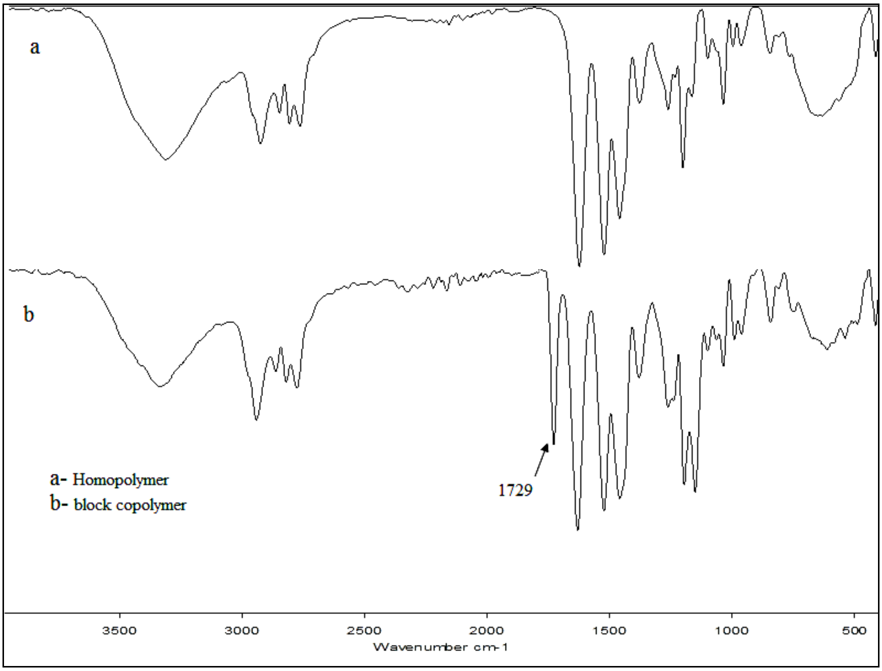


Figure 3. FT-IR spectra of synthesized homopolymer (a) PDMAPMA and diblock copolymer (b) P(DMAPMA-b-MMA).

RMN Analysis of diblock P(DMAPMA-b-MMA):

The PDMAPMA-I homopolymer was characterized by ^{1}H NMR and ^{13}C NMR in $CDCl_{3,}$ ^{1}H NMR spectra is given in Figure 4: ^{1}H NMR ($CDCl_3$, δ in ppm): 1.08-1.21 (H_a, $(–CH_2–)_n$), 0.97 (H_b, CH_3–C–), 3.50-3.05 (H_c ,NH), 1.66 (H_d, CH_2–), 2.37 (H_e,CH_2–N), 2.25 (H_f, CH_3-N), 1.66 (H_d, -CH_2-C-I).

As shown in Figure 5, ^{1}H NMR spectrum of the final copolymer, exhibits signals at 3.60 ppm which can be attributed to O-CH_3.

Figure 6 shows ^{13}C NMR spectrum of P(DMAPMA-b-MMA) diblock copolymer: ^{13}C NMR ($CDCl_3$, δ in ppm):177 ppm ($\underline{C}$=O of ester),176,5 ppm ($\underline{C}$=O of amide),51 ppm ($\underline{C}H_2$-N),44 ppm ($\underline{C}H_3$-O), 55 ppm (–CH_2-$\underline{C}$-CH_3), 18 ppm ($\underline{C}H_3$-C), 26 ppm (CH_2-$\underline{C}H_2$-).

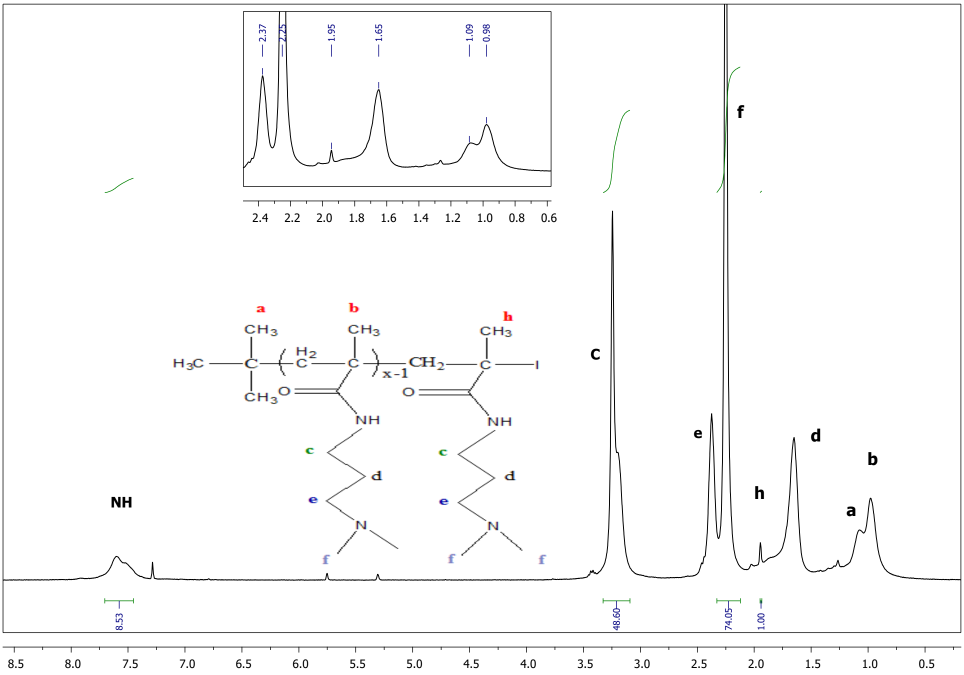


Figure 4. ^{1}H NMR spectrum of PDMAPMA-I homopolymer.

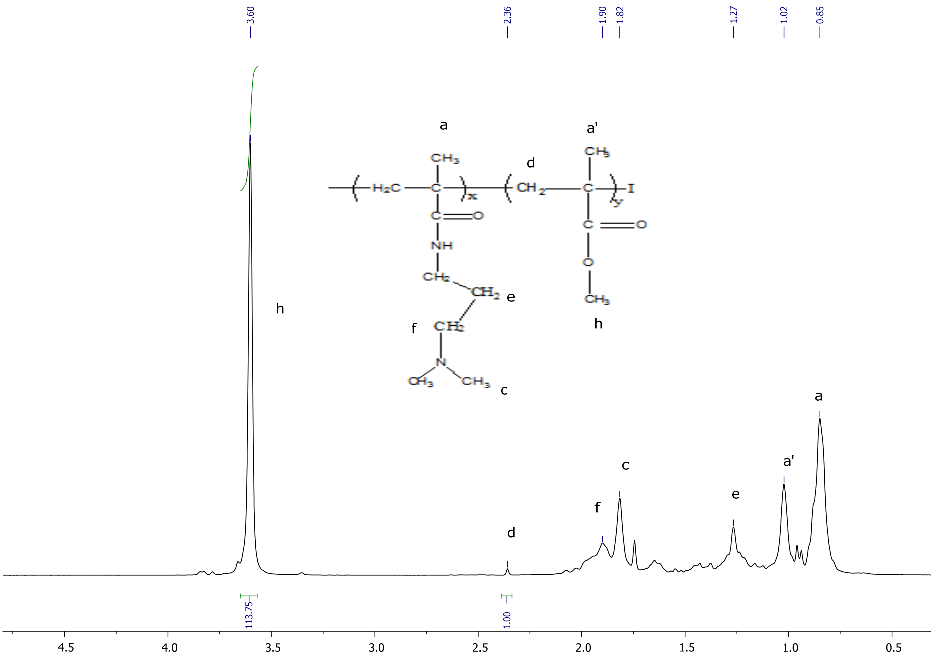


Figure 5. ^{1}H NMR spectrum of P(DMAPMA-b-MMA) diblock copolymer.

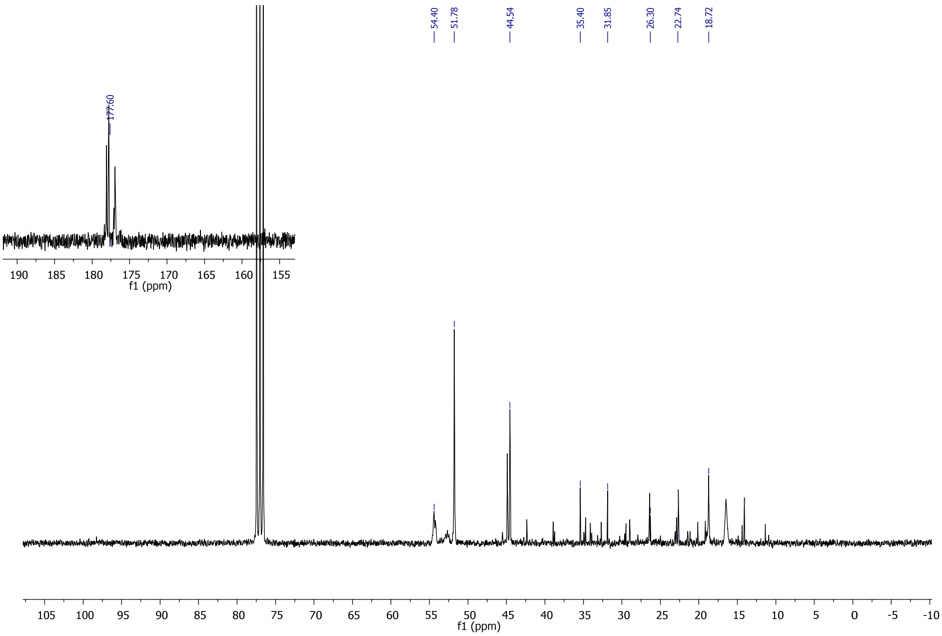


Figure 6. ^{13}C NMR spectrum of P(DMAPMA-b-MMA) diblock copolymer.

Viscosity: The purpose of this study was to analyse the influence of water content on viscosity for solutions of diblock amphiphilic copolymer in an organic solvent in the presence of an increasing proportion of water to determine the exact nature intra- or intermolecular aggregation.

The high solubility of this copolymer in pure acetone which is themselves soluble in water enabled a systematic study. Figure 7 shows the viscosity obtained in mixtures of solvent (acetone and water) for diblock copolymer. The most characteristic observation was that the reduced viscosity remained high as far as the solution water content was reach a particular water content above which the reduced viscosity increased fastly.

Indeed, if hydrophobic microdomains had been the result of intermolecular associations, as in the case of associative polymers, the reduced viscosities of the corresponding samples would have increased with content, since intermolecular associations tend to increase the hydrodynamic volume of the macromolecules.

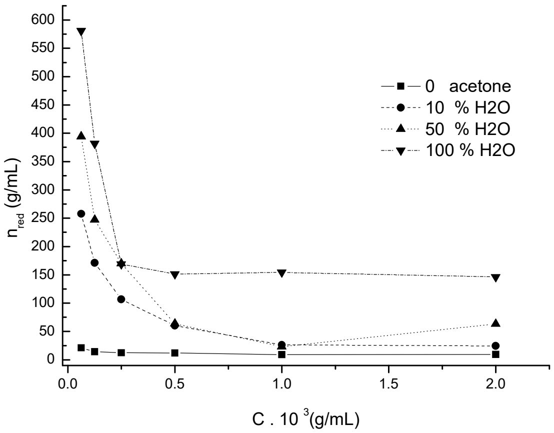


Figure 7. Variation of the reduced viscosity η_{red} of P(DMAPMA-b-MMA) with increasing water contents.

Surface activity: The surface active behaviour of amphiphilic diblock copolymer was studied by surface tension measurement. Figure 8 illustrates the equilibrium surface tension for amphiphilic diblock copolymer as a function of polymer concentration in aqueous solution. The plot shows surface tension of water gradually decreases as polymer concentration increases. As seen, the polymer exhibits a nearly constant surface tension value at low polymer concentrations which proves that molecular adsorption at the water/air interface is very weak. This adsorption becomes more prevalent when polymer concentration becomes higher than 0.78 10^{-3} g.mL^{-1}. As shown in Figure 8, a critical micellar concentration was found to be at 0.78 10^{-3} g.mL^{-1} which corresponds to γ_{CMC} (dyn.cm^{-1}) [31, 34].

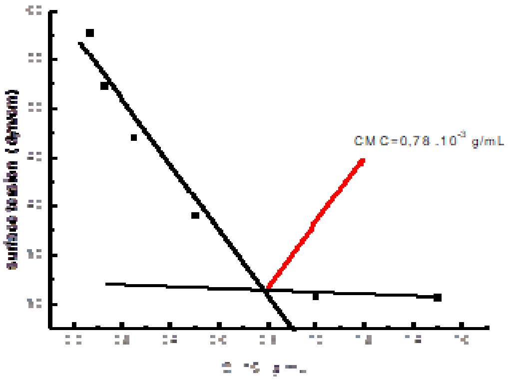
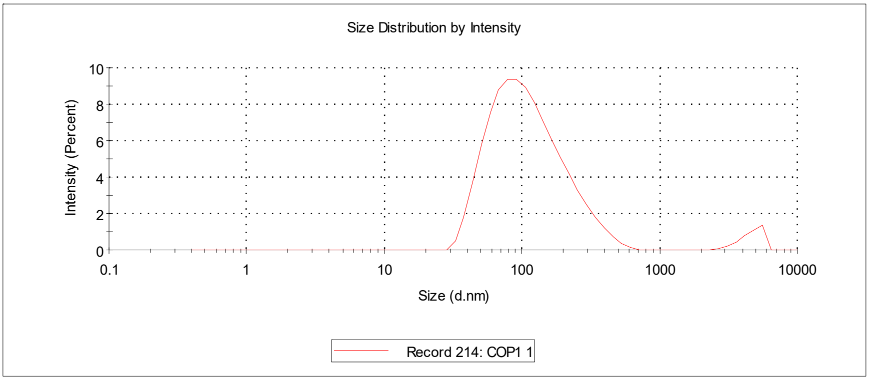


Figure 8. Variation of the equilibrium surface tension with copolymer P(DMAPMA-b-MMA) concentration in water solution.

Size of copolymer aggregates: To estimate the apparent hydrodynamic diameter of the micelle-like of structures formed by the amphiphilic P(DMAPMA-*b*-MMA) diblock copolymer in aqueous solution, Dynamic Light Scattering (DLS) studies were carried out in the concentration range of 0.002 g.mL^{-1} -0.00025 g.mL^{-1}. DLS analysis of aqueous solutions indicated the presence of micellar aggregates in the nanometer range. Figure 9 shows, size distributions examples for P(DMAPMA-b-MMA) diblock copolymer in the concentration at 0.002 and 0.0015 g.mL^{-1} in H_2O at T = 25 °C , respectively.



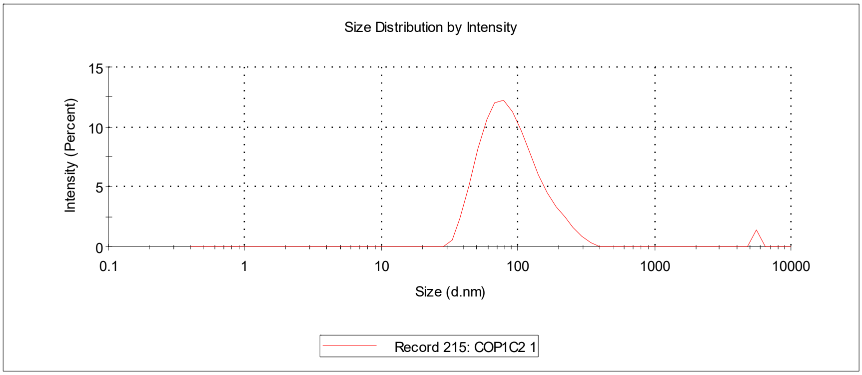


Figure 9. The size distributions of diblock copolymer in the concentration 0.002 and 0.0015 g.mL^{-1} in H_2O.

Figure 10 shows, the DLS measurements at different concentrations of the copolymer, we observe a slight decrease of the hydrodynamic diameter of aggregates with increasing concentrations. The average diameter is around 95 to 209 nm corresponding to the inter-chain aggregate of several polymer units, called as multiple polymeric micelles which usually grow in numbers as well as in size with increase in polymer concentration due to the stronger hydrophobic interaction resulting in an increase of hydrodynamic diameter with broad distribution, as reported by others.[43,44]

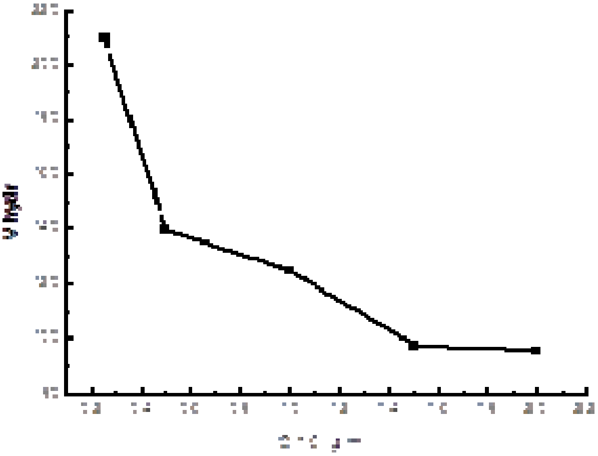


Figure 10. Diameter function concentration in the concentration range of 0,002 - 0.00025 g.mL^{-1}.

Conclusion

In the present work, a new amphiphilic copolymer consisting of a hydrophilic PDMAPMA block and a hydrophobic PMMA block was synthesized starting from a PDMAPMA macroinitiator through RITP method based on the *in situ* generation of transfer agents using molecular iodine I_2. The results illustrate that RITP is a suitable process for preparation of functional polymers.

The analysis by FT-IR and NMR confirmed that diblock copolymer combining hydrophilic/ hydrophobic segments was made. The tensioactive and viscosity properties of the copolymer allowed us to conclude that the amphiphilic block copolymer constitute a new class of tensioactive nonionic compounds. Dynamic light scattering technique allowed determining hydrodynamic size of the aggregates. It was observed that copolymer retain open conformation in the dilute solutions. However, with increase in concentration the intermolecular association becomes favorable towards the formation of more compact aggregates. Unlike the results reported in literature for structurally similar copolymers we have not observed very small aggregates, this could be due to the large size of the polymers.

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