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Synthesis of new amphiphilic cationic block copolymers and study of their behaviour in aqueous medium as regards hydrophobic microdomain formation

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Abstract

Block copolymers of *N*-hexadecyl-4-vinylpyridinium bromide ($4VPC_{16}Br$) and *N*,*N*-dimethylacrylamide (DMAA) were synthesised by nitroxide-mediated radical polymerisation using 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) as a control agent. The behaviour of such block copolymers in aqueous medium was then investigated in relation to the respective size of both the amphiphilic and the hydrophobic block. Viscosimetry, surface tension measurements, and fluorescence spectroscopy revealed that intramolecular hydrophobic microdomains were spontaneously formed by the pendent long alkyl chains. The properties of the corresponding microdomains were determined in terms of polarity and local cohesion, and were revealed to depend on the relative length of the blocks in the copolymer.

Keywords: Poly(*N*-hexadecyl-4-vinyl pyridinium bromide)-*b*-poly(*N*,*N*-dimethylacrylamide); Nitroxide-mediated radical polymerisation; Physico-chemical studies

1. Introduction

For the last 30 years, amphiphilic polymers have become a major subject of investigation [1], and their use has progressively developed to many fields, such as enhanced oil recovery [2,3] or biomedical substances [4,5]. Their widely extended range of potential industrial applications is a consequence of their particularly interesting tendency to self-associate in the aqueous medium [6–10], yielding microdomains with lowered polarity that can be incorporate and transport external hydrophobic molecules. Thus, previous work [11–13] on cationic amphiphilic species derived from polyvinylheterocycles (imidazole, pyridine) quaternised by long alkyl chains had led us to conclude that comb structures were particularly likely to induce intramolecular side chain aggregation leading to micelle-like pseudophases.

So far, amphiphilic polymers were all usually obtained by chemical modifications of previously existing macromolecules (e.g. natural polymers) or by (co)polymerisation of monomers that are themselves amphiphilic species. In the latter case, free radical polymerisation represented a significant synthetic pathway, but the obtained copolymers were more frequently random copolymers since block copolymers are not easily obtained by radical polymerisation. In the case of amphiphilic polyvinylimidazolium or polyvinylpyridinium salts, the introduction of hydrophilic units with a view to preparing copolymers proved a proper method to modulate the polymer properties. However, it was not possible to control the polymer microstructure unless conversion yield was drastically limited. Moreover, for each copolymer composition, the corresponding aggregation structure was much influenced by the different random insertion of hydrophilic units among hydrophobic ones. Thus, it seemed really interesting to examine the behaviour of block copolymers, in which each particular block would participate in the features of the whole macromolecule by its own characteristics.

This is the purpose of this article: investigations in the field of block copolymerisation required a different polymerisation method. For several years, pseudo-living radical polymerisation has offered an interesting outlook as regards the opportunity to synthesise block copolymers by radical reactions. Indeed, since Rizzardo's pioneering work [14], pseudo-living free radical polymerisation has become a frequently used strategy, providing controlled architectures

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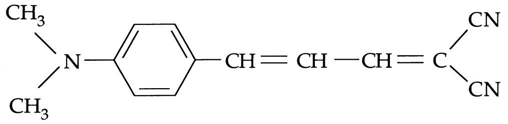


Scheme 1.

under very basic experimental conditions following different techniques. Among the latter, Nitroxide-Mediated Radical Polymerisation (NMRP) [15,16]was chosen owing to its applicability to different types of monomers. In NMRP, nitroxide radicals are used as capping agents, involving a mechanism based on the existence of dormant species formed by the reversible association of the growing chain with a stable free radical (in the present case, TEMPO). In our case, NMRP allowed the synthesis of a set of bi-block copolymers combining a poly(*N*-hexadecyl-4-vinylpyridinium bromide) amphiphilic block of constant size and a poly(*N*,*N*-dimethylacrylamide) block of varying size. This article describes these new amphiphilic structures and the physico-chemical properties related to their behaviour in the aqueous medium, based on surface tension measurements, viscometry and fluorescence spectroscopy.

2. Experimental

2.1. Materials

Commercial 4-vinyl pyridine and *N*,*N*-dimethylacrylamide (Aldrich) were distilled under reduced pressure (62–65°C/ 15 mmHg and 80–81°C/20 mmHg, respectively), in order to remove the stabiliser. Commercial 2,2,6,6,-tetramethyl-piperidin-1-oxyl (Aldrich) was used as received, and benzoyl peroxide (BPO), also purchased from Aldrich, was recrystallised from methanol. For fluorescence spectroscopy, the rotor 1,1-dicyano-(4′-dimethylaminophenyl)-1,3-butadiene (DMAC, Scheme 1) was synthesised according to a Knoevenagel's reaction between 4-(*N*,*N*-dimethylamino)-cinnamaldehyde and malonitrile with a 84% yield after recrystallisation from ethyl acetate (m.p. = 147°C; literature 146–148°C [17]). All solvents used for UV/visible absorption and fluorescence studies were of spectral grade and did not contain more than 0.1 wt% water.

2.2. Synthesis of the poly(4VP) macro-initiator

Using the same proportions as in our previous work on the kinetic study of the polymerisation of 4-vinylpyridine[16], a 100 ml reactor was charged with 370 mmol monomer, 0.96 mmol TEMPO and 0.74 mmol benzoyl peroxide (according to the literature [18], the molar ratio TEMPO/ BPO was thus equal to 1.3/1). The mixture was de-gassed by several freeze–thaw cycles, and finally left under argon. The vessel was then immersed in a pre-heated oil bath (inner temperature of the reactor: 138°C). Magnetic stirring and temperature control (±1°C) were used throughout the reaction. After the required duration, the reaction was stopped by cooling the flask. Excess monomer was evaporated under reduced pressure (1 mmHg) and the polymer was recovered as a powder after careful drying in a vacuum oven (0.5 mmHg, 65°C) for 24 h. The purity of the product was confirmed by ^{1}H NMR using a Bruker 200 MHz spectrometer. This TEMPO-terminated polymer was characterised by size exclusion chromatography ($\bar{M}_n = 65,000$ g/mol, $\bar{M}_w/\bar{M}_n = 1.18$) before being used as a macro-initiator in the copolymerisation with DMAA.

2.3. Synthesis of poly(4VP)-b-poly(DMAA)

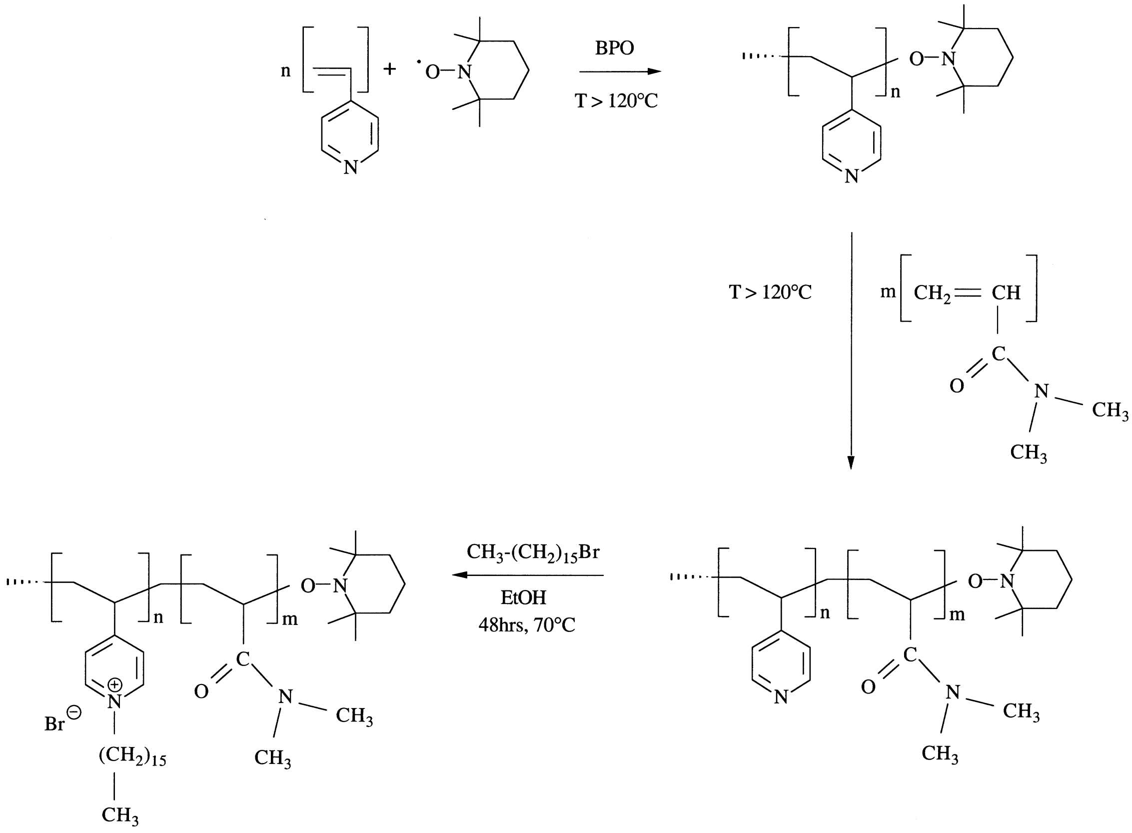
A 50 ml reactor was charged with 500 mg of macro-initiator (TEMPO-terminated poly(4VP)) dissolved in 4 ml comonomer (DMAA)). Excess nitroxide (0.096 mmol TEMPO) was also added since preliminary experiments had revealed that contamination of the copolymer by some DMAA-homopolymer could not be avoided otherwise. De-gassing and heating along with polymer recovery were then conducted under the same conditions as the ones used for 4VP-homopolymerisation. The copolymers were characterised by size exclusion chromatography, which allowed the determination of the proportion of DMAA units compared to that of 4VP units.

2.4. Size exclusion chromatography (SEC)

The homopolymers and copolymers were dissolved in dimethylformamide (DMF) (Fisher Scientific, 99.5%) and the solutions were filtered through PTFE membranes (Alltech, pore diameter: 200 nm) prior to injection. Measurements were performed at 35°C, on a Waters device equipped with a Styragel HR4 7.8 × 300 mm column (10^3 to 5×10^6 g/mol). DMF was used as eluent. The system had previously been calibrated with standard polystyrenes purchased from Polymer Standard Service. Sample detection was done with a Waters 410 differential refractometer. The results were processed using Millenium software.

2.5. Quaternisation of the block copolymers

A 100 ml reactor was charged with 1 g of block copolymer (poly(4VP)-*b*-poly(DMAA)), 20 ml of 1-bromohexadecane as an alkylating agent, and 25 ml ethanol as a solvent. The mixture was left to react for 48 h at 70°C under inert atmosphere and constant stirring. Once the reaction was stopped, excess ethanol and 1-bromohexadecane were evaporated under reduced pressure (1 mmHg). The quaternised block copolymer was dissolved in chloroform and precipitated in diethyl ether. The resulting powder was dried in a vacuum oven (0.5 mmHg, 65°C) for 24 h. Elementary analyses were obtained from the Service Central d'Analyse du Centre National de la Recherche Scientifique. They allowed the estimation of the quaternisation yields, which were all found superior to 95%.



Scheme 2.

2.6. Fluorescence spectroscopy

Absorption spectra were recorded on a Perkin Elmer (Lambda 2) UV/visible spectrophotometer. Fluorescence emission spectra were recorded on a Spex-fluorolog-2 spectrometer equipped with a thermostatically controlled cell at 25 ± 0.1°C. Stock solutions of polymer in propan-1-ol were first prepared at different concentrations (20, 10, 1 and 0.1 g/l). These solutions were then diluted with propan-1-ol and distilled water, so as to obtain a final solvent consisting in a water/propan-1-ol (97/3%, v/v) mixture. A stock solution of rotor (10^{-3} mol/l) was prepared. 10 μl of this solution were systematically added to 3 ml of each final polymer solution a few minutes before measurement. Thus, for all samples, the rotor concentration was 3.3×10^{-6} mol/l. All samples were excited at 495 nm. The spectra were recorded in the range 500–600 nm (slit width: 1.5 mm, $\Delta\lambda_{1/2} = 6$ nm) and consisted of a single fluorescence peak, the position and intensity of which was medium-dependent.

2.7. Surface tension measurements

Surface tensions were measured by the plate method at 25 ± 0.1°C with a Krüss K8 tensiometer. Typically, the samples were prepared in 50 ml vessels. A stock-solution of polymer (16.67 g/l) in propan-1-ol was prepared and diluted in ethanol and water with a view to obtaining a 0.5 g/l solution in a medium that was composed of distilled water, propan-1-ol and ethanol in the proportions 96/3/1 (v/v/v). This solution was then progressively diluted in a solvent of the same composition.

2.8. Viscometry

Viscosity measurements were performed in chloroform or in water/propan-1-ol mixtures at 25 ± 0.1°C using a Schott-Geräte AVS 310 viscometer. Intrinsic viscosities $[\eta]$ were obtained by extrapolation to zero concentration of the linear plots of reduced viscosity η_{red} vs polymer concentration. As to the study in chloroform, a stock-solution of polymer (7 g/l) was progressively diluted by addition of pure chloroform and systematically stirred to ensure a homogeneous dilution before measurement.

In the hydro-alcoholic medium, the concentration of all polymer solutions was 1 g/l.

3. Results and discussion

With a view to studying the physico-chemical behaviour in the aqueous medium of bi-block structures containing an amphiphilic block bound to a hydrosoluble block, poly(*N*-hexadecyl-4-vinylpyridinium bromide)-*b*-poly(*N*,*N*-dimethylacrylamide) copolymers were synthesised

Table 1
Features of the poly(*N*-hexdecyl-4-vinylpyridinium bromide)-*b*-poly(*N*,*N*-dimethylacrylamide) copolymers

Polymer #	$\bar{M}_n$ (g/mol)	$\bar{M}_w/\bar{M}_n$	4VP unit weight percentage	DMAA unit weight percentage
1	65,000	1.18	100.0	0.0
2	79,000	1.41	82.3	17.7
3	85,300	1.27	76.2	23.8
4	87,100	1.30	74.6	25.4
5	90,100	1.30	72.1	27.9
6	92,000	1.30	70.6	29.4
7	93,200	1.26	69.7	30.3
8	108,600	2.20	59.8	40.2

according to Scheme 2. The choice of *N*,*N*-dimethylacrylamide as the comonomer was the result of previous investigations, which had led us to conclude that DMAA, among other monomers that were likely to yield a neutral hydrosoluble block, was one of the rare monomers to be polymerisable by NMRP (former attempts, with *N*-vinylpyrrolidinone for instance, proved to be unsuccessful). For all the prepared copolymers, the polycationic first block was rigorously the same, whereas the poly(*N*,*N*-dimethylacrylamide) block varied in size, thus yielding structures with different hydrophilic/lipophilic balances. It must be recalled here that it was not possible to quaternise 4-vinylpyridine before polymerizing it as the first block, since 4-vinylpyridinium salts are not stable. This is why a post-polymerisation quaternisation was compulsory. Consequently, the preparation scheme consisted of three steps, the first one being the homopolymerisation of 4-vinylpyridine [8] initiated by benzoyl peroxide and controlled by TEMPO. Copolymerisation with *N*,*N*-dimethylacrylamide was then conducted using always the same TEMPO-terminated poly(4-vinylpyridine) as a macroinitiator ($\bar{M}_n = 65,000$ g/mol, $\bar{M}_w/\bar{M}_n = 1.18$). Finally, the heterocyclic rings of the first block were quaternised by 1-bromohexadecane. Table 1 summarises the features of the studied poly(*N*-hexadecyl-4-vinylpyridinium bromide)-*b*-poly(*N*,*N*-dimethylacrylamide) copolymer samples, as regards their chemical compositions, number average molar weights, and polydispersities.

3.1. Fluorescence spectroscopy

In order to study the aggregation phenomenon in the case of amphiphilic polymers in an aqueous medium, a widely-used technique is fluorescence spectroscopy using pyrene as a probe [19]. Yet, this polarity probe, which is particularly useful to study the behaviour of most molecules in solution,

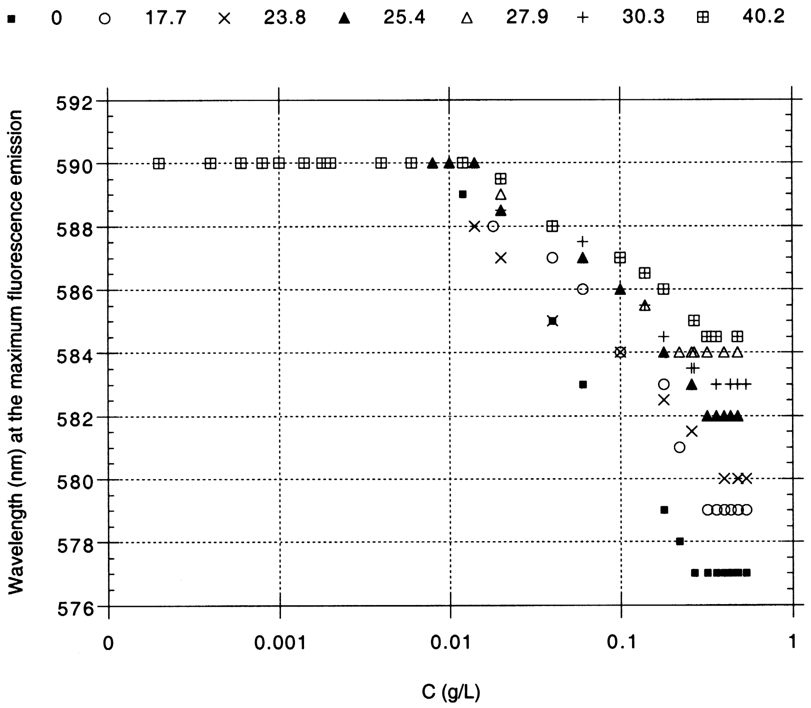


Fig. 1. Fluorescence spectroscopy: variations of the wavelength at the maximum fluorescence emission as a function of polymer concentration for different DMAA unit weight percentages; [DMAC] = 3.3×10^{-6} mol/l; $T = 25$°C, solvent — water/propan-1-ol (97/3%, v/v).

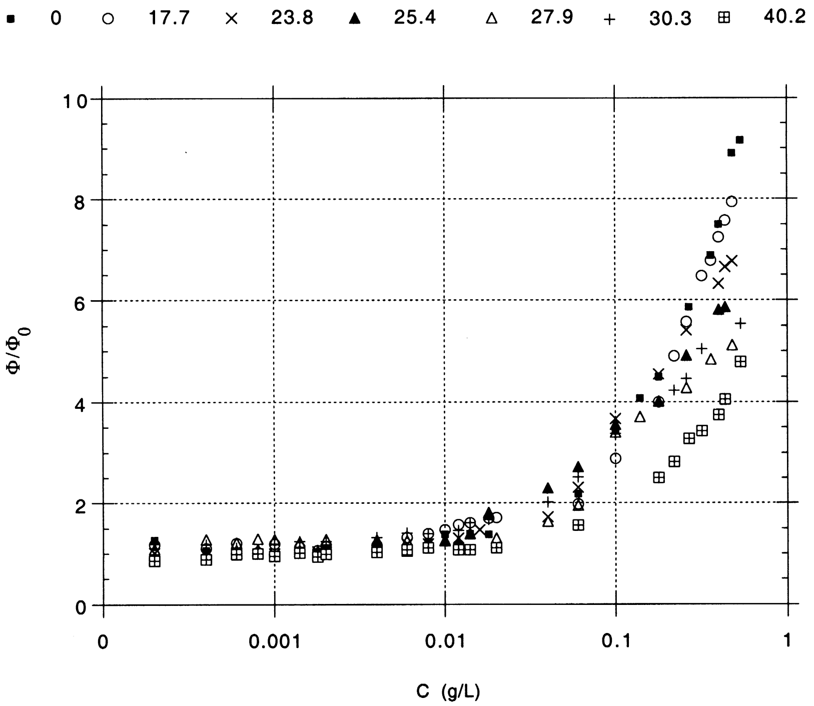


Fig. 2. Fluorescence spectroscopy: variations of the Φ/Φ_0 ratio as a function of polymer concentration for different DMAA unit weight percentages; [DMAC] = 3.3×10^{-6} mol/l; $T = 25°C$, solvent — water/propan-1-ol (97/3%, v/v).

has been proved ineffective for poly(alkylvinylpyridinium salts) [20,21], since long-alkyl-chain-quaternised pyridine rings are responsible for pyrene quenching. In order to circumvent the quenching process, molecular rotors were chosen as fluorescent probes, given, first, their sensitivity to solvation, polarity, and molecular mobility changes, and, second, their very low excited state lifetimes (from 0.01 to 5 ns) [22–28]. As regards DMAC, the single-peak fluorescence emission spectrum yields two pieces of information: the wavelength at the maximum emission is related to the polarity of the microenvironment of the probe, and the emission intensity can be directly linked with the fluorescence quantum yield, and, thus, to the microdomain cohesion [29,30]. Indeed, an increase in the microdomain cohesion, i.e. a decrease in the free-volume of the medium, with a subsequent slowing down of the motion of the rotor, leads to a diminution of the non-radiative relaxation processes with a consequent increase in the fluorescence quantum yield Φ, since fluorescence is the only means of relaxation left when the motion of the rotor is struck.

It is now commonly known that the lower the polarity in the microenvironment of the probe, the lower the wavelength at the maximum fluorescence emission λ_{max} [21]. Fig. 1 presents the evolution of the latter as a function of polymer concentration for different weight percentages in DMAA units ranging from 0 (poly(4VPBr) homopolymer) to 40.2. It is particularly remarkable that, up to 0.01 g/l polymer concentration, no variation of λ_{max} is observed, which tends to prove that hydrophobic microdomains are not yet detectable. For higher concentrations, the rotor witnesses a decrease in the medium polarity, which would indicate that it is located in more hydrophobic areas resulting from the exclusion of water by hydrophobic parts, and, thus, that microdomains are being formed in a substantial manner. For polymer concentrations exceeding 0.2 g/l, the plot reaches a final plateau. It is to be noticed that the wavelength value in the final plateau, which is in direct relationship with the polarity of the formed microdomains, is higher as DMAA is in a higher proportion in the block copolymer. This is quite expected, since DMMA is the hydrophilic polar part of the polymer. Thus, it can be inferred that the higher the proportion of DMAA, the more polar the microenvironment of the probe.

Similar remarks can be made about Fig. 2, which represents the fluorescence quantum yield ratio Φ/Φ_0 (Φ_0 being the fluorescence quantum yield without polymer, i.e. when the mixture water/propan-1-ol alone is excited). Here, the higher the proportion of DMAA in the block copolymer, the lower the ratio Φ/Φ_0. This is quite logical, since a higher proportion of hydrophilic units triggers an easier intrusion of water in the microdomain, thus resulting in a less cohesive structure.

Another interesting observation is that both the concentration for which microdomains appear (i.e. the concentration for which the wavelength value begins to decrease and the Φ/Φ_0 ratio begins to increase) and the concentration for which the λ_{max} vs concentration plot reaches its final plateau are independent of the DMAA proportion. Indeed, all λ_{max} vs concentration plots tend to go down when polymer

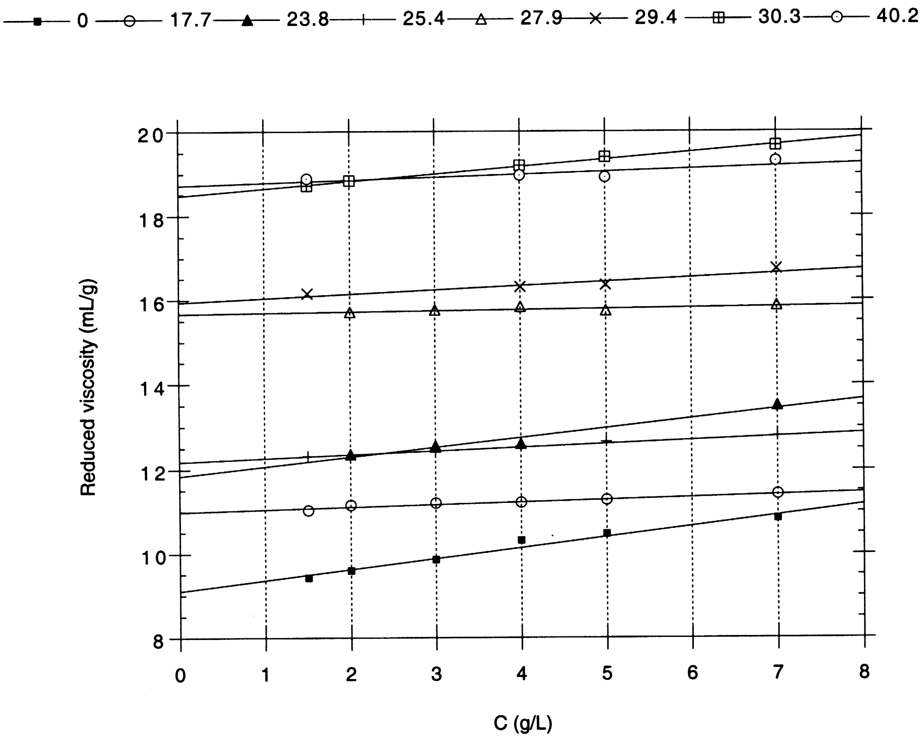


Fig. 3. Viscometry: variations of the reduced viscosity of the polymer solutions as a function of polymer concentration in chloroform for different DMAA unit weight percentages.

concentration approximately reaches the same value, i.e. 0.01 g/l, and tend to stabilise for concentrations above 0.2 g/l. This proves that microdomain formation itself is governed mainly by the poly(4VPBr) block, and not by the poly(DMAA) block, since the only constant parameter for all copolymers is the size of the amphiphilic block. These results are worth comparing with the ones obtained for statistic amphiphilic copolymers [21]. In the latter case, the concentration for which microdomains were detected was directly dependent on the hydrophilic/hydrophobic proportion.

Finally, it is worth noticing that, whereas the λ_{max} vs concentration plot reaches a plateau for concentrations above 0.2 g/l, the Φ/Φ_0 ratio value is still increasing. This would somehow indicate that, even for concentrations above 0.2 g/l, the cohesion of the microdomains is still evolving towards a more compact structure.

Table 2
Intrinsic viscosities of the quaternised block copolymers in chloroform at 25°C

Polymer #	$\bar{M}_n$ (g/mol)	DMAA unit weight percentage	$[\eta]$ (ml/g)
1	65,000	0.0	9.1
2	79,000	17.7	11.0
3	85,300	23.8	11.8
4	87,100	25.4	12.2
5	90,100	27.9	15.7
6	92,000	29.4	15.9
7	93,200	30.3	18.5
8	108,600	40.2	18.7

3.2. Viscometry

The objective of our study of the viscosimetric behaviour of the copolymers in an organic solvent in the presence of an increasing proportion of water was to determine the exact nature (intra- or intermolecular side chain aggregation) of the micelle-like pseudophases.

Preliminary experiments were carried out in chloroform to confirm the characterisation of our polymers by size exclusion chromatography and the regular viscometric behaviour of the copolymers in a purely organic polar solvent. Linear plots of reduced viscosity η_{red} vs polymer concentration were observed (Fig. 3). The intrinsic viscosities corresponding to the extrapolation to zero concentration have been gathered in Table 2. No Mark–Houwink relationships were available for this type of copolymer, which prevented us from approximating the molar weight of our samples by a method other than SEC. Yet, the overall evolution of intrinsic viscosities seems to be in quite good agreement with what was observed in size exclusion chromatography.

Fig. 4 summarises the variations of the reduced viscosity of the polymer solutions (1 g/l) as a function of water content in the water/propan-1-ol mixture for different DMAA unit weight percentages. Logically, for an identical composition of the solvent mixture, the reduced viscosity of the sample is higher as the size of the macromolecule is important, i.e. as the second block is long. It is to be noticed that all plots tend to follow the same curvature. The maximum

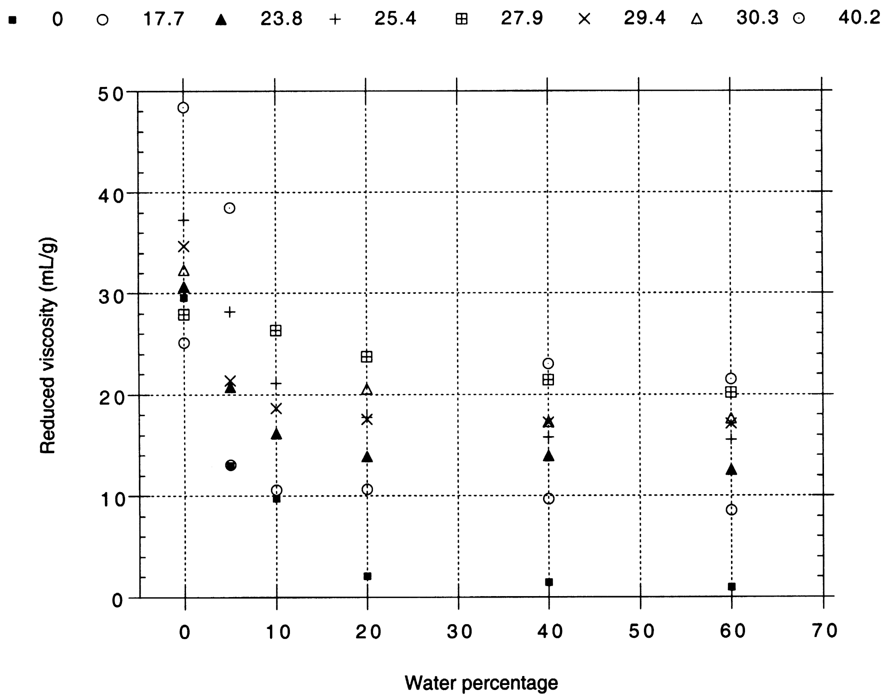


Fig. 4. Viscometry: Variations of the reduced viscosity of the polymer solutions (polymer concentration — 1 g/l) as a function of water content in propan-1-ol for different DMAA unit weight percentages.

reduced viscosity is obtained in pure propan-1-ol, which is a good solvent. The addition of water, even in small amounts, triggers a strong decrease of the reduced viscosity. This can be accounted for by the fact that water is not as good a solvent as propan-1-ol, especially as far as the poly(4VPBr) block is concerned. Consequently, the addition of water tends to cause the apolar long alkyl chains to gather in a more cohesive manner in intramolecular hydrophobic

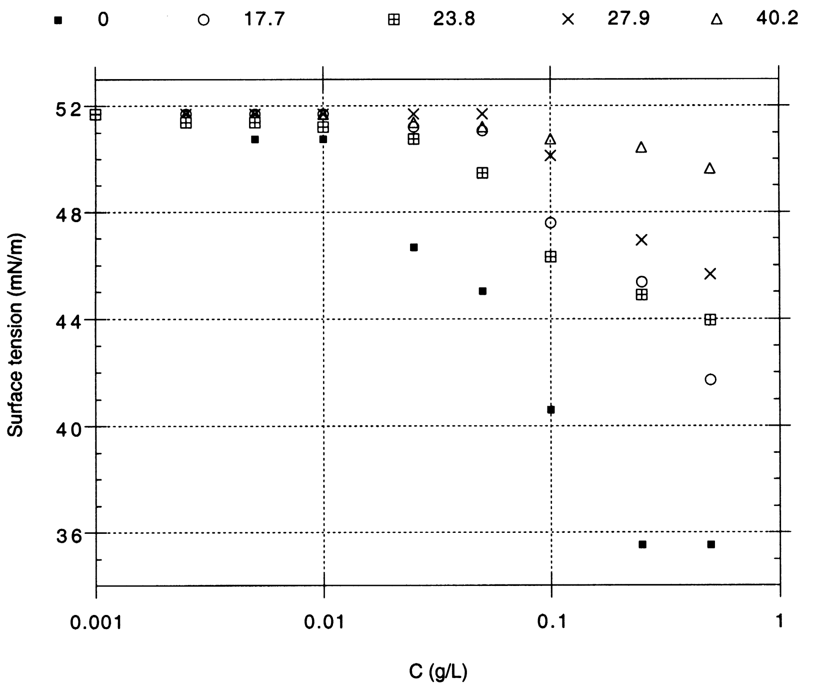


Fig. 5. Surface tension of the polymer solutions as a function of polymer concentration, solvent — water/propan-1-ol/ethanol (96/3/1%, v/v/v) for different DMAA unit weight percentages.

microdomains. Thus, the hydrodynamic volume of the macromolecule in solution is strongly reduced by folding effects.

Fig. 4 is also particularly interesting in the way that the overall curve shape (i.e. a diminution of the reduced viscosity as water becomes more prevalent) reveals the presence of intramolecular aggregates. 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 water content, since intermolecular associations tend to increase the hydrodynamic volume of the macromolecules.

Furthermore, it is to be noticed that all curves are superimposable, which means that the hydrophobic part of the polymer alone governs the diminution of the reduced viscosity as a function of water content, whereas the length of the second block influences the position of the curve for a given water content, but not its shape.

3.3. Surface tension measurements

Fig. 5 presents some results concerning surface tension measurements for polymer solutions at different concentrations in a water/propan-1-ol/ethanol (96/3/1%, v/v/v) mixture. Whatever the DMAA unit weight percentage, the first part of the plot (at low polymer concentrations) is at a nearly constant surface tension value, which proves that molecular adsorption at the water/air interface is very weak. This adsorption becomes more prevalent when polymer concentration becomes higher than 0.01 g/l, which was also the critical value observed by fluorescence spectroscopy as regards the formation of hydrophobic microdomains. The most surprising result that can be read in Fig. 5 is the evolution of the tensio-activity of the solutions as a function of the DMAA unit percentage. Indeed, the reduction of surface tension is all the more important as the proportion of DMAA in the block copolymer is low. Thus, among all the synthesised polymers, the most tensio-active is the homopolymer poly(4VPBr), which is quite an unexpected observation. Indeed, amphiphilic polymers in solution can be considered to be submitted to two opposite influences, the first one being the hydrophobic effect resulting in microdomain formation, and the second one being the tendency of the hydrophobic parts to adsorb at the surface of the liquid in order to limit any contact with water. Hence, one would have thought that the polymers that were the most likely to form cohesive microdomains (i.e. copolymers with a high proportion of 4VPBr) would also be the least tensio-active. Nevertheless, it could be argued that, as the proportion of DMAA units increases, the hydrophobic part is getting more and more attracted in water by the hydrophilic block, which could explain the reduction in adsorption.

4. Conclusion

Nitroxide-mediated radical polymerisation proved to be a very satisfactory route to allow the synthesis of amphiphilic cationic block copolymers. Such bi-block structures are not so often encountered in the literature concerning amphiphilic species, and yet, can be of major interest, especially as regards their physico-chemical properties, when compared to random copolymers composed of the same type of units. Indeed, as shown by our study of the intramolecular microdomains formed by poly(*N*-hexadecyl-4-vinylpyridinium bromide)-*b*-poly(*N*,*N*-dimethylacrylamide)s, the amphiphilic block on its own can govern the aggregation mechanism, letting the other block modulate the ultimate properties. Hence, contrary to what is observed with random copolymers, bi-blocks are likely to preserve the intimate behaviour of each unit. Varying different parameters in similar structures (relative block length, side chain length, chemical composition) should probably soon allow the control of the very properties of the microdomains themselves.

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