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Influence of the alkyl-chain size on the amphiphilic behaviour of poly(3-alkyl-1-vinylimidazolium) bromide in aqueous medium

C. Leddet[1], A. Fischer[*,1], A. Brembilla[2], P. Lochon[1]

[1] Laboratoire de Chimie-Physique Macromoléculaire, UMR CNRS-INPL 7568, Groupe ENSIC,
1, rue Grandville, BP 451, 54001 Nancy Cedex, France
Fax: 33 (0)3.83.37.99.77, e-mail: Arnaud.Fischer@ensic.inpl-nancy.fr
[2] Laboratoire d'Etude des Systèmes Organiques et Colloïdaux, UMR CNRS-UHP Nancy I 7565,
BP 239, 54506 Vandoeuvre-les-Nancy Cedex, France

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Summary

Several 3-alkyl-1-vinylimidazolium bromides differing by the length of the alkyl chain were prepared and polymerized using a free radical route. The behaviour of the obtained homopolymers in aqueous medium was investigated by several physico-chemical methods including viscosimetry, surface tension measurements and fluorescence spectroscopy. These experiments highlighted a strong influence of the length of the pendent alkyl chain on the side-chain aggregation tendency which is a property of such amphiphilic comb polymers. Fluorescence experiments were also conducted on the surface active analogues, in order to compare their behaviour to that of the polymers.

Introduction

For the last thirty years, amphiphilic polymers have become a major subject of investigation (1), and their use has progressively expanded to many fields, such as enhanced oil recovery (2-3) or biomedical substances (4-5). This widely-extended range of potential industrial applications is a consequence of their particularly interesting tendency to self-associate in aqueous medium (6-10), yielding micelle-like structures which can be able to incorporate and transport external hydrophobic molecules. Previous work (11-14) on cationic amphiphilic species obtained by polymerization of quaternized 1-vinylimidazole had led us to conclude that the latter were particularly likely to yield intramolecular hydrophobic microdomains, and, thus, to dissolve lipophilic substances. Yet, their solubility in water was much inferior to that of classical surface-active agents. Consequently, in order to test if a decrease in the length of the long alkyl pendent chain could grant an increase in polymer solubility without inhibiting the aggregation tendency, we decided to investigate, first, the influence of the chain-length on the behaviour of our polymers in aqueous medium. We report here the results of experiments concerning various physico-chemical studies *i.e.* surface tension measurements, viscosimetry and fluorescence spectroscopy. In all cases, a comparison between polymers with different chain lengths will be discussed. A comparative study between each homopolymer and its surface active analogue is also conducted as regards fluorimetry.

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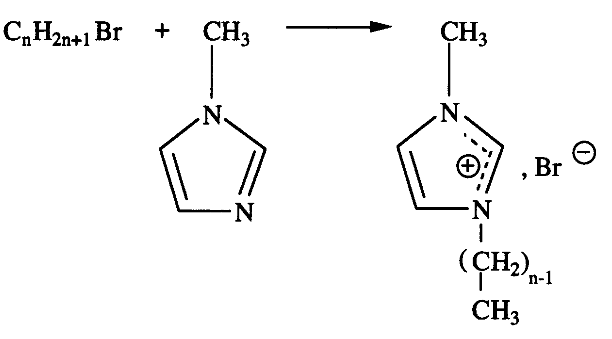
[*] Corresponding author

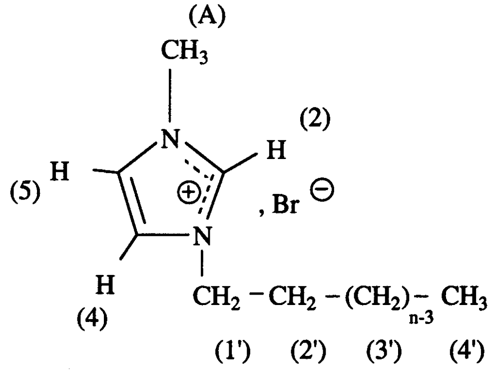
Experimental

Materials

1-vinylimidazole was purchased from Aldrich and distilled under reduced pressure (b.p. : 78-79°C/13 mm Hg) before use. So were the alkyl bromides (octyl bromide : b.p. = 80°C/13 mm Hg ; decyl bromide : b.p. = 110°C/13 mm Hg ; pentadecyl bromide : b.p. = 159-160°C/5 mm Hg). Pyrene was purchased from the Community Bureau of Reference (N°177). All solvents used for fluorescence studies were of spectral grade.

Synthesis of the 3-alkyl-1-methylimidazolium bromides (MIC$_n$Br)





MIC$_8$Br and MIC$_{10}$Br (viscous liquids) :

A mixture consisting of 5 g 1-methylimidazole (60.9 mmol), 13.3 g octyl bromide (68.9 mmol) (resp. 18.0 g *i.e.* 81.3 mmol decyl bromide), 3 mL acetonitrile and 6 mL chloroform was heated at 60°C for 72 hours. The obtained product was precipitated in diethyl ether (yields : 93.0 % and 93.3 % respectively). Further purification consisted in dissolution in chloroform, precipitation in ethyl acetate and residual solvent evaporation under vacuum (0.5 mm Hg).

^{1}H NMR (CDCl$_3$, TMS) :

MIC$_8$Br : δ (ppm) 0.78 (3 H, t, CH3 (4')) ; 1.21 (2 H, m, CH$_2$ (3')) ; 1.84 (2 H, m, CH$_2$ (2')) ; 4.25 (2 H, t, CH$_2$ (1')) ; 4.05 (3 H, s, CH$_3$ (a)) ; 7.43 (1 H, H (5)) ; 7.61 (1 H, H (4)) ; 10.20 (1 H, s, H (2)).

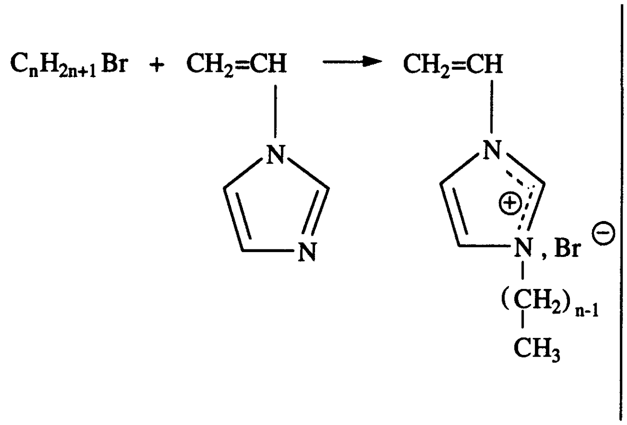
MIC$_{10}$Br : δ (ppm) 0.86 (3 H, t, CH$_3$ (4')) ; 1.28 (2 H, m, CH$_2$ (3')) ; 1.90 (2 H, m, CH$_2$ (2')) ; 4.31 (2 H, t, CH$_2$ (1')) ; 4.12 (3 H, s, CH$_3$ (a)) ; 7.33 (1 H, H (5)) ; 7.47 (1 H, H (4)) ; 10.51 (1 H, s, H (2)).

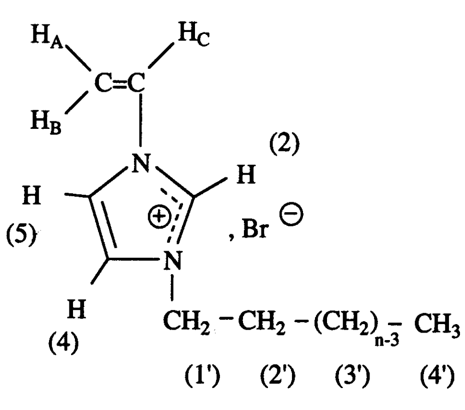
MIC$_{15}$Br (white solid, m.p. : 70°C) :

A mixture consisting of 5 g 1-methylimidazole (60.9 mmol), 23.0 g pentadecyl bromide (79.0 mmol), 3 mL acetonitrile and 6 mL chloroform was heated at 60°C for 72 hours. The obtained product was precipitated in diethyl ether (yield : 91.1 %). Further purification consisted in two successive recrystallizations in ethyl acetate and a careful drying in a vacuum oven under reduced pressure (0.5 mm Hg).

^{1}H NMR (CDCl$_3$, TMS) : δ (ppm) 0.87 (3 H, t, CH$_3$ (4')) ; 1.29 (2 H, m, CH$_2$ (3')) ; 1.91 (2 H, m, CH$_2$ (2')) ;4.31 (2 H, t, CH$_2$ (1')) ; 4.13 (3 H, s, CH$_3$ (a)) ; 7.26 (1 H, H (5)) ; 7.36 (1 H, H (4)) ; 10.62 (1 H, s, H (2)).

Synthesis of the 3-alkyl-1-vinylimidazolium bromides (VIC$_n$Br)





VIC$_8$Br and VIC$_{10}$Br (viscous liquids) : a mixture consisting of 5 g 1-vinylimidazole (60.9 mmol), 13.3 g octyl bromide *i.e.* 68.9 mmol (resp. 18.0 g decyl bromide *i.e.* 81.3 mmol), 3 mL acetonitrile and 2 mL chloroform was heated at 40°C for 96 hours. The obtained product was precipitated in diethyl ether (yields : 23.5 % and 94.5 % respectively). Further purification consisted in dissolution in chloroform, precipitation in ethyl acetate and residual solvent evaporation under vacuum (0.5 mm Hg).

^{1}H NMR (CDCl$_3$, TMS) :

VIC$_8$Br : δ (ppm) 0.84 (3 H, t, CH$_3$ (4')) ; 1.29 (2 H, m, CH$_2$ (3')) ; 1.94 (2 H, m, CH$_2$ (2')) ; 4.37 (2 H, t, CH$_2$ (1')) ; 5.38 (1 H, dd, H (A), J_B = 2.93 Hz, J_C = 8.77 Hz) ; 6.00 (1 H, dd, H (B), J_A = 2.92 Hz, J_C = 15.70 Hz) ; 7.49 (1 H, dd, H (C), J_A = 8.76 Hz, J_B = 15.70 Hz) ; 7.56 (1 H, H (5)) ; 7.89 (1 H, H (4)) ; 10.91 (1 H, s, H (2)).

VIC$_{10}$Br : δ (ppm) 0.86 (3 H, t, CH$_3$ (4')) ; 1.30 (2 H, m, CH$_2$ (3')) ; 1.95 (2 H, m, CH$_2$ (2')) ; 4.40 (2 H, t, CH$_2$ (1')) ; 5.40 (1 H, dd, H (A), J_B = 3.10 Hz, J_C = 8.58 Hz) ; 5.97 (1 H, dd, H (B), J_A = 2.92 Hz, J_C = 15.70 Hz) ; 7.50 (1 H, dd, H (C), J_A = 8.76 Hz, J_B = 15.70 Hz) ; 7.46 (1 H, H (5)) ; 7.77 (1 H, H (4)) ; 11.06 (1 H, s, H (2)).

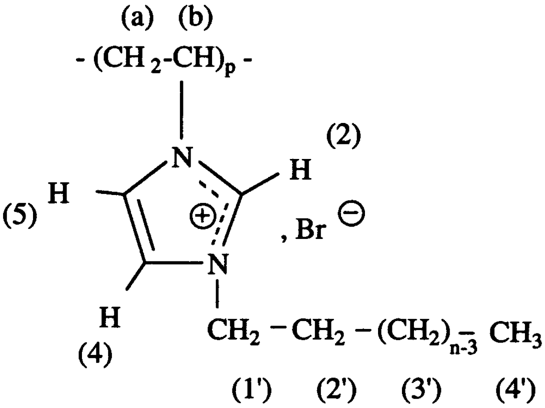
VIC$_{15}$Br (white solid, m.p. : 65°C) : a mixture consisting of 5 g 1-vinylimidazole (60.9 mmol), 23.0 g pentadecyl bromide (79.0 mmol), 15 mL acetonitrile and 12 mL chloroform was heated at 40°C for 96 hours. The obtained product was precipitated in diethyl ether (yield : 22.2 %). Further purification consisted in a double recrystallization in toluene and careful drying in a vacuum oven under reduced pressure (0.5 mm Hg).

^{1}H NMR (CDCl$_3$, TMS) : δ (ppm) 0.88 (3 H, t, CH$_3$ (4')) ; 1.33 (2 H, m, CH$_2$ (3')) ; 1.95 (2 H, m, CH$_2$ (2')) ;4.41 (2 H, t, CH$_2$ (1')) ; 5.43 (1 H, dd, H (A), J_B = 3.11 Hz, J_C = 8.59 Hz) ; 5.92 (1 H, dd, H (B), J_A = 2.93 Hz, J_C = 15.71 Hz) ; 7.51 (1 H, dd, H (C), J_A = 8.76 Hz, J_B = 15.70 Hz) ; 7.32 (1 H, H (5)) ; 7.57 (1 H, H (4)) ; 11.30 (1 H, s, H (2)).

Polymerization of the 3-alkyl-1-vinylimidazolium bromides

AIBN (1 mol. percent with respect to monomer) was added to a solution of monomer in ethanol (1 mol/L). The system was degassed by several freeze-thaw cycles. The mixture was then left to react for two days at 70°C. The polymer was recovered by successive dissolutions in chloroform and precipitations from acetonitrile, and finally dried under reduced pressure (0.5 mm Hg) in a vacuum oven (yields : 68 %, 98 % and 85 % for PVIC$_8$Br, PVIC$_{10}$Br, and PVIC$_{15}$Br, respectively).

^{1}H NMR ($CDCl_3$, TMS) :



$PVIC_8Br$: δ (ppm) 0.88 (3 H, t, CH_3 (4')) ; 1.28 (2 H, m, CH_2 (3')) ; 2.00 (2 H, m, CH_2 (2')) ; 4.19 (2 H, t, CH_2 (1')) ; 2.27 (2 H, CH_2 (a)) ; 4.88 (1 H, CH (b)) ; 7.10 (1 H, H (4)) ; 8.41 (1 H, H (5)) ; 10.04 (1 H, H (2)).

$PVIC_{10}Br$: δ (ppm) 0.89 (3 H, t, CH_3 (4')) ; 1.28 (2 H, m, CH_2 (3')) ; 2.00 (2 H, m, CH_2 (2')) ; 4.24 (2 H, t, CH_2 (1')) ; 2.28 (2 H, CH_2 (a)) ; 4.88 (1 H, CH (b)) ; 7.14 (1 H, H (4)) ; 8.48 (1 H, H (5)) ; 10.05 (1 H, H (2)).

$PVIC_{15}Br$: δ (ppm) 0.88 (3 H, t, CH_3 (4')) ; 1.26 (2 H, m, CH_2 (3')) ; 1.95 (2 H, m, CH_2 (2')) ; 4.17 (2 H, t, CH_2 (1')) ; 2.27 (2 H, CH_2 (a)) ; 4.92 (1 H, CH (b)) ; 7.12 (1 H, H (4)) ; 8.51 (1 H, H (5)) ; 10.08 (1 H, H (2)).

Surface tension measurements : Typically, the samples were prepared in 50 mL vessels. Preliminary dissolution of the polymer in 1-propanol was followed by a dilution in ethanol and water (final composition : water, 1-propanol and ethanol (96/3/1, v/v/v)). This solution was then progressively diluted with a solvent of the same composition. Surface tensions were measured by the plate method at 25±0.1°C with a Krüss K8 tensiometer. A kinetic study had previously been performed in order to assess the time needed to obtain reproducible measurements and, eventually, one hour proved sufficient to ensure equilibrium after the plate had been partially immersed in the alcohol/water mixture.

Fluorescence spectroscopy : 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 1-propanol were first prepared at different concentrations (10, 1 and 0.1 g/L). These solutions were then diluted with 1-propanol and distilled water. A stock solution of pyrene (10^{-3} mol/L) was prepared in 1-propanol. 5 µL of this solution were systematically added to 5 mL of each final polymer solution. Thus, for all samples, the pyrene concentration was 10^{-6} mol/L, and the composition of the samples was 97/3 (water/1-propanol, v/v). All samples were excited at 334 nm and vibronic peaks n°1 and 3 were observed at λ_1 = 372 nm (Intensity I_1) and λ_3 = 382 nm (Intensity I_3). The slit width was 0.5 mm ($\Delta\lambda_{1/2}$ = 2 nm). No excimer band was observed.

Viscosimetry : Viscosity measurements were performed in chloroform or in water/1-propanol mixtures at 25±0.1°C using a Schott-Geräte AVS 310 viscosimeter. Intrinsic viscosities [η] were obtained by extrapolation to zero concentration of the linear plots of reduced viscosity η_{red} *vs* polymer concentration. A stock-solution of polymer in chloroform was progressively diluted by addition of pure chloroform and systematically stirred to ensure a homogeneous dilution before measurement. In hydro-alcoholic medium, the concentration of all polymer solutions was 1 g/L.

Results and discussion

Surface tension measurements

Figure 1 presents the results concerning surface tension measurements for polymer solutions at different concentrations in a water/1-propanol/ethanol (96/3/1 percent, v/v/v) mixture. At very low polymer concentrations, the surface tension value decreases, which proves that molecular adsorption at the water/air interface is getting more and more prevalent. It is particularly surprising to read on figure 1 that the most tensioactive polymer is PVIC$_{15}$Br. Indeed, as regards amphiphilic polymers in solution, it is usually admitted that molecules are 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 could have thought that the polymers which were the most likely to form microdomains (*i.e.* copolymers with a long alkyl chain) would also be the least tensioactive. In fact, the longer the chain, the bigger the tensioactive effect.

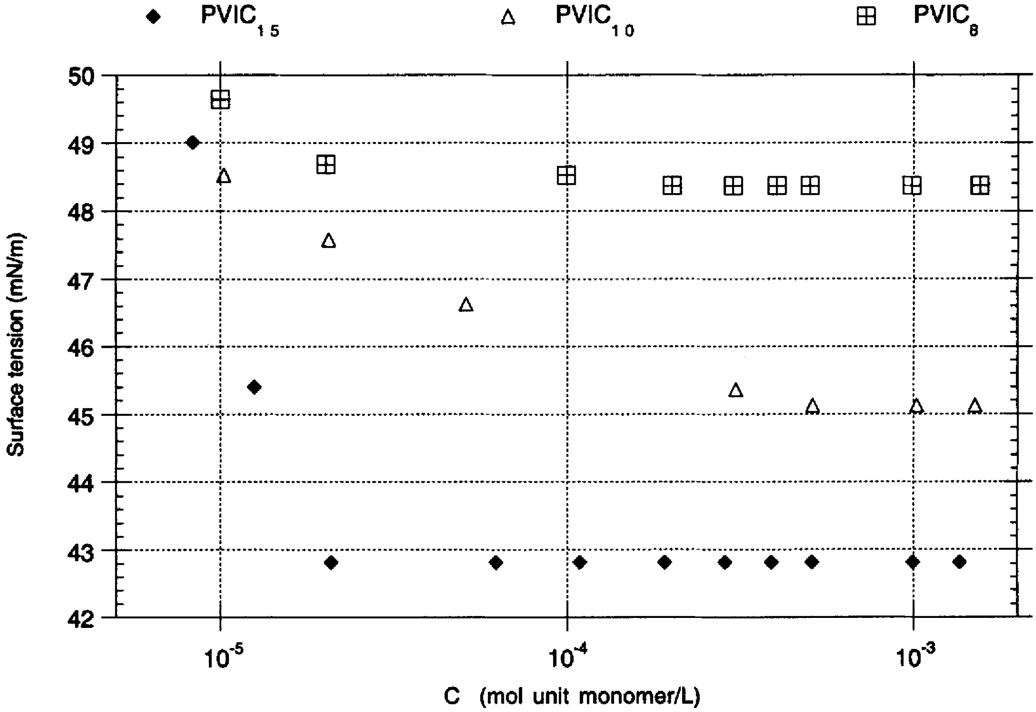


Figure 1 : Surface tension of the polymer solutions as a function of polymer concentration. Surface tension of pure solvent (water/1-propanol/ethanol, 96/3/1 percent, v/v/v) = 51.8 mN/m

Fluorescence spectroscopy

In order to study the aggregation phenomenon in the case of amphiphilic polymers in aqueous medium, a widely-used technique is fluorescence spectroscopy using pyrene as a probe (11, 14-16). It is now commonly known that a decrease in the polarity of the micro-environment of the probe triggers a decrease in the I_1/I_3 ratio, I_1 and I_3 respectively standing for the intensities of the first and third vibronic peaks in the fluorescence emission spectrum of pyrene. As regards poly(3-alkyl-1-vinylimidazolium bromide)s, our results have been summarized in Figure 2.

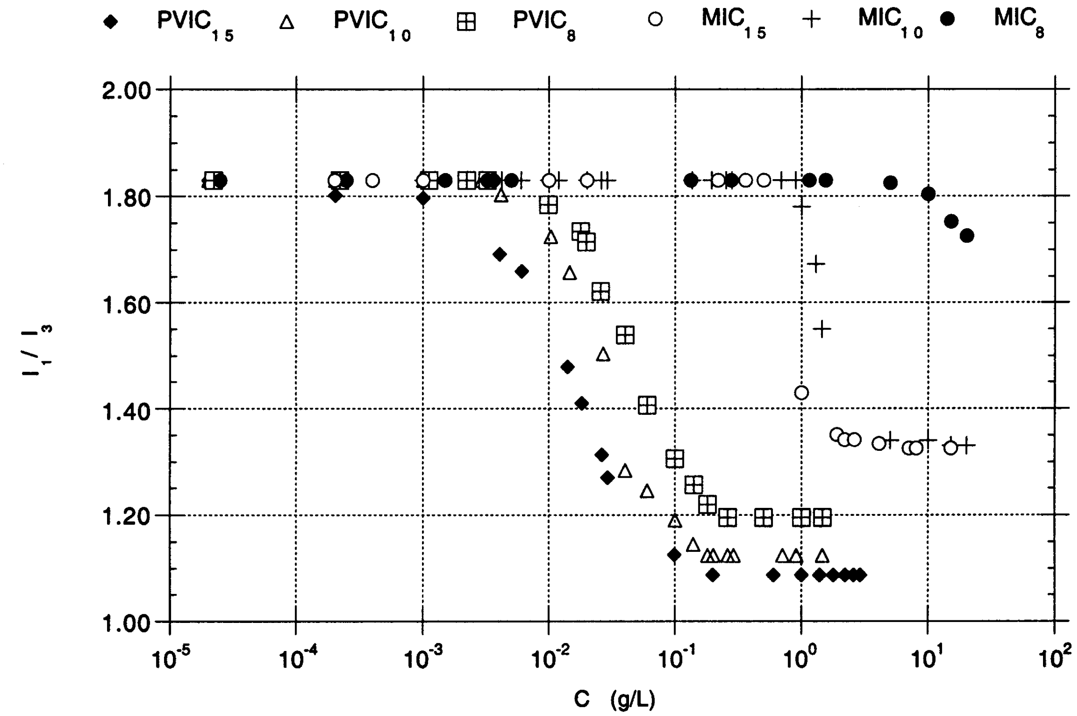


Figure 2 : Fluorescence spectroscopy : Variations of the I_1/I_3 ratio as a function of polymer or surfactant concentration for different species ([Pyrene] = 10^{-6} mol/L ; T = 25°C ; solvent : water/1-propanol, 97/3, v/v).

For polymer concentrations below 10^{-3} g/L, it is particularly obvious that no real variation is detected as regards the environment of the probe. When polymer concentration increases, a transition occurs for all species, consisting in a diminution of the I_1/I_3 ratio. This decrease, which is representative of a decrease in the polarity of the surrounding of the probe, is commonly attributed to the formation of hydrophobic microdomains. Finally, all curves reach a plateau, the position of which is also medium-dependent.

From the three plots I_1/I_3 *vs* concentration concerning polymers, it can be inferred that the transition is likely to take place all the earlier as the alkyl chain is long. In the same perspective, the longer the chain, the lower the I_1/I_3 ratio value in the final plateau. These observations clearly indicate that, when the chain is longer, hydrophobic microdomains are formed earlier, and the fluorescent probe is in a less polar microenvironment.

A similar conclusion was inspired by experiments concerning the tensio-active analogues MIC_8Br, $MIC_{10}Br$ and $MIC_{15}Br$. Yet, it must be noticed that, for the $MIC_{10}Br$ and $MIC_{15}Br$ analogues, the transition which is representative of microdomain formation - in this very case, of micellization - occurs much later than for the corresponding polymers. As to MIC_8Br, no micellization was observed within the studied concentration range.

Viscosimetry

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) of the side-chain aggregation which was responsible for the micelle-like pseudophase formation. Preliminary experiments were carried out in chloroform in order to assess the viscosimetric molar weight of our polymers, and to confirm their regular viscosimetric behaviour in a purely organic polar solvent. Linear plots of reduced viscosity η_{red} *vs* polymer concentration were observed, and enabled us to approximate the molar weights of our species (table 1) by using a Mark-Houwink-type relation, which had been established (17) for another type of amphiphilic cationic polymer. It is to be noticed that experiments in our laboratory showed that there was a very good agreement between values calculated from this relation and values corresponding to $PVIC_{12}Br$ obtained from poly(vinylimidazole)s whose molecular weights were known and which had been quaternized up to at least 98 percent by dodecylbromide.

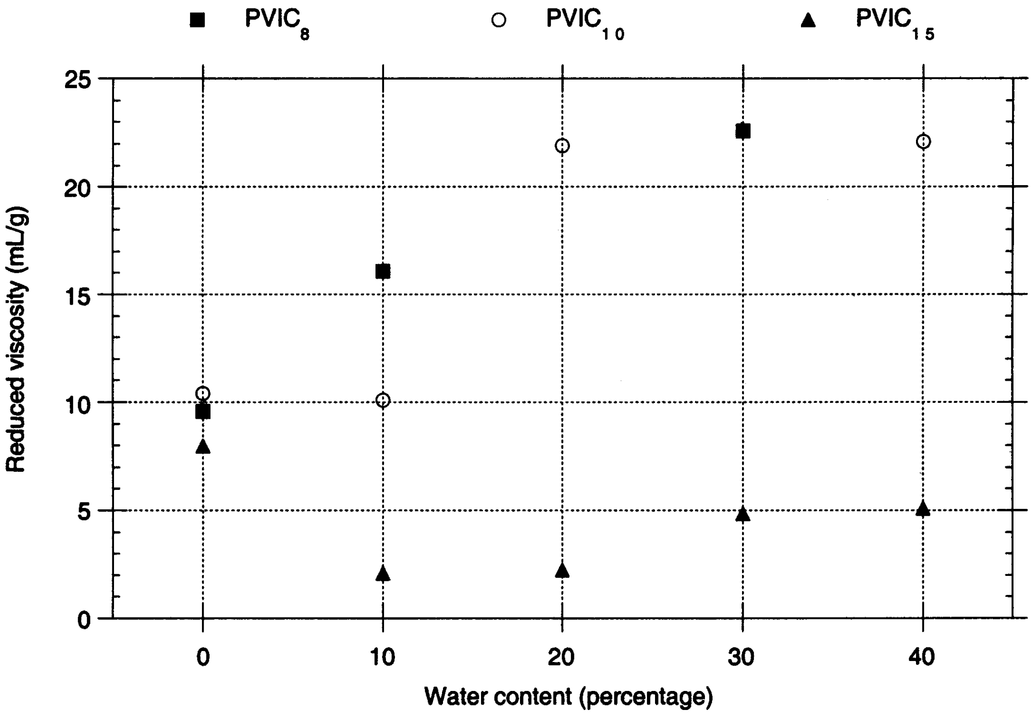


Figure 3 : Viscosimetry : Variations of the reduced viscosity of the polymer solutions (polymer concentration : 1 g/L) as a function of water content in 1-propanol

Polymer	[η] (mL/g)	M_v (g/mol)
$PVIC_8Br$	8.60	87000
$PVIC_{10}Br$	10.01	105000
$PVIC_{15}Br$	6.21	57000

Table 1 : Intrinsic viscosities and viscosimetric molar weights of the $PVIC_nBr$ after experiments in chloroform at 25°C

As shown in figure 3, the nature of the side-chain aggregations in aqueous medium is very dependent on the length of the pendent alkyl chain and can be interpreted by considering the concurrence between hydrophobic effect and ionic interactions. In the case of the longest alkyl chain ($PVIC_{15}Br$), the hydrophobic effect is very important and the addition of low amounts of water (10 percent) triggers an intramolecular aggregation, which corresponds to internal molecular foldings. This is the reason why the viscosity decreases. This behaviour is very similar to that of the high-molecular weight hexadecyl compound which has been extensively described in previous papers (11). As far as the shortest two chains are concerned ($PVIC_8Br$ and $PVIC_{10}Br$), the polyelectrolyte character of the macromolecule is likely to be more prevalent than the hydrophobic effect. In this case, the polymer adopts a more extended conformation, and, consequently, tends to behave as an associative species, notably showing an increase in viscosity when water is added.

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