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Poly(*N*-alkylacrylamide-*co*-vinylpyridinium): synthesis and aqueous solution properties

Christine Damas, Alain Brembilla*, Pierre Lochon, Francis Baros† and Marie-Laure Viriot†
Laboratoire de Chimie-Physique Macromoléculaire, CNRS-URA-494 and †Département de Chimie-Physique des Réactions, CNRS-URA-328, ENSIC-INPL, 1 Rue Grandville, BP 451, 54001 Nancy Cedex, France
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Copolymers of 4-vinylpyridine and *N*-alkylacrylamides (alkyl chain bearing 6, 10 and 12 carbon atoms) were prepared by bulk free radical copolymerization using 2,2'-azobisisobutyronitrile and 2,2'-azobis(2,4-dimethylvaleronitrile) as initiators. Poly(*N*-alkylacrylamide-*co*-4-vinylpyridine)s were then converted into cationic copolymers by quaternization of the pyridine rings with methylbromide. Their amphiphilic properties in dilute aqueous media were studied by viscosimetry, fluorescence and tensiometry. In selected solvents (water + methanol), the association phenomenon was investigated as a function of the solvent composition and the chemical structure of the copolymers.

(Keywords: *N*-alkylacrylamides; 4-vinylpyridine; copolymers)

INTRODUCTION

The cationic amphiphilic polymers belong to a subclass of the polyelectrolytes and have been the focus of many studies in the last three decades[1,2]. From their properties, of self-associating (e.g. micelle-like structure formation) or of allowing the incorporation of external hydrophobic molecules and in other respects often related to those of surface-active agents, these polymers are of great interest in a large number of potential applications in industrial fields. However, only in recent years has attention been focused on understanding the behaviour of this type of polymer in aqueous media which strongly depends on their chemical structure.

An examination of the literature shows that these compounds can be essentially classified into four structure types, namely block, graft, comb and random[3,4]. In the latter case, the preparation of such a copolymer is carried out by the copolymerization of a hydrophilic monomer with a hydrophobic comonomer that allows wide synthesis possibilities. In the present work, we describe the synthesis and the solution properties of a new cationic amphiphilic copolymer series, poly(*N*-alkylacrylamide-*co*-1-methyl-4-vinylpyridinium bromide)s, whose hydrophobic part is composed of *N*-alkylacrylamide units differing by their chain length (C_6, C_{10} and C_{12} atoms) and whose hydrophilic part is composed of pyridinic moieties, quaternized by methylbromide. These copolymers were prepared by free radical copolymerization using 2,2'-azobisisobutyronitrile (AIBN) or 2,2'-azobis(2,4-dimethylvaleronitrile) (ADVN) as initiators. Preliminary investigations of the behaviour of these compounds were conducted in aqueous media using fluorescence probe experiments, viscosimetry and interfacial tension measurements. A first approach to the study of the influence of the structure of these copolymers by varying the *N*-alkylacrylamide chain length and their composition on the association phenomenon and the surface active properties will also be discussed.

EXPERIMENTAL

Elemental analyses were obtained from the Service Central d'Analyse du CNRS. ^1H n.m.r. spectra were recorded on a Bruker AC-200 P spectrometer for D_2O or $CDCl_3$ solutions. Chemical shifts were given in δ scale, downfield from TMS. *FT*i.r. spectra were recorded on a Bruker IFS 25 spectrophotometer. All the melting points were determined on a Reichert heating plate microscope without correction.

Synthesis of N*-alkylacrylamide monomers*

The *N*-alkylacrylamides were prepared by the reaction of acryloyl chloride on the corresponding *n*-alkylamine, according to the method described by McCormick *et al.*[5]. However, decyl and dodecylacrylamides (respectively, denoted C_{10}AAM and C_{12}AAM) were purified first by two recrystallizations from heptane without heating above 50°C for dissolution. C_{10}AAM recrystallized after cooling the solution slowly at -25°C and for C_{12}AAM at 0°C (C_{10}AAM m.p. = 42°C, lit.[5] = 45–46°C; C_{12}AAM m.p. = 58°C, lit.[5] = 55.5–56.5°C), hexylacrylamide (C_6AAM) was recrystallized twice from diethylether at -25°C (m.p. = 32°C). As a final purification the compounds were chromatographed on silica gel or alumina column with ethyl acetate as an eluent.

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*To whom correspondence should be addressed

4-Vinylpyridine

4-Vinylpyridine (4-VP) from Aldrich was distilled in the presence of calcium hydride by transfer on a cold condensing surface (30°C, 2 mmHg).

Copolymerization

Copolymerization of $C_{12}AAM$ and 4-VP. C_{12}AAM (1.456 g, 6.1×10^{-3} mol) and 4-VP (2.766 g, 2.6×10^{-2} mol) were introduced into a reactor (25 ml) and degassed by the application of the freeze–thaw technique. Then, AIBN (4.36 mg, 2.65×10^{-5} mol) was added under an Ar atmosphere and the waterproof reactor, under magnetic stirring, was immersed in a thermostatically controlled bath at 80°C for 24 h. The mixture began to solidify after a reaction time of 2 h. The polymer was recovered by dissolution in pyridine (50 ml) followed by precipitation with heptane or chloroform (600 ml) to produce a white fibrous material. Finally the polymer was filtered off and dried under vacuum at 50°C for 24 h.

Composition determination. The *N*-alkylacrylamide–4-VP copolymers were prepared by varying the comonomer ratios: *N*-alkylacrylamide/4-VP ranging from 10/90 to 50/50. The composition was determined from elemental analysis and ^{1}H and ^{13}C n.m.r. spectra by integration of methylene and methyl peaks. For simplicity, the copolymers were referred to as C*n*AAMVP*N*, where C*n*AAM denotes the *N*-alkylacrylamide monomer ($n = 6$, 10 and 12) and *N* is the final percentage of 4-VP units or quaternized pyridinium sites.

Quaternization

Copolymer $C_{12}AAMVP90$. In a reactor, copolymer C_{12}AAMVP90 (0.91 g, 7×10^{-3} mol based on the pyridine units) was dissolved in a *N,N*-dimethylformamide/chloroform medium (18 ml DMF/8.5 ml $CHCl_3$). The mixture was stirred at 50°C until complete dissolution of the copolymer. Then the reactor was purged with an Ar flow and plunged into liquid nitrogen. Then, methyl bromide (10 g, 0.105 mol) was added to the reaction mixture. The reaction was performed at 60°C for 5 days. After cooling, the solvent was removed and the polymer was purified by redissolution in methanol and precipitation by a $CHCl_3$/acetone medium (60/40 v/v).

DMF was purified by allowing it to stand in contact with potassium hydroxide for 2 days and then distilled at reduced pressure over tolylene 2,4-diisocyanate. Chloroform was distilled over calcium chloride.

Surface tension

The interfacial tensions were measured by the ring method at 30 ± 0.1°C with a Krüss K8 tensiometer at the interface water/methylcyclohexane. Typically the samples were prepared in volumetric flasks (20 ml) by dissolution of the copolymers in methanol (1 ml) for C_{12}AAMVP90, C_{12}AAMVP84, C_{10}AAMVP83 and C_6AAMVP76 or 1-propanol (1 ml) for C_{12}AAMVP67. Then the polymer aliquots were made up to 20 ml with aqueous KBr solutions (0.0526 M).

Viscosities

The viscosity measurements were performed in water/methanol (MeOH) mixtures containing KBr (0.05 M in the final solution) using a Schott-Geräte AVS 310 viscosimeter. Intrinsic viscosities ($[\eta]$) were obtained by extrapolation to zero concentration of the linear plots of reduced viscosity (η_{red}) *versus* polymer concentrations. Huggins coefficients (k_H) were evaluated from the Flory–Huggins equation[6]:

$$\eta_{red} = [\eta] + [\eta]^2 k_H c \qquad (1)$$

Fluorescence measurements

Fluorescence emission spectra were recorded on a Spex fluorolog-2 spectrometer equipped with a thermostatically controlled cell compartment at 30°C. Pyrene (Community Bureau of Reference, BCR No. 177) was used as the probe. At the fixed concentration (1.1×10^{-6} M in the final solution), no emission band due to excimer fluorescence was observed. All the samples were excited at 332 nm and the emission spectra of pyrene show vibronic peaks at approximately $\lambda_1 = 372$ nm (intensity I_1) and $\lambda_3 = 382$ nm (I_3) (slit width = 0.05 mm; $\Delta\lambda_{1/2} = 2$ nm). The I_1/I_3 ratio was used as a measure of the polarity of the microenvironment[7–9]. Sample solutions were prepared by dissolving the copolymers (at various concentrations) in MeOH or 1-propanol (5%) and adding 95% of a KBr aqueous solution (0.05 M). In order to study the influence of the water content in the system water/MeOH or 1-propanol/KBr, the polymer concentration was fixed at 0.15 wt%.

RESULTS AND DISCUSSION

Poly(*N*-alkylacrylamide-*co*-1-methyl-4-vinylpyridinium bromide)s were synthesized in two steps: first, the polybases [poly(*N*-alkylacrylamide-*co*-4-vinylpyridine)] were prepared by copolymerization of the *N*-alkylacrylamides and 4-VP by using AIBN as the free radical initiator. Owing to the low melting point of the *N*-alkylacrylamide comonomers, several experiments using ADVN as initiator gave similar results. By varying both the initial composition of the two comonomers and the chain length of the acrylamides, a complete series of copolybases was prepared whose chemical composition was characterized by elemental analysis, *FT*i.r., ^{1}H and ^{13}C n.m.r. (*Table 1*).

*FT*i.r.: typical copolymer (acrylamide unit): NH (broad) 3300 cm^{-1}; amide I (broad) 1635 cm^{-1} (m); amide II (broad) 1530–1540 cm^{-1} (m); -$(CH_2)_n$- 2945 cm^{-1} (s), 2840 cm^{-1} (m); (pyridine unit): 1590 cm^{-1} (s), 1550 cm^{-1} (m); -(CH_2)- chain 2920, 2850 cm^{-1} (w).

^{1}H n.m.r.: (pyridine unit): -N=CH-, 8.3 ppm; -N-CH-*CH*- 6.43 ppm; -CH- chain 2 ppm; -CH_2- 1.5 ppm; (acrylamide unit): NH- 6.5 ppm; N-CH_2- 3.06 ppm, -N-CH_2-*CH_2*- 1.47 ppm; -$(CH_2)_n$- 1.23 ppm; CH_3 0.87 ppm.

^{13}C n.m.r. (pyridine): -CH- chain 40.5 ppm; -CH_2- 43 ppm; (acrylamide): -(CH_2)- 23–40 ppm; -C=O 175 ppm; -CH_3- 14 ppm; -CH- chain 43 ppm.

The second step was the typical quaternization of the pyridine units. This reaction was performed in a DMF/$CHCl_3$ medium. DMF was selected because high conversion yields (practically quantitative) are reported in the literature for the quaternization of polystyrene–poly(4-vinylpyridine) block copolymers using ethyl bromide[10] and methyl iodide[11]. It was known that the use of DMF, a solvent a priori favourable for this type of reaction, particularly because of its high relative permittivity (36.7 at 25°C), led to the drawbacks first of obtaining coloured products by formation of charge-transfer complexes as demonstrated by Boucher and

Table 1 Polymerization parameters and compositions of the copolymers

Comonomer	Initial composition in VP	Initiator (%)[a]	Temperature (°C)	Time (h)	Recovery solvent/ non-solvent	Yield (%)	Final composition in VP	$[\eta]$ (ml g^{-1})[b]
	100	AIBN 0.08	80	48	Pyridine/benzene then acetone	68.6	100	194
6AAM	67.8	AIBN 0.08	70	22	n-BuOH/petroleum ether	70	76^{e} 75.4^{c} 77.8^{d}	–
	49.4	ADVN 0.1	50	24	$CHCl_3$/sulfuric ether	–	53.2^{c} 57^{e}	115
10AAM	71	ADVN 0.09	50	24	$CHCl_3$/sulfuric ether	46.3	83.5^{c} 87^{e}	320
	49.4	ADVN 0.11	50	24	$CHCl_3$/sulfuric ether	41	64.5	–
12AAM	83.5	AIBN 0.42	80	6	$CHCl_3$/sulfuric ether	68	89^{c} 90.8^{e}	154
	81.2	AIBN 0.08	80	6	Pyridine/heptane	80.9	87.1^{c}	214
	81	AIBN 0.49	80–100	4.5	$CHCl_3$/heptane	64.3	82.2^{c} 85.3^{d}	
	58.4	AIBN 0.83	80	24	THF/AcOEt	35.7	58.8^{c} 59.3^{d}	
	54	AIBN 0.43	80	24	THF/heptane	66.9	66.5^{c} 66.7^{d} 64^{e}	128
	49	AIBN 0.47	70	24	$CHCl_3$/petroleum ether	43.1	66.2^{c} 68.3^{d} 67^{e}	207
	90.2	ADVN 0.09	68	24	$CHCl_3$/benzene petroleum ether	87.2	92.6^{c} 93.9^{d}	193
	80.2	ADVN 0.1	68	24	$CHCl_3$/petroleum ether	37.6	83.4^{c} 83.7^{f}	
	79.6	ADVN 0.11 solvent benzene	50	24	$CHCl_3$/petroleum ether	39	85.6^{c} 84.7^{d}	147

[a] Percentage based on the total amount of monomers
[b] Solvent $CHCl_3$, $T = 30°C$
[c] ^{1}H n.m.r. δCH_3
[d] ^{1}H n.m.r. δCH_2
[e] Elemental analysis
[f] ^{13}C n.m.r. δCH_3

Mollett[12] and secondly for its possible involvement in side reactions[13–15]. In our case the copolymers are not completely soluble in DMF, so that it has been necessary to dissolve them in mixtures containing $CHCl_3$. In order to avoid numerous side reactions, these solvents were carefully purified (see Experimental). Moreover, with the aim of the reaction going to completion, a very large excess of methyl bromide (10–20 times) was used. Despite these preventive measures, a very pale yellow colour always disappeared in the reaction mixture while after recovery the copolymers were white. The chemical purity of the quaternized copolymers was tested by elemental analysis (C, H, N, Br), *FT*i.r. and ^{1}H and ^{13}C n.m.r.

*FT*i.r.: (pyridinium): $-N^{+}-CH_3$ 1470 cm^{-1}; ^{1}H n.m.r.: $-N^{+}-CH_3$ 4.3 ppm; ^{13}C n.m.r.: $-N^{+}-CH_3$ 50.4 ppm; $-C{=}O$ 177.4 ppm.

The quaternization rate was determined by the titration of bromine [after complete decomposition of the copolymers the bromide ions were titrated by silver nitrate (5×10^{-3} M)]. The results show that in all cases the extent of side reactions does not exceed 0.8%.

The behaviour of these copolymers in aqueous media has been studied as a function of the hydrophilic/hydrophobic balance. To make sure of a complete solubilization, viscosimetric studies were carried out in mixtures (water/MeOH) incorporating a minimum of 5% methanol. The influence of the 'quality' of the solvent medium was studied essentially by acting on the composition of the mixture (water/MeOH). Moreover, in contrast to observations on the decreasing viscosity of some amphiphilic polymer solutions with time, no significant variation was observed with aged solutions[4,16–18].

As shown in *Figure 1*, in the case of the copolymer C_{12}AAMVP90 the plots of the reduced viscosity *versus* polymer concentrations for different solvent composition media exhibited straight lines in all cases, the extrapolation of which allowed the determination of the intrinsic viscosity and then the calculation of k_H. *Figures 2* and *3* represent, respectively, the variation of $[\eta]$ and k_H for the different copolymers as a function of the solvent composition. For the copolymers bearing a C_{10} or C_{12} alkyl chain, C_{10}AAMVP83 and C_{12}AAMVP90, the increasing percentage of water in the medium causes a significant variation of the intrinsic viscosity up to a water content of ~70% for C_{10}AAMVP83 and almost 80% for C_{12}AAMVP90. For higher percentages, a sharp decrease of $[\eta]$ was observed in both cases, which indicates the appearance of an association phenomenon. This change occurs with a lower proportion of water for C_{10}AAMVP83 than C_{12}AAMVP90, which is in agreement with its structure including a larger hydrophobic part. At the same time, the k_H variations for the two copolymers are demonstrated by the fact that there is a slight decrease when the water content increases. Above 70 and 80%, respectively, a sharp increase was observed for this

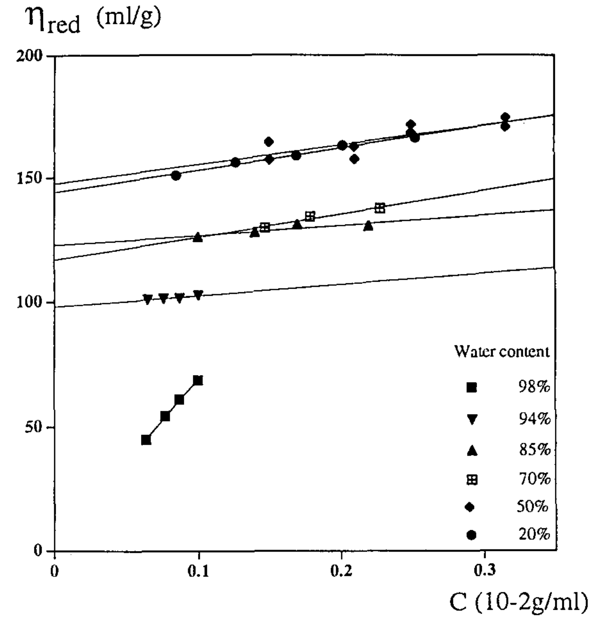

Figure 1 Reduced viscosity as a function of copolymer concentration and solvent composition (MeOH/water) for C_{12}AAMVP90 (T= 30°C; [KBr] = 5 × 10^{-2} M)

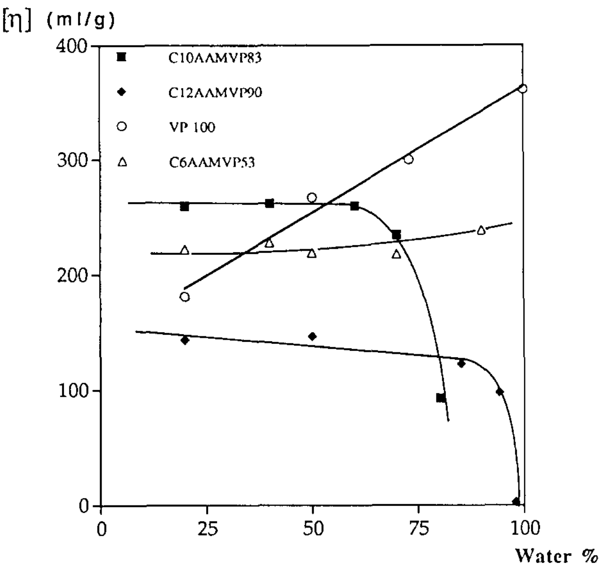

Figure 2 Dependence of intrinsic viscosity on solvent composition for copolymers C_{12}AAMVP90, C_{10}AAMVP83 and C_6AAMVP53. Poly(1-methyl-4-vinylpyridinium bromide) (VP 100) is shown for comparison (T= 30°C; [KBr] = 5 × 10^{-2} M)

coefficient. These results can be interpreted assuming that at low water contents, the medium begins to become a worse solvent for the acrylamide moieties and consequently the macromolecules tend to collapse in order to minimize the interactions between hydrophobic *N*-acrylamide chains and the water molecules and at the same time the hydrophilic parts protect the hydrophobic cores. In fact, a first assumption is that the low hydrophobic content (≤17%) means that the coiling is not important and does not significantly influence the hydrodynamic volume of the macromolecules. Consequently, the intrinsic viscosity of the copolymer is not really affected but on the other hand, a slight decrease of the Huggins coefficient is observed. The possibility of intermolecular interactions may also be considered. Indeed, a strong increase in water content in the medium is capable of inducing local 'precipitations' of the hydrophobic moieties[19,20]. In this case, the *N*-acrylamide chains must be protected from water and the macromolecule cannot by itself ensure an efficient protection. In order to maintain the hydrophobic parts in solution the molecules are forced to associate. The result is that the decrease in the hydrodynamic volume, due to the coiling of the macromolecules, is compensated by the higher hydrodynamic volume of the associated molecules and consequently the intrinsic viscosity remains unchanged. The result of an efficient protection of the *N*-acrylamide chains by many associated molecules means that k_H decreases. When the water content increases beyond 70 and 80% for C_{10}AAMVP83 and C_{12}AAMVP90, respectively, a very sharp decrease in $[\eta]$ is observed. indeed, when the water is in a larger proportion than MeOH, the hydrophobic parts contract further and tend to form more and more compact aggregates which have a greater difficulty to remain in solution. This result is illustrated by a very sharp increase in k_H. Thus the precipitation of the copolymers can occur when the water content exceeds 95%. For the copolymer C_6AAMVP53 whose hydrophilic/hydrophobic balance is approximately equal to 1, an increase in water content in the medium has no significant effect on $[\eta]$, while k_H passes through a maximum for a 50/50 (vol/vol) composition of the water MeOH mixture. Indeed, MeOH can be considered as a good solvent for the hydrophobic parts of the macromolecules so that when the water content increases (MeOH content remaining dominant) the greater proportion of *N*-acrylamide chains causes these chains to have trouble associating in order to reduce the hydrophobic chains/water interactions as reflected by the observed increase of k_H. For the maximum value of this coefficient, the hydrophobic chains/MeOH interactions on one side and the hydrophilic moieties/water interactions on the other side balance each other. When the percentage of water exceeds 50%, the great affinity of water for the pyridinium sites favours the solubility of the whole copolymer and consequently a decrease of k_H is observed indicating an increase in solvent quality.

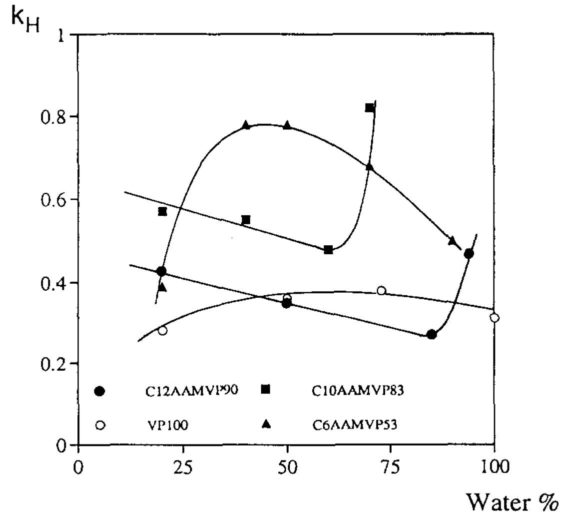

Figure 3 Variations of the Huggins coefficient k_H with solvent composition (MeOH/water) (T= 30°C; [KBr] = 5 × 10^{-2} M)

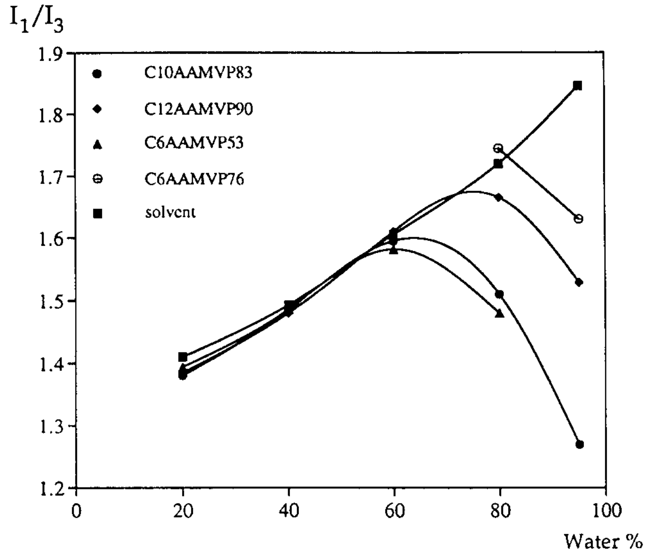

Figure 4 Variations of I_1/I_3 for pyrene with solvent composition (MeOH/water) ($T = 30°C$; $[KBr] = 5 \times 10^{-2}$ M)

Fluorescence

The transitions shown previously (changes of the quality of the solvent) were corroborated by fluorescence spectroscopy. We studied the variations in the ratio I_1/I_3 for the copolymers as a function of the composition of the mixture MeOH/water (copolymer concentration fixed at 0.15 wt%). As shown in *Figure 4*, for high MeOH contents in the medium, no association phenomenon was detected whatever the copolymer. The measured polarity corresponds to that of the solvent medium (MeOH/water). When the water content increases, the polar character of the medium increases until the detection of the association phenomenon. At this point, for all the copolymers studied, the water ratio exceeds 50%, and the pyrene, which is hardly soluble in water, has a greater affinity for the hydrophobic microdomains. Its behaviour explains the I_1/I_3 ratio value corresponding to a less and less polar environment. However, one must keep in mind that at high MeOH contents, no association phenomenon is detected because of the greater affinity of the pyrene for MeOH than for the hydrophobic microdomains, and the absence of I_1/I_3 variation (in comparison with the polarity of the medium) must not be interpreted as a total absence of hydrophobic microdomains. It is interesting to note the particular case of the copolymer C_6AAMVP53 for which the viscosity studies did not reveal significant variations with regard to the mixture composition. The great sensitivity of the fluorescence spectroscopy technique showed that the acrylamide chains, despite their short length, are still inclined to associate to form hydrophobic microdomains.

The influence of the copolymer composition on the I_1/I_3 ratio was studied by using a MeOH/water medium with a water content equal to 95% so that all the copolymers remain soluble (*Figure 5*). Under these conditions, the polarity variation of the microenvironment of the probe with regard to the copolymer concentration shows that the association phenomenon occurs for all the copolymers whatever the comonomer composition or the chain length of the acrylamide unit from C_6 to C_{12}. For copolymers with similar composition and differing only by their *N*-acrylamide chain length (e.g. C_6AAMVP76, C_{10}AAMVP83 and C_{12}AAMVP84) the formation of the hydrophobic microdomains occurs at lower concentrations especially since the acrylamide chain length is longer. From the plot I_1/I_3 as a function of the copolymer concentration[21], we can determine for each compound the concentration corresponding to the start of aggregates formation. These concentrations were found to be equal to 3.4×10^{-5}, 8.25×10^{-5}, 1.5×10^{-4}, 4.1×10^{-4} and 5.6×10^{-4} g ml^{-1} for C_{12}AAMVP67, C_{12}AAMVP84, C_{10}AAMVP83, C_{12}AAMVP90 and C_6AAMVP76, respectively.

Interfacial tension

In the system (water–MeOH 5%)/methylcyclohexane, no significant variation in interfacial tension was observed. On the other hand, the addition of KBr (0.05 M) induces for C_{12}AAMVP90 and C_{10}AAMVP83 a decrease in the interfacial tension from 30×10^{-3} to $\sim 7 \times 10^{-3}$ J m^{-2}. These values are comparable to that measured for ethylene and propylene oxide block copolymers[22]. A more detailed study for C_{12}AAMVP90 shows that the plot of interfacial tension (γ) *versus* ln concentration (C) can be divided into three distinct domains: at very low copolymer concentrations, the surface tension does not vary significantly and then with increasing concentrations, a linear decrease is observed (*Figure 6*). The slope demonstrates the adsorption of the macromolecules at the interface according to the Gibbs adsorption isotherm, defined by the equation:

$$\Gamma = -1/RT(\partial\gamma/\partial \ln C)_T \qquad (2)$$

which is applicable in the presence of an electrolyte (e.g. KBr)[23]. This portion is followed by a second linear domain with a lower slope indicating that the copolymer association always occurs before surface saturation. Indeed, generally in the case of a normal surfactant this portion is parallel to the concentration axis and indicates that the adsorption is inoperative when micelles are formed, the breaking point thus defining the critical micelle concentration. In the case of C_{12}AAMVP90 this point appears at a concentration superior to that observed by fluorescence for the formation of microdomains

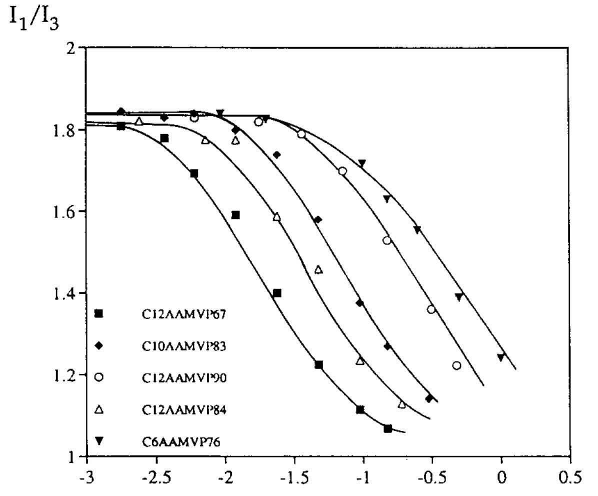

Figure 5 Variations of I_1/I_3 for pyrene with concentration of the copolymers ($T = 30°C$; MeOH/water; MeOH 5%; $[KBr] = 5 \times 10^{-2}$ M)

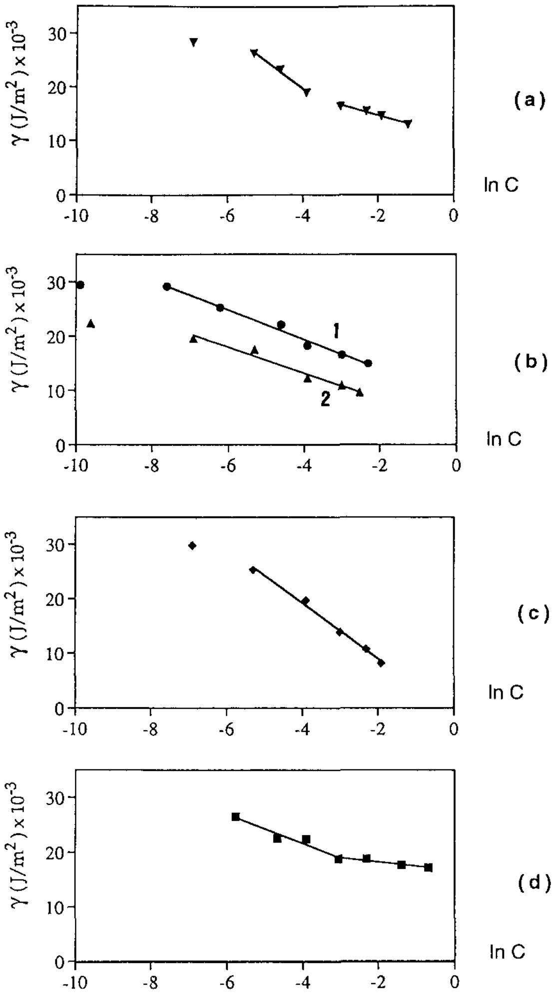

Figure 6 Concentration dependence of the interfacial tension γ for: (a) C_{12}AAMVP90; (b1) C_{12}AAMVP84; (b2) C_{12}AAMVP67; (c) C_{10}AAMVP83; (d) C_6AAMVP76. Interface (water, MeOH 5%, [KBr] = 5×10^{-2} M/methylcyclohexane); $T = 30°C$

Table 2 Surface concentration and area per group adsorbed

	1st slope		2nd slope	
Copolymers	Γ_1 ($\times 10^6$) (mol m^{-2})	A_1 (nm^2)	Γ_2 ($\times 10^6$) (mol m^{-2})	A_2 (nm^2)
C_{12}AAMVP90	2.11	0.78	0.76	2.2
C_{12}AAMVP84	1.1	1.54	–	–
C_{12}AAMVP67	0.94	1.76	–	–
C_{10}AAMVP83	2.0	0.83	–	–
C_6AAMVP76	1.1	1.57	0.29	5.64

(*Figure 5*). So, one can suggest that in the first linear part of the curve, the microdomains can be formed as shown by the results of fluorescence spectroscopy but the interactions between the chains within the macromolecules are weaker than those between the organic phase and the copolymer. Consequently, the macromolecules are adsorbed more easily at the interface especially since the hydrophobic chains have a high affinity for methylcyclohexane. In the second linear portion, the association phenomenon continues up to saturation. It had to be noted that because of their precipitation at higher concentrations, saturation is never reached with the present copolymers. These observations can be confirmed in a more quantitative way by the calculation (from the slopes) of the minimal areas occupied by the macromolecules (A) and their concentration (Γ) in the two phases corresponding to the linear sections. In the later section, the desorption of the macromolecules is observed as shown by the decrease in the surface concentration Γ_2 (*Table 2*). In the first case, the area per molecule was found to be 0.78 nm^2 (this area being comparable to that of a low molecular weight compound) whereas it was equal to 2.2 nm^2 in the second section. By increasing slightly the proportion of hydrophobic moieties in the copolymer (C_{12}AAMVP84), the effects on the interfacial tension remain similar to those observed for C_{12}AAMVP90. On the other hand, the curve profile can be assimilated to a pure straight line. For the C_{12}AAMVP67 copolymer, an identical variation was observed but with lower surface active properties. For these two copolymers (C_{12}AAMVP84 and C_{12}AAMVP67), the microdomains are formed at lower concentrations (than for C_{12}AAMVP90) (*Figure 5*) for which the adsorption of macromolecules also occurs at the interface. In both cases the calculation of the minimal area occupied per molecule provides intermediary values when compared to those previously found for C_{12}AAMVP90 (*Table 2*). The copolymer bearing a C_{10} *N*-acrylamide chain (C_{10}AAMVP83) behaves identically to that observed for C_{12}AAMVP90 at low concentrations but with a greater surface activity. When the chain length of the acrylamide unit becomes too short (e.g. C_6AAMVP76), no significant effect on the interfacial tension is observed.

Thus, the more the hydrophobic moieties increase, the less the copolymer adsorbs at the interface and at a lower concentration with the quasi-simultaneous appearance of hydrophobic microdomains. In the case that the polymer contains only a few hydrophobic side chains, the rather weak hydrophobic interactions within the polymer can explain the migration of the macromolecules to the interface before the formation of the microdomains.

CONCLUSIONS

The nature of the solvent plays a fundamental role in the association phenomenon of copolymers studied, as shown by the viscosity and fluorescence spectroscopy studies. Interfacial tension characteristics strongly depend upon the hydrophilic/hydrophobic balance, i.e. the ratio between the two comonomers and the chain length of the acrylamide unit. These two latter properties are essential in governing the formation and the stability of the hydrophobic microdomains which are both in competition with the adsorption of the macromolecules at the water/methylcyclohexane interface. This kind of compromise between chain–chain interactions in the copolymer and the chain–organic phase has been evidenced in the case of the copolymer C_{10}AAMVP83 whose surface active properties, although weak, remain interesting.

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