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Viscosity and Electrical Conductivity of Cationic Amphiphilic Polyacrylamide Derivatives in Hydroalcoholic Medium

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ABSTRACT

A series of different copolymers of N-[3-alkyldimethylammoniopropyl] methacrylamide bromides (DPMAA) and N,N-dimethylacrylamide were prepared by free radical copolymerization at 60°C in toluene varying the composition feed. The polymers obtained were characterized by spectroscopic methods infrared and ^{1}H NMR, elemental analysis, conductivity and by viscometry. Viscosity was used to study the hydrophobic microdomain formation in hydroalcoholic medium. Conductivity for aqueous solution of synthetics polymer as functions of their concentration was studied.

Key words: *Cationic amphiphilic polymer, Radical copolymerization, Viscosity, Electrical conductivity.*

1. INTRODUCTION

The interest in the synthesis and characterization of amphiphilic polymers has increased enormously in the last years. Amphiphilic polymers consisting of hydrophilic and hydrophobic segments are self-assembling materials, which are capable of forming polymer assemblies into microdomains, micelles, and vesicles in aqueous solutions. Depending on their amphiphilic behavior, they can be classified into two broad categories: Macrosurfactants [1] and polysoaps [2]. Amphiphilic polymers have become a major subject of investigation [3], and their use has progressively developed to many fields, such as enhanced oil recovery [4,5] or biomedical substances [6,7].

Nevertheless, since the pioneering works by Strauss *et al.* [8,9-12] cationic amphiphilic polymers have been much less investigated than anionic ones. It has also been reported that the presence of cationic charges can increase significantly the reaction kinetics between reactants dissolved in the hydrophobic nanodomains [13-15]. Polymeric quaternary ammonium compounds represent a class of amphiphilic polyelectrolytes that derive unique properties mainly from the density and distribution of positive charges along a macromolecular backbone [16].

Thus, previous work [17,18] on cationic amphiphilic species derived from poly methacrylamides quaternized by long alkyl chains had led us to conclude that comb structures were particularly likely to induce intramolecular side chain aggregation leading to microdomains. A lot of these microdomain forming polymers contain repeating units which are themselves amphiphilic. They correspond to polysoaps with comb-like structures which are more or less dense in alkyl side chains.

Here, we report the radical copolymerization of N-[3-alkyldimethylammoniopropyl] methacrylamide bromides (DPMAA) with N,N-dimethylacrylamide (DMAA) at 60°C using 2,2'-Azobis isobutyronitrile (AIBN) as initiator in toluene as solvent. The aim of this work was to study the effect of the chemical structures on the viscometry and the electrical conductivity of solutions of cationic polyelectrolytes.

2. EXPERIMENTAL

2.1. Materials

Commercial (DPMAA, Aldrich) was distilled under reduced pressure (80-85°C/0.2 mmHg) to remove the stabilizer under argon atmosphere. The polymerization initiator, AIBN, Acros Organics was purified by recrystallization from methanol, dried under vacuum at room temperature, and stored at −20°C. Hydroquinone (Aldrich). 1-bromoalkanes (Aldrich) were used as received. DMAA (Fluka Chemika).

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2.2. Measurements

Fourier transform infrared (FTIR) spectrum of the monomers and polymers was recorded on FTIR SCHIMADZU 8300 spectrometer with KBr disc in the range of 400-4000 cm^{-1}.

^{1}H NMR spectra were recorded using a Bruker Avance instrument using $CDCl_3$ as the solvent at 300 MHz.

Elemental analysis was carried out using an elemental analyses system in (Centre de Microanalyses de l'Université de Rennes-1, France).

The molar mass of polymer was characterized relatively with intrinsic viscosity, and the intrinsic viscosity of polymer was determined using an Ubbelohde viscometer with chloroform as solvent and the concentrations of the polymer were in the range of 0.00025-0.003 g.dl^{-1} at 30.0 ± 0.1°C.

2.3. Synthesis and Characterization

2.3.1. Synthesis of monomers N-[3-alkyldimethyl-ammoniopropyl] methacrylamide bromides

The monomers DPMAACn were prepared according to literature procedures [18-19]. N-[3-(dimethyl-amino)propyl] methacrylamide is quaternized with selected 1-bromoalkane in the presence of acetonitrile as the reaction solvent including the high polarity promotes nucleophilic substitutions (SN_2) and a small amount of hydroquinone to avoid polymerization reaction. Operating at T = 50°C for about 72 h. The solvents were then removed in vacuum below 40°C, and the oily remaining product left to stand and washed several times with dry diethyl ether. The amphiphilic monomers were characterized by ^{1}H NMR [18].

2.3.2. Synthesis of copolymers

Four different copolymers in composition were prepared by radical polymerization using AIBN in toluene as solvent. The monomers DPMAACn and DMAA were copolymerized at 60°C under N_2 atmosphere during 24 h (Figure 1). Different feed compositions were used to modify the charge density in the copolymers. The copolymers were purified by three cycles solution-precipitation from chloroform into a large excess of heptane. The resulting precipitates were filtered off and dried at 50°C to constant weight.

Table 1 reports the most results obtained by varying the experimental conditions. The structural characterizations of copolymers were done by FTIR (Figure 2) and ^{1}H NMR spectroscopy (Figure 3).

The IR spectrum of the copolymer exhibited peaks at 3435 cm^{-1} and 1637 cm^{-1}, which are due to N-H stretching and -NC=O stretching vibrations, respectively. The peaks at 2928 cm^{-1} and 2854 cm^{-1} are due to alkyl side chain DPMAACn of monomer. The peak at 1058 cm^{-1} is assigned to N-H vibration of the amide group.

3. RESULTS AND DISCUSSION

3.1. Polymer Synthesis and Characterization

The amphiphilic monomers were obtained by nucleophilic substitution of the tertiary amine group of the precursor monomer with the appropriate 1-bromoalkane. The nucleophilic substitution was carried out at temperature 50°C in acetonitrile and in the presence of hydroquinone. These monomers behaved similarly as ionic liquids; they were perfectly purified by repeated washings in diethyl ether. Then the amphiphilic monomers are copolymerized with hydrophilic comonomer DMAA at different molar ratio.

The copolymers are easily soluble in methanol, ethanol, acetonitrile, chloroform, and dichloromethane but insoluble in heptane, acetone, dioxane, benzene, tetrahydrofuran, ethyl acetate, and water. All polymers displayed regular viscosity behavior in solution in chloroform for a large concentration, therefore, allowing determining an intrinsic viscosity.

The compositions of the copolymers were derived from the conductivity and elemental analysis data.

3.2. Conductimetric Titration

The quaternization degree was estimated from a simple titration method. We dose the bromide ions of copolymers using $AgNO_3$ solution (5.10^{-3} mole) as titrant. The Figure 4 represents the variation of conductivity of copolymer P(DPMAAC$_8$-co-DMAA) with $AgNO_3$ volume added χ =f (V_{AgNO3}). The results are presented in Table 2.

Titration of P(DPMAAC$_8$-co-DMAA) by $AgNO_3$ leads, therefore, to a gradual replacement of the bromide ions $Br^-_{(aq)}$, highly conductive, which react with silver ions $Ag^+_{(aq)}$ to give precipitates of silver bromide (AgBr) are replaced by nitrate ions NO_3^- less drivers. Accordingly, the conductivity decreases until the end point is reached (Figure 4). Further, the excess of $AgNO_3$ brings about a gradual increase of conductivity. Whereas, that the quaternizing bromoalkyle has reacted completely and no side reactions have occurred during the bromoalkylation. The equivalence volume lies at the intersection of the two linear branches of the titration curve. Equivalence volume determined according to Figure 4 will be employed for calculating the quaternization degree.

Table 2 shows the results of comonomers ratio in the copolymers using conductimetric titration.

3.3. Elemental Analysis

Elemental analysis was performed to determine the percentage of carbon, hydrogen, and nitrogen and

Table 1: The experimental percentages of copolymers with different ratios.

Polymers	Copolymer molar ratio (DPMAAC$_n$/DMAA)	Conversion %	[η] (mL.g^{-1})^{a}	M$_w$ 10^{-5} Daltons^{b}
P(DPMAAC$_8$-co-DMAA)	(50/50)	69	64.60	10.11
P(DPMAAC$_8$-co-DMAA)	(40/60)	73	78.46	10.42
P(DPMAAC$_{10}$-co-DMAA)	(50/50)	78	29.88	4.18
P(DPMAAC$_{10}$-co-DMAA)	(40/60)	64	37.86	5.65

DPMAAC$_8$: Monomer (dimethylamino propylmethacrylamide) quaternized with 1-bromooctane, DPMAAC$_{10}$: Monomer (dimethylamino propylmethacrylamide) quaternized with 1-bromodecane, ^{a}[η]: Intrinsic viscosity measured in chloroform at 30°C, ^{b}M$_w$ calculated from the following Mark-Houwink equation: Where $K=1.0810^{-5}$ mL.g^{-1} and a=0.79 at T=30°C [20]

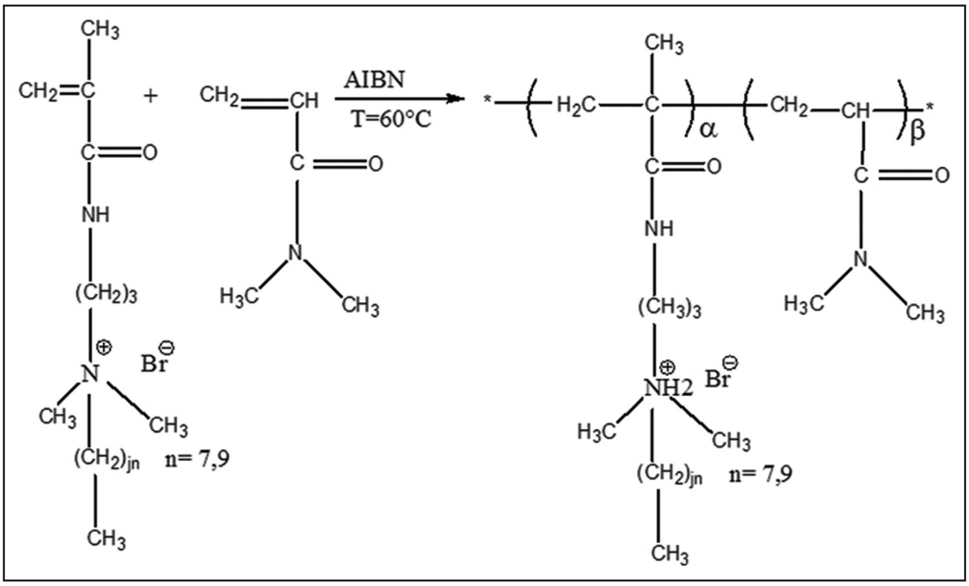

Figure 1: Copolymerization of DPMAACn with N,N-dimethylacrylamide.

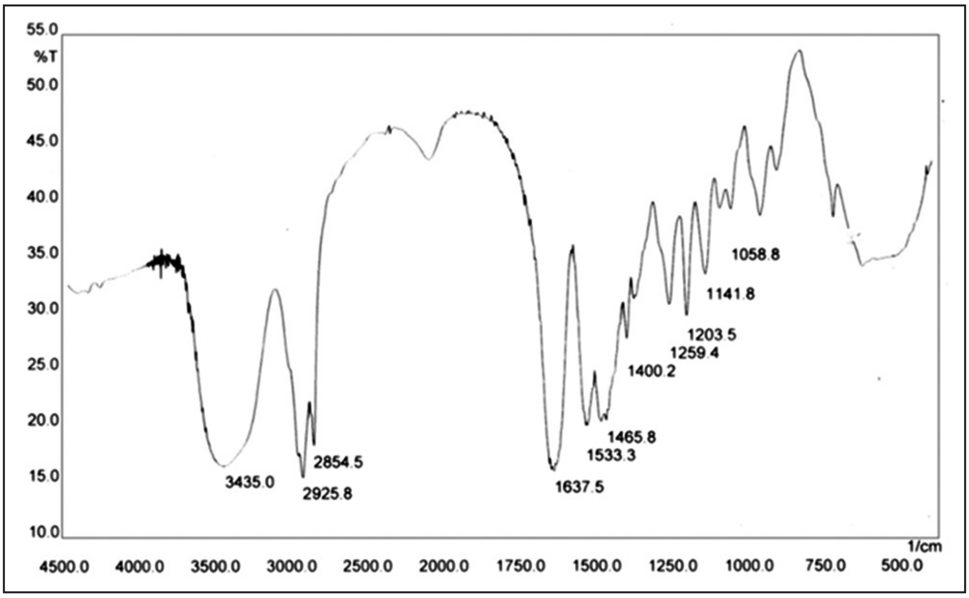

Figure 2: FTIR (KBr) spectrum for P(DPMAAC10-co-DMAA).

then the degree of quaternization. Table 3 shows the results of elemental analysis experiments. We used elemental analysis to verify the complement of the conductimetric titration. Moreover, elemental analysis

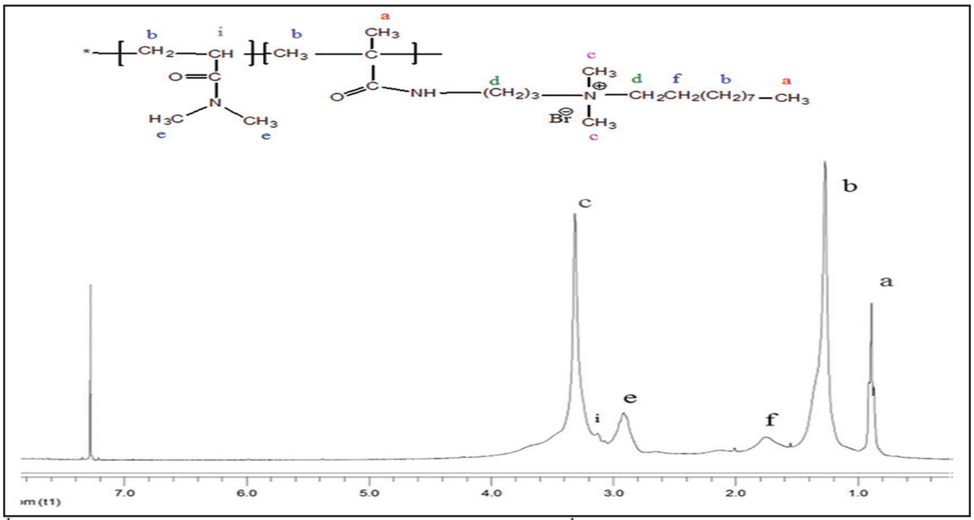

Figure 3: ^{1}H NMR spectrum for P(DPMAAC$_{10}$-co-DMAA). ^{1}H NMR (CDCl$_3$, δ in ppm): 0.95 (Ha, CH$_3$-C and CH$_3$-CH$_2$-), 1.15-1.60 (Hb, (-CH$_2$-)n and -CH$_2$- main chain), 1.7 (Hf, N$^+$-CH$_2$-CH$_2$) , 3.15 (Hc, CH$_3$-N$^+$), 3.60-4.00 (Hd, NH-CH$_2$-), 2.9 (He, CH$_3$-N).

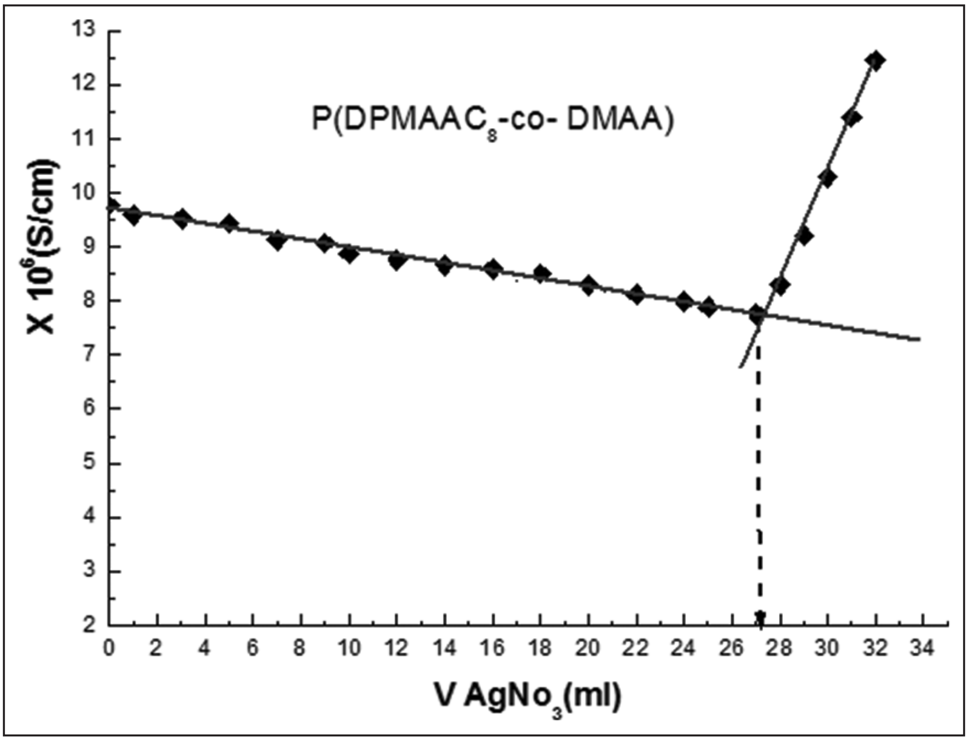

Figure 4: Schematic presentation of the titration curve for the titration of P(DPMAAC$_8$-co-DMAA) against AgNO$_3$ volume.

of the products indicates that the copolymers contain DPMAACn and DMAA. Conductimetric provided similar values were confirmed by elemental analysis. This assumption is in agreement with conductimetric titration method.

3.4. Viscosity

In Figures 5-8, the reduce viscosity in solvent mixtures of methanol and water for amphiphilic copolymers are shown, respectively. The reduced viscosity η_{red} of polymer solutions as a function of polymer concentration C shows typical behavior of polyelectrolyte, increasing with decreasing C. However, the reduced viscosity η_{red} decreasing extremely when water is added. These phenomena may be due to hydrophobic effect responsible for intramolecular aggregation of alkyl side chains. Thus, the hydrodynamic volume decreased and the reduced viscosity decreased consequently. The polymers P(DPMAAC$_8$-co-DMAA), P(DPMAAC$_{10}$-

co-DMAA) are differenced in the length of their alkyl side chains. Hence, it was easily observed that this particular water content decreased with an increase in the length of alkyl side chains. The result showed that the intramolecular aggregation producing for hydrophobic effect easiness when the length of alkyl side chains decrease. Therefore, the hydrodynamic volume decreased and the reduced viscosity decreased consequently. Otherwise; the effect of hydrophilic DMAA comonomer reduces the formation of intramolecular aggregation (e.g., P(DPMAAC$_{10}$-co-DMAA): The formation of aggregation at 50% water content is easy when the copolymer is more dense (α = 93% of quaternization). The values were low that they were hardly measurable. These phenomena are due to hydrophobic effect responsible for intramolecular aggregation of alkyl side chains.

3.5. Conductivity

All polymer solutions were prepared in methanol/water mixture (50v/50v). Deionized water was used in all preparation (c = 0.89 10^{-6} s/cm).

Specific electrical conductivity $\chi(\Omega^{-1}.cm^{-1})$ was measured experimentally at 25°C ± 1, for aqueous solutions of cationic quaternary ammonium polyacrylamide derivatives with Br^- as countrions, the relationship between specific electrical conductivity and its corresponding equivalent electrical conductivity $\Lambda(\Omega^{-1}\ eq^{-1}\ cm^2)$ being: L = 1000c/C (1) where C is the polyion equivalent concentration.

In Figures 9 and 10, the plots of equivalent electrical conductivity L versus the square root of polyion equivalent concentration $C^{1/2}$ for three series are shown. It can be seen that equivalent conductivities L are found to increase with decreasing C values.

3.5.1. Effect of percentage of quaternization

Figures 9 and 10 show that conductivities decrease with increasing in percentage of quaternization. For example; the conductivity of P(DPMAAC$_{10}$-co-DMAA) (50/50) is lower than the conductivity of P(DPMAAC$_{10}$-co-DMAA) (40/60). It can be explained by the formation of compact structure of the hydrophobic aggregation of alkyl side chains.

Table 2: Coefficients α and β founded from conductimetric titration of P(DPMAAC8-co-DMAA).

Polymers	V_e^a (mL)	α	β
P(DPMAAC$_8$-co-DMAA) (50/50)	27.00	0.93	0.07
P(DPMAAC$_8$-co-DMAA) (40/60)	25.55	0.76	0.24
P(DPMAAC$_{10}$-co-DMAA) (40/60)	18.74	0.40	0.60
P(DPMAAC$_{10}$-co-DMAA) (50/50)	25	0.82	0.18

α and β: Molar fraction of each monomer incorporated in copolymer P(DPMAAC$_n$-co-DMAA)

3.5.2. Effect of alkyl side chain

The copolymers P(DPMAAC$_8$-co-DMAA), P(DPMAAC$_{10}$-co-DMAA) are differenced in the length of their alkyl side chains. It was easily observed that the conductivity decrease with an increase of the length of alkyl side chains. The effect of the chain length can be explained in term of a hydrophobic/

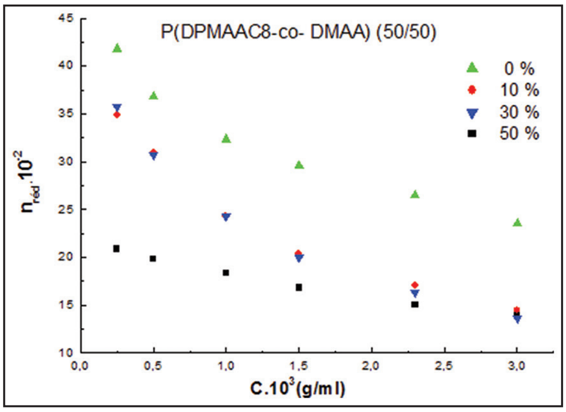

Figure 5: Influence of water content on the reduced viscosity η_{red} of P(DPMAAC$_8$-co-DMAA) (50/50) as a function of polymer concentration at 30°C.

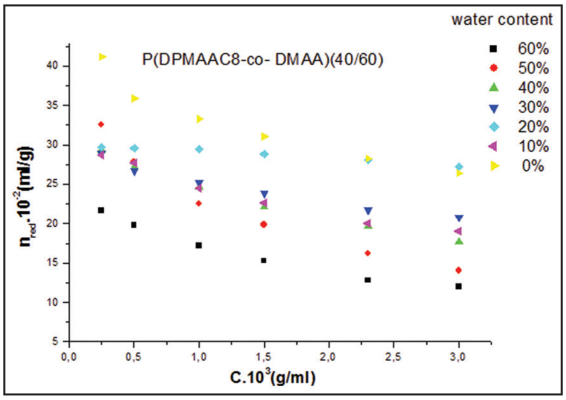

Figure 6: Influence of water content on the reduced viscosity η_{red} of P(DPMAAC$_8$-co-DMAA) (40/60) as a function of polymer concentration at 30°C.

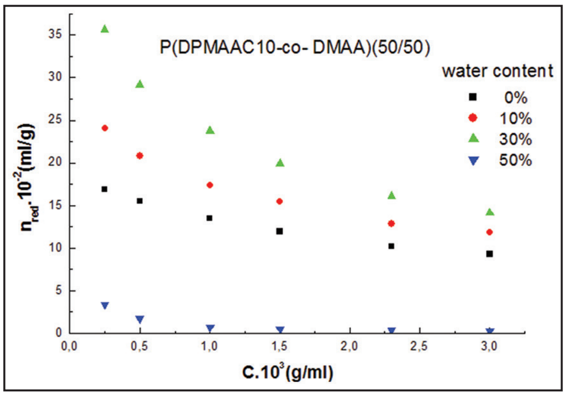

Figure 7: Influence of water content on the reduced viscosity η_{red} of P(DPMAAC$_{10}$-co-DMAA) (50/50) as a function of polymer concentration at 30°C.

Table 3: Element analysis of P(DPMAAC$_{10}$-co-DMAA).

Copolymer	% C	% H	% N	α	β
P(DPMAAC$_{10}$-co-DMAA) (50/50)	53.7	9.0	7.46	0.84	0.15

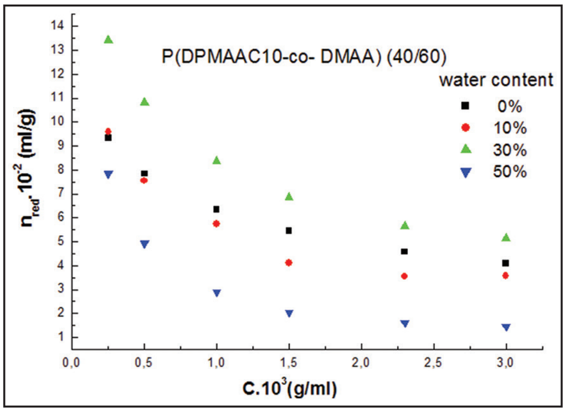

Figure 8: Influence of water content on the reduced viscosity η_{red} of P(DPMAAC$_{10}$-co-DMAA) (40/60) as a function of polymer concentration at 30°C.

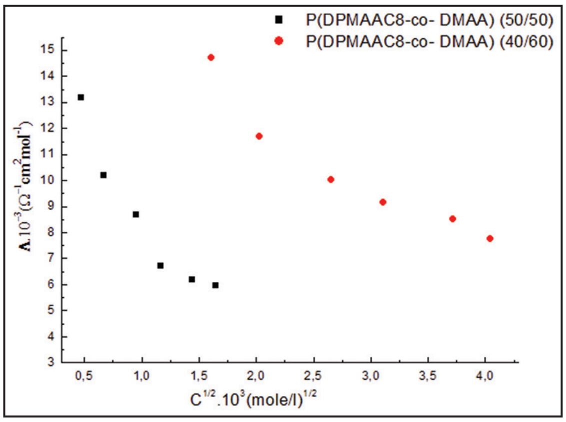

Figure 9: The equivalent conductivity (L) of P(DPMAAC$_8$-co-DMAA) as a function of polymer concentration at 30°C.

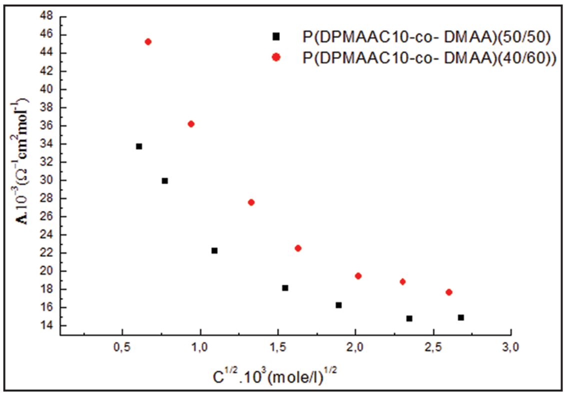

Figure 10: The equivalent conductivity (L) of P(DPMAAC$_{10}$-co-DMAA) as a function of polymer concentration at 30°C.

hydrophilic balance of copolymer. Indeed, when the hydrophobic character of copolymer increases the copolymer acquires an aggregation form. Indeed, the conductivity was more important when the chain length of alkyl bromide decreases.

4. CONCLUSION

Four amphiphilic copolymers were prepared by copolymerization of DPMAAC$_n$ (n = 8, 10) and DMAA at 60°C using AIBN as initiator in toluene. Viscosity measurements carried out with aqueous solutions of a polymer revealed intramolecular associative properties. In particular, the variation of the reduced viscosity of polymer solutions reflected the formation of hydrophobic microdomains in water. Hence, the low conductivities suggested the ion-binding due to hydrophobic interaction with alkyl side chains. Experimental results of molar conductivity L for aqueous solution of synthetics polymer are plotted as functions of the square root of concentration. It is clear that this system follows typical polyelectrolyte behavior. The molar conductivity exhibits a slight increase with decreasing concentration, followed by a rapid increase at higher dilutions.

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***Bibliographical Sketch**

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