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Effect of solvent nature and spacer structure from zwitterionic moieties on the conformation of some poly(carboxybetaines) based on poly(n-vinylimidazole)

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A light-scattering study on the solutions of two poly(carboxybetaines) based on poly(N-vinylimidazole) was performed. Distilled water, 0.5 M NaCl and methanol were used as solvents. From Zimm or Guinier plots molar masses ($\overline{M}_w$), radius of gyration (R_G) and second virial coefficients (A_2) were determinated. The values of the above-mentioned parameters allowed an assignment of the conformation of two poly(carboxybetaines) dissolved in the above-mentioned solvents. Thus, in distilled water these polymers form aggregations by interchain associations, the addition of NaCl leads to the dissociation of the aggregations while methanol is the best thermodynamic solvent.

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1. Introduction

Polybetaines are zwitterionic polymers where each pair of covalently bonded anion and cation is located in the same repeat unit and the two oppositely charged groups are not adjacent.

Typically the cationic moiety is a quaternary ammonium group and for the poly(carboxybetaines) the anionic group is carboxylate one.

Poly(carboxybetaines) may be synthesized by the reaction of the tertiary amine monomers/polymers which haloalkylcarboxylates [1], haloalkylcarboxylic esters [2,3], lactones [4] and α, β- unsaturated carboxylic acids [5-8].

The first synthetic poly(carboxybetaine) was reported by Landenheim and Morawetz in 1957, it being based on poly(4-vinylpyridine) [9].

Polybetaines are regarded as a well-identified class of high dipolar polymeric materials with a wide spectrum of unique and specific properties. Studies on the solution properties of the poly(carboxybetaines) mainly include solubility investigation and viscosity measurements in different environments (additional salt, different pH values) for solution properties whereas the thermal analysis and X-ray studies being for the bulk properties.

If some studies show that intermolecular and intramolecular aggregations do not seem to play a significant role in the properties of the poly(carboxybetaines) except when longer alkyl spacers are involved [10,11], however a recent publication using laser light-scattering reveals a significant interchain aggregation of poly(carboxybetaine) with poly(N,N-dimethyl ((methacrylamido) propyl) ammonium propiolactone)) [12].

The present work deals with a light-scattering study performed on the solutions of two poly(carboxybetaines) based on poly(N-vinylimidazole) containing different spacers in their zwitterionic moieties. The used solvents were bidistilled water, 0.5 M NaCl and methanol. By this study the molar masses ($\overline{M}_w$), radius of gyration (R_G) and second virial coefficients (A_2) were determinated. From the values of the above-mentioned parameters an assignment on the conformation of the respective poly(carboxybetaines) in the three solvents were pictured.

2. Experimental

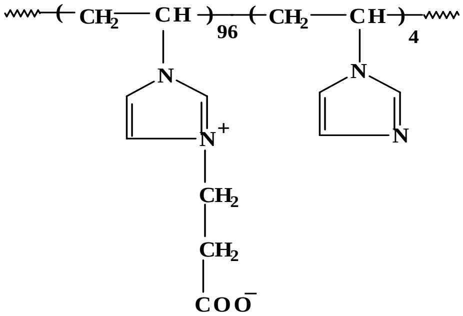
The synthesis of the poly(carboxybetaines) was previously shown [6,8].

Light-scattering measurements were determined with ALV/DLS/SLS-5000F monomode fiber compact goniometer system, equipped with an ALV-500 correlator and COMPASS 315M-150 Coherent solid-state laser Nd:YAG (output power = 150 mW at λ = 532 nm). Measurements were made in an angular region from 30^0 to 140^0, in steps of 10^0. The value was dn/dc = 0.168 mL/g. All measurements were carried out at 20 ^{0}C.

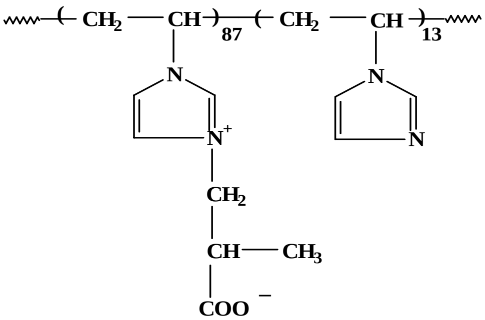
The poly(carboxybetaines) were dissolved in bidistilled water, 0.5 M NaCl solution or methanol to yield solutions of 2 to 10 mg/mL concentration. Prior to measurements, all solutions were repeatedly filtered through 1,2 μm Acrodisc syringe filters with Versapor membrane – Sigma Aldrich.

3. Results and discussion

Fig. 1 shows the chemical structures of two polycarboxybetaines based on poly(N-vinylimidazole) used in this work.



PNVIB-2



PNVIB-3

Fig. 1. Chemical structures of the studied poly(carboxybetaines).

From Fig. 1 it can be observed that PNVIB-2 possesses a spacer in the zwitterionic moiety of two methylene groups while PNVIB-3 contains a side $-CH_3$ group into the spacer of two methylene groups.

The data of light-scattering were analyzed by the Zimm procedure using Debye equation (1):

$$\frac{Kc}{R_\theta} = \frac{1}{\overline{M}_w}\left(1 + \frac{q^2 R_G^2}{3}\right) + 2A_2 c \qquad (1)$$

where, K = an optical contrast constant determined by equation (2);

c = the polymer concentration;

R_θ = Rayleigh ratio used to calculate the scattering function, Kc/R_θ according to equation (3);

q = scattering vector calculated by equation

$$q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$$

λ = wavelength of the light in the solution.

$$K = \frac{4\pi^2}{\lambda_0^4} n_0^2 \left(\frac{dn}{dc}\right)^2 \frac{1+\cos^2\frac{\theta}{2}}{2} \qquad (2)$$

where λ_0 = the wavelength of the primary beam in vacuum;

n_0 = the solvent refractive index;

dn/dc = the refractive index increment;

θ = scattering angle.

$$R_\theta = \left(\frac{i_\theta}{I_0}\right) r^2 \qquad (3)$$

where I_0 = the primary beam intensity;

i_θ = the corresponding scattering intensity at scattering angle θ and r is the distance of the detector from the centre of the scattering volume.

Figs. 2-4 show Zimm plots for PNVIB-2 dissolved in bidistilled H_2O, 0.5 M NaCl solution and methanol, respectively.

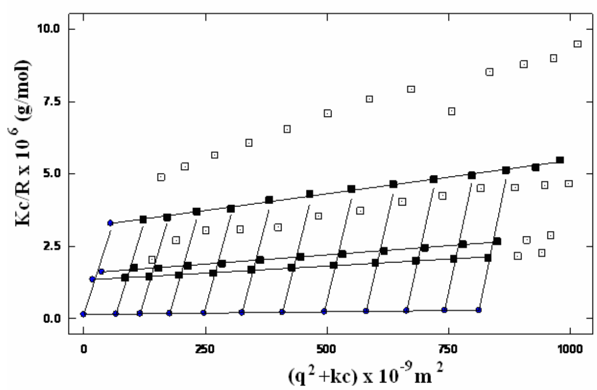


Fig. 2. Zimm plot of PNVIB-2 in bidistilled water for concentration of c = 2 to 10 mg/mL, k= 9.236.

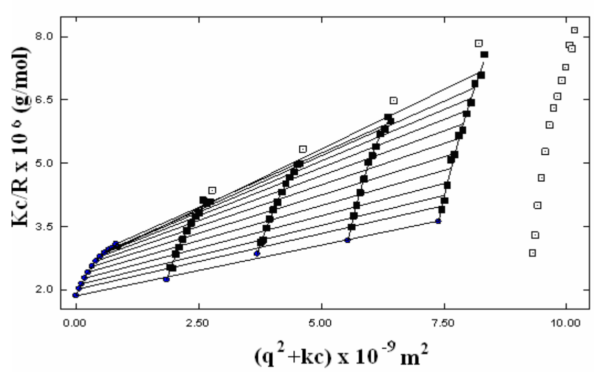


Fig. 3. Zimm plot of PNVIB-2 in 0.5 M NaCl for concentration of c = 2 to 10 mg/mL, k= 923.6.

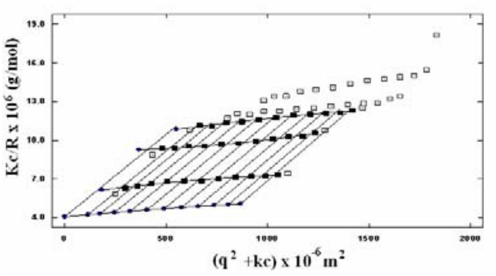


Fig. 4. Zimm plot of PNVIB-2 in methanol for concentration of c = 2 to 10 mg/mL, k= 90.77, $\overline{M}_w$ = 2.464 x 10^5 g/mol, A_2 = 5.808 x 10^{-7}mol·dm^3/g^2, R_G = 32.3 nm.

Figs. 2 and 3 show that the Zimm plots exhibit an abnormal features and no reasonable extrapolate was possible, in contrast to the case when methanol was used as solvent (Figure 4).

For PNVIB-2 dissolved in bidistilled H_2O and 0.5 M NaCl solution the corresponding Guinier representations were used (Figures 5 and 6).

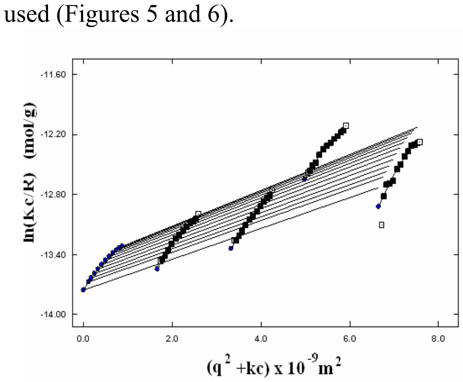


Fig. 5. Guinier plot from PNVIB-2 in water for the concentration of c = 2 to 10 mg/mL. Accurate determination of the molecular parameters became possible. $\overline{M}_w$ = 9.422 x10^5 g/mol, A_2 = 0.6798x10^{-7}mol·dm^3/g^2, R_G = 46.61 nm.

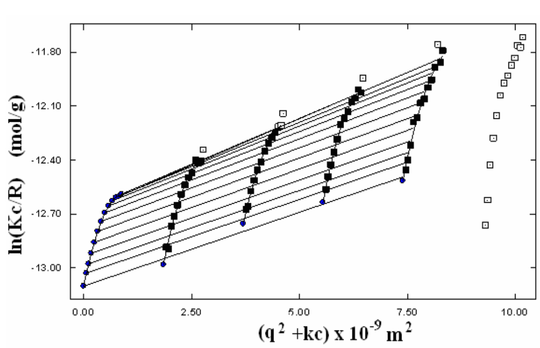


Fig. 6. Guinier plot from PNVIB-2 in 0.5 M NaCl for the concentration of c = 2 to 10 mg/mL. Accurate determination of the molecular parameters became possible. $\overline{M}_w$ = 4.900 x10^5 g/mol, A_2 = 0.7753x10^{-7}mol·dm^3/g^2, R_G = 58.48 nm.

From the high $\overline{M}_w$ value (942,200 g/mol) together with a very low R_G value of 46 nm for PNVIB-2 (Figure 5) we assume that this polymer in bidistilled water exists as aggregations of polymer chains with sphere conformations. The addition of NaCl reveals a major decrease of $\overline{M}_w$ value and an increase of R_G (Fig. 6) indicating a dissociation of the interchain aggregations.

The methanol can be considered the best thermodynamic solvent because PNVIB-2 dissolved in this solvent has the lowest value of $\overline{M}_w$ and R_G and the highest value of A_2. These findings could be attributed to a complete dissociation of the aggregations and an extension of the individual chains.

The results of the light-scattering measurements are in good agreement with those from our previous viscometric study [13]. Thus, PNVIB-2 dissolved in bidistilled H_2O and 0.5 M NaCl has a typical viscometric behaviour of hard-sphere suspensions, namely it is insensitive to the polymer concentrations, while PNVIB-2 dissolved in CH_3OH has a polyelectrolyte behaviour. Also, the higher [η] value in H_2O than 0.5 M NaCl solution was observed.

Fig. 7 illustrates our assignment for the conformations of the polymer chains of PNVIB-2 dissolved in the three solvents.

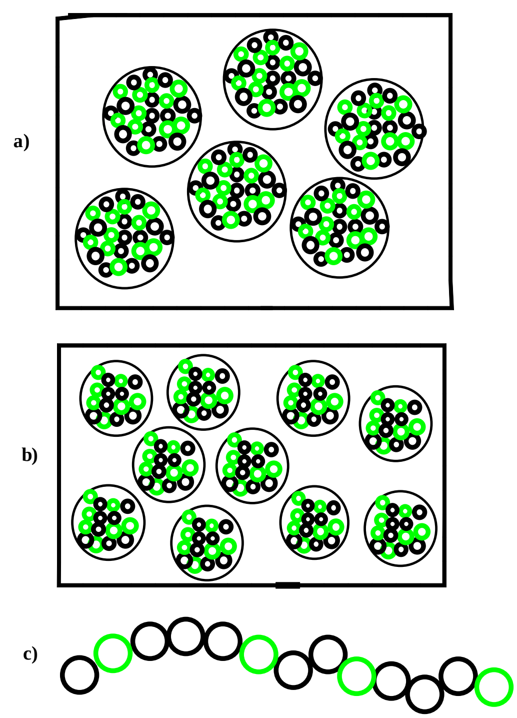


Fig. 7. The conformation models of PNVIB-2 in a) bidistilled H_2O, b) 0.5 M NaCl, c) CH_3OH.

Figs. 8 and 9 illustrate Guinier plots for PNVIB-3 dissolved in H_2O and 0.5 M NaCl, respectively.

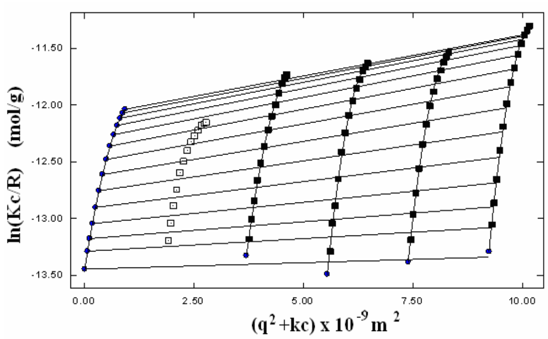


Fig. 8. Guinier plot from PNVIB-3 in water for the concentration of c = 2 to 10 mg/mL. Accurate determination of the molecular parameters became possible. $\overline{M}_w = 6.920 \times 10^5$ *g/mol,* $A_2 = 0.0761 \times 10^{-7}$ *mol·dm^3/g^2,* $R_G = 85.69$ *nm.*

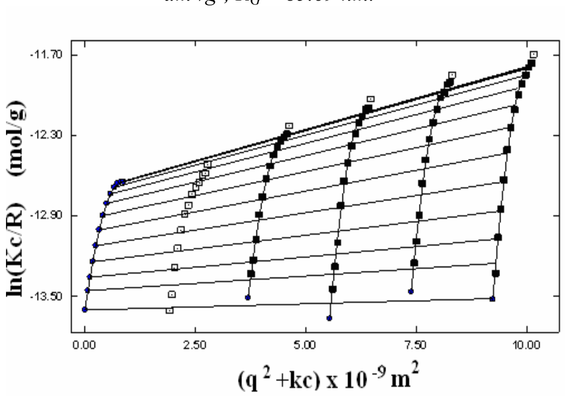


Fig. 9. Guinier plot from PNVIB-3 in 0.5 M NaCl for the concentration of c = 2 to 10 mg/mL. Accurate determination of the molecular parameters became possible. $\overline{M}_w = 8.059 \times 10^5$ *g/mol,* $A_2 = 0.0592 \times 10^{-7}$ *mol·dm^3/g^2,* $R_G = 82.58$ *nm.*

A contrary result wais observed for PNVIB-3 poly(carboxybetaine) which exhibits a higher $\overline{M}_w$ value in 0.5 M NaCl than in bidistilled H_2O. Also, the A_2 value is higher in H_2O than 0.5 M NaCl. These aspects means that 0.5 M NaCl is a poorer solvent than bidistilled H_2O for PNVIB-3 and therefore, sodium chloride ensures a certain association degree of the polymer chain.

4. Conclusions

This paper provides informations about the conformations of the polymer chains of two poly(carboxybetaines) based on poly(N-vinylimidazole) by means with of a light-scattering study. From Zimm or Guinier plots $\overline{M}_w$, R_G and A_2 were determinated.

The influences of the spacer structure and solvent nature on the conformations are shown. Bidistilled water and 0.5 M NaCl solution are poor solvents for PNVIB-2 and therefore, the polymer chains form interchain aggregations while the methanol is a good thermodynamic solvent. PNVIB-3 forms interchain aggregations only in 0.5 M NaCl solution.

The knowledge of the poly(carboxybetaine) chains conformation is important because these polymers are used in H_2O, saline media or organic solvents in textile, medical, sewage treatment, soil conditioning, paper reinforcement.

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