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Research Article

Thermo-associative Behavior of Poly (4-Vinylpyridine)-g-poly(ethylene oxide) [p4vp-poe] Copolymers

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ABSTRACT

Poly(4-vinylpyridine) (P4VP) consists of organic macromolecules that do not dissolve in water. However, modifying these polymers by incorporating polyethylene oxide (PEO) side chains results in novel water-soluble copolymers. The attachment of PEO chains to the P4VP backbone significantly enhances its affinity for water. A distinctive feature of PEO is its decreasing solubility in water as temperature rises. In this study, we examine whether this thermal response is preserved in P4VP-PEO copolymers, leading to their thermoassociative behavior. Monomethyl polyethylene oxide (molecular weight: 6000 g/mol) undergoes functionalization via tosylation. The resulting tosylated PEO is then employed in the quaternization process of P4VP. The rheological properties of the synthesized P4VP-6000-Ts copolymer solutions are analyzed using viscometry. Initial findings suggest a promising thermoassociative system. The variation in reduced viscosity depends on polymer concentration, defining three key concentration regions: **C < C***, **C = C***, and **C > C***. At **C***, the influence of temperature on reduced viscosity becomes evident. A sharp decline in viscosity is directly correlated with the self-association behavior of PEO chains at elevated temperatures.

Keywords: Polyelectrolyte, poly(4-vinylpyridine),viscosity,thermo-association

INTRODUCTION

Jordan et al., Berkowitz et al., and Boyes et al. [1-3] have explored the viscometric properties of poly(4-vinylpyridine) (P4VP) in solution across various solvents and temperatures. Their research indicates that the intrinsic viscosity of P4VP in ethanol declines as temperature rises [4]. On the other hand, numerous investigations have focused on polyethylene oxide (PEO) in dilute solutions [5,6]. However, a comprehensive theoretical-experimental comparison remains incomplete, preventing the establishment of general conclusions regarding the conformational behavior of polyelectrolyte chains in solution. The influence of ionic strength and counter-ion properties remains insufficiently characterized [7]. Variations in viscosity and the emergence of associative structures can result from electrostatic screening, counter-ion condensation, and interactions between or within polymer chains.

OBJECTIVES

This study details the synthesis and characterization of a novel P4VP-PEO copolymer, alongside an analysis of its viscosity behavior in aqueous solutions across different temperatures. A distinguishing feature of PEO is its reduced solubility in water as temperature increases. This work seeks to verify whether this property persists within the P4VP-PEO system, contributing to its thermoassociative nature. We specifically examine how the reduced viscosity of the P4VP-6000-Ts[PVCPAM6TS]copolymer varies with temperature, neutralization degree (α), and concentration (Cp) in aqueous solutions

EXPERIMENTAL PART

1.1 Preparation of POE6000 Ts [AM 6Ts]:

a/ Preparation of anhydrous toluene:

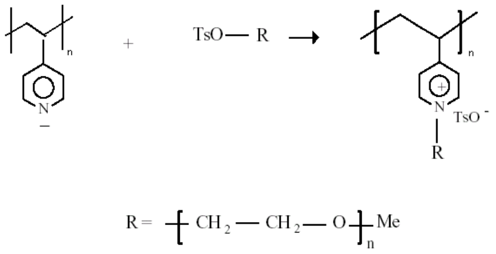
The evaporation of water in Toluene is carried out using a flask equipped with a Dean-Stark flask. The Toluene used is supplied by Rectapur (Prolabo).

b/ Tosylation :

In a dry 500ml three-necked flask, equipped with a condenser, place the PEO (4.103-mol, 24g) in toluene (250ml), cool using an ice-water bath. In a dropping funnel, place the tosyl chloride solution (4.95.10-3mol, 0.94g) in 5ml of pyridine.

The addition is carried out drop by drop over 1 hour, the temperature of the ice-water bath must be kept below 2°C during the addition. Stirring is continued for 24 hours at room temperature. Gently add the reaction mixture to 250ml of water and ice containing 35% hydrochloric acid (100ml). Shake well and separate the organic phase. Extract the aqueous phase three times with chloroform (250 ml). Dry the organic phase over anhydrous sodium sulfate, then filter and dry the solvent. The product is washed with methanol and precipitated several times in diethyl ether.

c/ Quaternization of poly(4-vinylpyridine) [P4VP] by POE-Ts*:*



In a 500ml dry three-necked flask, fitted with a condenser, place the PEO6000Ts (2g) in 95% ethanol (20ml). Bubble in nitrogen for 15 min. In a dropping funnel, place a solution of P4VP (Mw = 160,000g/mol, 2g) in 95% ethanol previously bubbled in nitrogen for 15 minutes. Add the solution to the flask. Both solutions are stirred and kept at a temperature of 70°C in an oil bath for 4 days. Precipitate the product in diethylene ether several times. Dry the resulting product.

1.2 Apparatus

Viscosity measurements were conducted using a capillary viscometer, specifically the Ubbelhode-Schott Gerat AVS400 [7], at the Laboratoire d'Application des Electrolytes et des Polyélectrolytes Organiques (LAEPO). The system was maintained at a controlled temperature with a thermostatic bath (±0.1°C). The reduced viscosity ($\eta_{red} = \eta_{sp} / c$) was determined by dividing the specific viscosity—where η represents the viscosity of the solution and η_o that of the solvent—by the polyelectrolyte concentration (expressed in g/ml). Products and reagents Poly(4-vinylpyridine) polymer (P4VP) was prepared by radical polymerization, using AIBN or Benzoyle peroxyde as initiators, in toluene at 60°C following a described procedure [8] . P4VP samples were fractionnated by successive dissolution-precipitation in the following solvents: chloroforme/hexane or methanol/ethylacetate. Fractionation has provided ten P4VP fractions P4VP1 to P4VP10, which have been used in a previous paper [7-8]. Only one of these is used in this work. Mw was determined by Light Scattering in ethanol (λ=632nm, constant apparatus: K=0,735). The polymer was then characterized by 1HNMR spectroscopy (in $CDCl_3$). The following commercial solvents and products were used without any later purification: Polyethyleneoxide (PEO, Mw=6000g/mole), Hydrochloric acid HCl 37.5% and Methanol.

1.3 General preparation of P4VP-6000Ts Solution:

A 100mg of P4VP-6000-Ts and 1ml of ethanol 95% are introduced into a graduated flask of 20ml. 0,5ml of HCl 0.2M solution is added to the copolymer, to reach α=0.1. We fill to 20ml with water and agitate during 48 hours at ambient temperature. Agitation is engaged and the solution is then filtered using an usual filter paper.

RESULTS AND DISCUSSIONS

1 Viscosimetry behavior of P4VP600TS copolymer:

The neutralization degree α represents the quantity of added protons H+ compared to the P4VP polymer concentration. In the present work, we have only studied the case $\alpha = 1$. Thus, we have used, in each case, the same concentrations for protons H+ than for the P4VP. Under these conditions, we traced the variation of the reduced viscosity of this copolymer P4VP-6000-Ts as a function of its concentration.

2 Concentration effect:

Figure 1.1 shows the reduced viscosity variation of P4VP-6000-Ts [P4VPAM6Ts] aqueous solutions, as a function of the copolymer concentration (Cp) for neutralisation degree (α =1), at temperatures T=25, Figure 1.2 shows the reduced viscosity variation of P4VPAM6Ts aqueous solutions, as a function of the copolymer concentration (Cp) for neutralisation degree (α =1), at different temperatures T=25 (35, 45, 55, 65, 70, 75°C). We observe three variation concentration domains, as mentioned on the figure 1.0:

- C< C*: one macromolecular chain occupes a space more important than its needing volume.

- C*: a maximum limit is observed. It is due the extended macromolecular form. This effect has been studied by Flory-Huggins [14]. The reduced viscosity when the concentration decreases in our case, this behaviour is also due to the PEO chain associations under the temperature effect.

- C> C*: the concentration increases and the reduced viscosity decreases rapidly. The macromolecular chains change their physical structure electrostatically as detailed by Edwards [10]. In fact, semi-diluted solutions of charged macromolecules have been analysed, in theoretical point of view, by several authors [11-12], but never considered experimentally. For copolymer concentration values superior thane 0.1mg/ml, PEO chain associations lead to the macromolecular collapse [12-13] and to a decrease of the reduced viscosity. Tosylate ions seem be free in the solution.

The condensation of this counter-ion is screened by the PEO side-chains [4]. When the polymer concentration is increased, we move from a dilute regime (where the chains are isolated) to a semi-dilute regime (where they become entangled).[11-14]

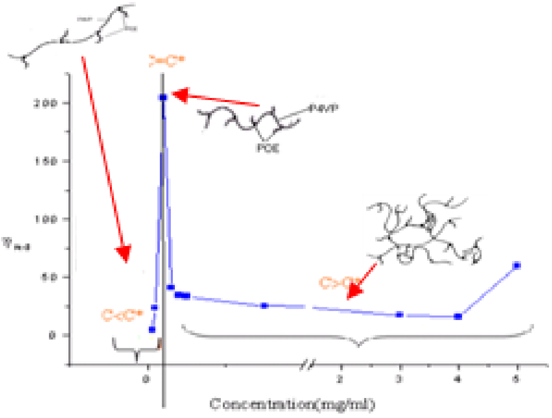


Figure 1.1. Reduced viscosity of P4VPAM6Ts copolymer as a function of concentration for a neutralization degree α=1 at T=25°C

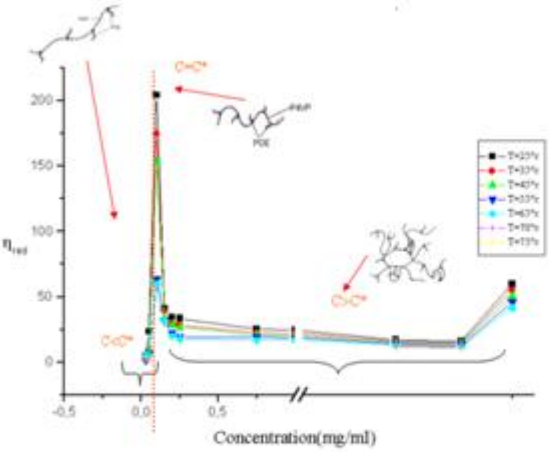
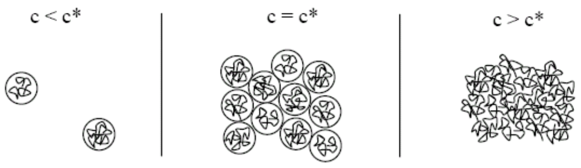


Figure 1.2. shows the reduced viscosity variation P4VPAM6Ts aqueous solutions, as a function of the copolymer concentration (Cp) for neutralisation degree (α =1), at different temperatures (T=25, 35, 45, 55, 65, 70, 75°C)

$$c^{*}_{p} = \frac{M}{N_{av}\frac{4}{3}\pi R^{3}_{g}}$$

Where N_{av} is Avogadro's number and Cp is the polymer concentration per unit volume.

In the semi-dilute regime, the chains are interpenetrated and form a temporary network. Edwards [10] introduced the correlation (or screening) length ζ, which also represents the mesh of the network:



Diluted diet Semi-diluted diet

Figure 1.0: Diagram simplifying the transition of polymer solutions from dilute to semi-dilute regimes

It should be noted that this phenomenon has never been observed for P4VP-POE.

3 Influence of the degree of neutralizations α:

To study the influence of the degree of neutralization α, we plotted the variation of the reduced viscosity of the copolymer P4VPAM6Ts as a function of the concentration at T=25°c as a function of the degree of neutralization α As they are represented in the previous figures 2.

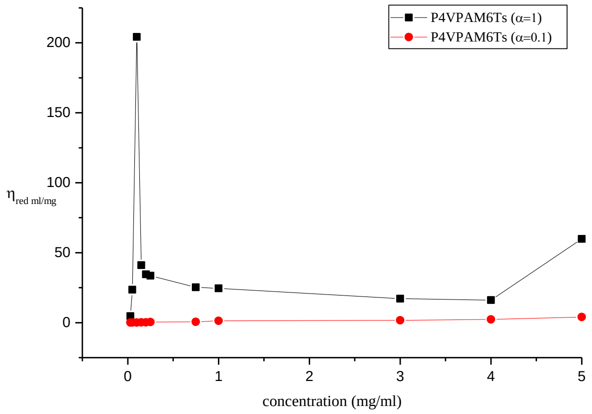


Figure 2: Comparison of reduced viscosity of P4VPAM6Ts copolymer as a function of concentration for neutralization degree α=1 and α=0.1 at T=25°C

We note that for α =1 the values are 100 times higher than those for α =0.1, and this can be explained by the effect of the charge rate carried by the P4VP. This phenomenon greatly increases the volume occupied by the chain which will have difficulty moving in this state and its viscosity increases rapidly around c* [10-14]. In this case, the counterions would be free to move longitudinally along the chain. [7], on the other hand for α =0.1 this effect of repulsion of the charges of the polyion does not exist which explains the significant drop in the viscosity values. To confirm this hypothesis, we studied the viscometric behavior of the polymers alone and separately.

Figure 2.1 shows Reduced viscosity of P4VP polymer as a function of concentration for a neutralization degree α=1 at T=25°C, this polymer in aqueous solution shows a behavior similar to that of polyelectrolytes [2]. Indeed, its reduced viscosity remains constant and equals approximately 10 ml/mg in a wide concentration range, then by diluting the solution of this polyelectrolyte its reduced viscosity increases abruptly from 0.15 mg/ml.

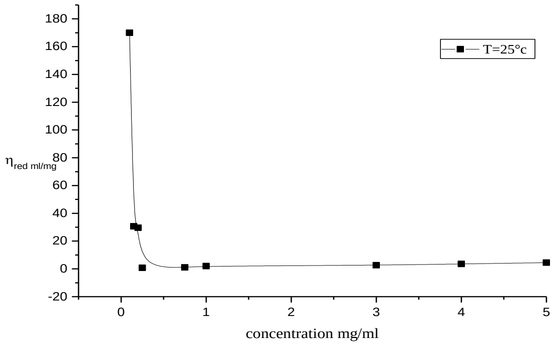


Figure2.1: Reduced viscosity of the P4VP polymer as a function of concentration for a degree of neutralization α=1 at T=25°C

Figure 2.2 shows the Reduced Viscosity of POE polymer as a function of Concentration at T=25°C, this polymer in aqueous solution shows a behavior similar to that of neutral polymers in solution [2]. Indeed, its reduced viscosity remains practically constant and very low. An increasing variation is observed with a very low speed.

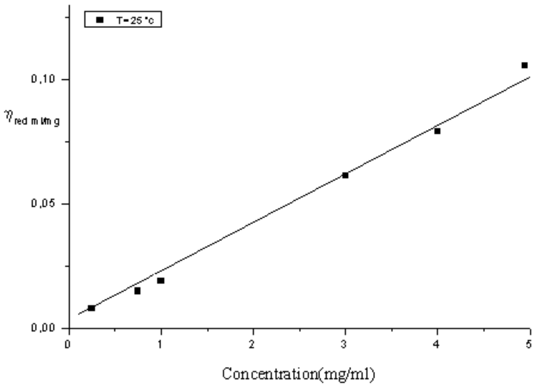


Figure 2.2 Reduced viscosity of POE polymer as a function of concentration at T=25°C

Figure 2.3 shows the comparison of the reduced viscosity of the copolymer P4VPAM6Ts, P4VP and POE as a function of concentration for the degree of Neutralization α=1 at T=25°C:

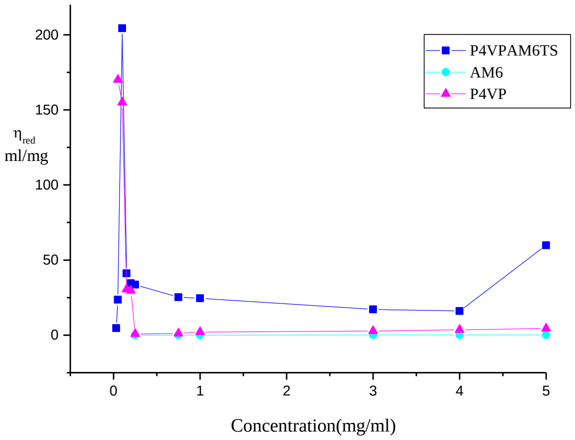


Figure 2.3: comparison of the reduced viscosity of the copolymer P4VPAM6Ts, P4VP and POE as a function of concentration for the degree of Neutralization α=1 at T=25°C.

In conclusion, it is noted that this phenomenon described in Figure 1.1 and 1.2 was observed after the copolymerization between P4VP and PEO. This phenomenon has not been cited in the literature.

4 Temperature effect:

In general, a lost of viscosity is observed with heating the solutions [6]. As observed in figure1, we have three concentration domains. The temperature effect can be clearly seen at C* concentration, where reduced viscosity decreases when temperature increases. At this concentration, we are below the overlap concentration and the observed behaviour is explained by the intramolecular PEO associations. Thus, macromolecular copolymer chains collapse under these associative interactions. This phenomenon is accompagned by the effect of the polyioncounter-ions condensation [15]. Numerous patents have described thickning phenomenon, when heating solutions, for block copolymers containing poly(ethyleneoxyde), like for (PEO poly(propylene)). Therefore, thermo associative properties observed for P4VP-6000-Ts (figure 3) are based on the PEO chains nature.

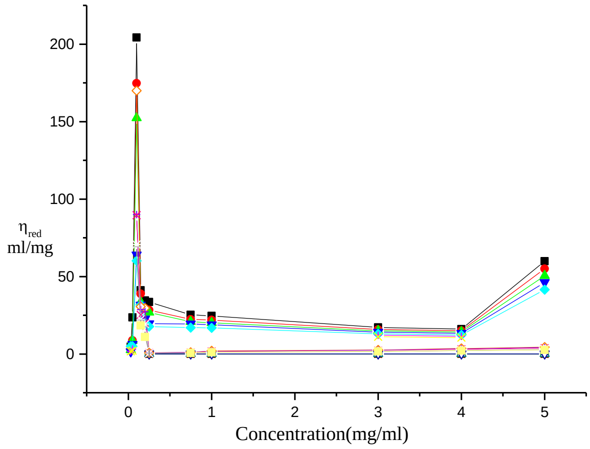


Figure 3. Reduced viscosities comparison of P4VPAM6Ts with each polymer P4VP or PEO alone as a function of concentration at different temperatures (T=25, 35, 45, 55, 65, 70, 75°C) for the neutralization degree α=1

In fact, it must be due to the actual physical properties of the polyelectrolytes. It is well known that the condensation of counterions on polyelectrolytes tends to reduce the number of free ionic species. It has been shown [17] that PEO chains exert a steric effect on tosylate counterions, which seems reasonable to assume that PEOs have a steric effect on counterions. Moreover, the size of the tosylate counterions is relatively large (7 to 8 Å) [17]. The high grafting density of these chains in a good solvent (water) encourages repulsion between them and thus their extension. However, it should not be forgotten that PEOs contain oxygen atoms that can be considered electronegative, which explains their complexing properties with cations. The actual conformation of PEO side chains is therefore probably the result of a subtle balance between, on the one hand, the monomer-monomer interaction that favors chain extension and, on the other, the interaction with cationic charges that favors their "collapse" around the backbone. These form a screen between the counterions and the polycation charges [18] (figure 4). These results are interesting in that they show that polyelectrolyte behavior and hence polyionic-counterion associations can be controlled by adjusting side-chain length, grafting rate and counterion size [19]. It can be concluded that the main skeleton is extremely taut, and increasing concentration increases viscosity under the effect of the PEO structure. The following diagram describes such a structure.

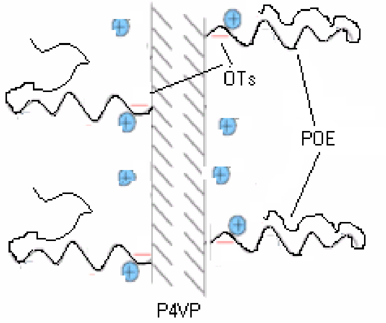


Figure 4. Representation of the P4VP-POE copolymer - stretched chain

A number of patents have reported the thickening behavior of solutes during heating with poly(ethylene oxide) of (PEO)-poly(propylene) block copolymers during heating due to their loss of solubility. On this basis, the thermos associative concept for the P4VPAM6Ts copolymer (figure 3-5), is based on the association properties of POE chains in the copolymer characterized by a low critical solution temperature (LCST) [19] . The concept of associative thermos, or thermostimulation of copolymers has been described in the literature [17, 20], and can be described as highly water-soluble, due to the side chain of the P4VPAM6Ts copolymer. Indeed, PEO forms blocks that exhibit LCST and thermos associative behavior with each other [19], and can undergo reversible microphase segregation with increasing temperature, which explains the reduced viscosity.

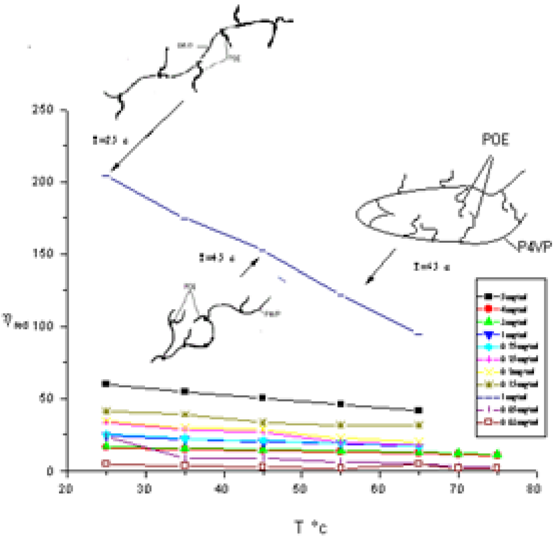


Figure 5: Reduced viscosity of the P4VPAM6Ts copolymer as a function of temperature at different concentrations (CC=0.03, 0.05, 0.1, 0.15, 0.20, 0.25, 0.75, 1, 2, 3, 4, 5mg/ml) for a degree of neutralization α=1.

For polymer concentrations higher than C*, the transition causes a change in solution viscosity due to associations between chains of the same macromolecule. Viscosity is very slightly influenced by increasing temperature. A slight drop is observed with temperature, due to internal associations, showing that intermolecular associations are not favored. Reduced viscosities comparison of P4VPAM6Ts with each polymer P4VP or PEO alone. There is no temperature effect on the reduced viscosity of the P4VP polymer. It shows the same curve for all temperature values. The PEO shows linear variation in its very weak reduced viscosity. All these observations lead to deduce that the reduced viscosity variation is directly linked to the P4VPAM6Ts copolymer structure.

CONCLUSION

This study has identified the *critical aggregation concentration (C)*, a parameter that has not been experimentally established in previous literature. The findings confirm the presence of thermo-associative interactions among PEO chains. Additionally, evidence suggests that PEO molecules can organize into hydrophobic domains, formed by the clustering of chain segments. Furthermore, the results indicate that hydrophobic associations between PEO groups counteract the electrostatic repulsions arising from tosylate ions (TsO^-) and pyridinium groups (N^+). The behavior of associative polyelectrolyte solutions appears to be significantly impacted by variations in ionic strength. Further investigation into this aspect is planned as part of the ongoing research. Additionally, this study has demonstrated the influence of the neutralization degree (α) on the system.

The P4VPAM6Ts copolymer exhibits a strong tendency toward inter-polymer associations, which can result in a marked increase in solution viscosity as polymer concentration rises. This phenomenon has not been cited in the literature**.**

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REFRENCES

[1] Jordan D.O. and Col., J Polymer Sci. 1956, 21, 473.
[2] Boyes A. G. and Col., J.Polymer Sci. 1956, 22, 463.(
[3] Berkowitz J.B. and Col., J.PolymerSci. 1958, 21, 69.

[4] Aubry T., M. Moan and B. Largenton, Rheology, Quebec City,1996, 492-3.
[5] O. Braun, J. Selb, F. Candau, Polymer, Volume 42, Issue 21, 2001, Pages 8499-8510.
[6] a- D. Hourdet, F. L'alloret, R. Audebert, Polymer 1997, 38, 2535-2547.
b- F. L'alloret, D. Hourdet, R. Audebert, Colloid Polym. Sci. 1995,273, 1163-1173.
[7] a- K. Benmansour, A. Mansri and J. François, Polymer International 2003, 52, 1403-1422.
b- K. Benmansour, K. Medjahed, L. Tennouga, A. Mansri, Eur.Polym. J. 2003, 39, 1443-1449.
[8] A. Mansri, L. Tennouga, J. Desbrières, Polymer Bulletin, 2008, 61, 771–777

[9] Bock J., Valint Jr P.L., Pace S.J., Siano, D.B., Schulz D.N., Turner S.R., G. A. Stahl, D. N. Schulz, Plenum Press 1988, Chap 9, 147, New York.
[10] McCormick C.L., Nonaka T., Johnson C.B., 1988, Polymer, 29(4), 731-739.
[11] Iliopoulos I., Wang T.K., Audebert R.; Langmuir 1991, 7(4), 617-619.
[12] Jenkins R.D., DeLong, L. Mark, Bassett, David R., Advances in Chemistry. American Chemical Society, 1996, 23, 425-447.
[13] Biggs S., Selb J., Candau F., Langmuir1992, 8(3), 838-847.
[14] Aubry T., Moan M., J. Rheol. 1994, 38(6), 1681-1692.
[15] Persson K., Bales B.L., J. Chem. Soc. Faraday 1995 91(17), 2863-2870.
[16] B. Bouras, T. Hocine, K. I. Benabadji, L. Tennouga and A. Mansri, Rev. Roum. Chim, 2020, 65(9), 839-846
[17] a- Lombardo, D.; Munaò, G.; Calandra, P.; Pasqua, L.; Caccamo, M. T. Evidence of Pre-Micellar Aggregates in Aqueous Solution of Amphiphilic PDMS–PEO Block Copolymer. *Phys. Chem. Chem. Phys.* 2019, *21* (22), 11983–11991.

b- Pike, S. J.; Bond, A. D.; Hunter, C. A. Solvatomorphism of Reichardt's Dye. *CrystEngComm* 2018, *20* (21), 2912–2915.

[18] Zubanova EM, Rubtsov DA, Golubeva EN, Relationship between the structure of nitroxyl radicals and their localization in solutions of heat-resistant polymers, Himalayan Physics Journal, Vol 42, No 7, 2023
[19] Karga, M.-E.; Kargaki, M.-E.; Iatrou, H.; Tsitsilianis, C. pH-Responsive, Thermo-Resistant Poly(Acrylic Acid)-g-Poly (boc-L-Lysine) Hydrogel with Shear-Induced Injectability. Gels 2022, 8, 817.
[20] Little, Hunter, Patel, Sanjay, Suh, David, Duhamel, Jean, Accurate Determination of the Average Rate Constant of Pyrene Excimer Formation for Pyrene-Labeled Macromolecules from the Analysis of Individual Fluorescence Decays with Sums of Exponentials, The Journal of Physical Chemistry, American Chemical Society, 1520-6106, 2024.