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Posted Date: 4 August 2025

doi: 10.20944/preprints202508.0138.v1

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Micellization Studies of Block Copolymers of Poly(N-vinyl Pyrrolidone) and Poly(Vinyl Esters) Bearing n-alkyl Side-Groups in Tetrahydrofuran

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Abstract

The association behavior of amphiphilic block copolymers of N-vinyl pyrrolidone, NVP and various vinyl esters, VEs, PNVP-*b*-PVEs, namely vinyl butyrate, VBu, vinyl decanoate, VDc, and vinyl stearate, VSt, was studied in tetrahydrofuran, THF, which is a selective solvent for the PVEs blocks. Static, SLS, and dynamic light scattering, DLS, techniques were employed as the tools to investigate the micellar assemblies and acquire information regarding the degree of association, the hydrodynamic radii and the shape of the aggregates. In addition, CONTIN analysis provided insights concerning the association equilibria in THF solutions. The effect of the nature of the PVE corona forming block on the association process was investigated. Finally, the experimental results were compared with those obtained in previous studies describing the micellization properties of block copolymers of PNVP with polymethacrylates in the same selective solvent.

Keywords: poly(N-vinyl pyrrolidone) (NVP); poly(vinyl esters) (VEs); block copolymers; micelles; light scattering

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1. Introduction

The most fascinating class of polymeric materials is without any doubt the family of block copolymers [1,2]. This is attributed to the following main reasons: a) Block copolymers are composed of two or more different polymer chains that are covalently bonded together. This unique structure allows them to exhibit a wide range of properties, depending on the specific polymers used and their arrangement [3,4]. b) There are several architectures that can be synthesized, such as diblock copolymers, triblock copolymers, triblock terpolymers, multiblock copolymers, star-block copolymers etc. This architectural diversity further expands the applicability of these materials and offers the possibility to manipulate the behavior in solution and in the solid state by changes in the macromolecular architecture [5–10]. c) There are numerous combinations of different blocks that can be combined in one structure, such as hydrophilic, hydrophobic, amorphous, crystalline, flexible, rigid materials etc. [11,12] d) There is a huge variety of polymerization techniques and their combinations that can be adopted for the synthesis of well-defined copolymers, with narrow molecular weight distributions and low chemical heterogeneity including anionic, cationic, controlled radical, ring opening, ring opening metathesis and coordination polymerization [13–29]. e) Block copolymers have the unique ability to promote self-assembly. In other words, they are organized either in bulk or in selective solvents [30,31]. In bulk, the self-assembly process leads to specific microstructures, such as cylinders, spheres, lamellae, cubic phases etc. [32,33], whereas in selective solvents to the formation of micelles [34–38]. The micelles usually adopt the core-corona structure [39–41]. The core is formed from the insoluble block, whereas the corona is consisted by the surrounding protective soluble block.

Amphiphilic block copolymers is a special class of copolymers consisting of one water soluble block and another one water insoluble block [42–49]. The characteristic of these structures is that they offer the possibility to self-assemble both in aqueous solutions and in organic solvents. For this reason, countless applications have appeared in the literature based on these materials, such as in the fields of drug delivery and the biomedical sector (nanocarriers for gene therapy, stimuli-responsive drug carriers, biodegradable hydrogels etc.), coatings and surface modification (antifouling coatings, self-healing applications etc.), nanotechnology and electronics (nanoreactors, nanocatalysis, organic electronics, flexible displays etc.), cosmetics and personal care products (surfactants, emulsifiers, encapsulation of active ingredients etc.), water purification systems etc. [50–60]

In previous works, the synthesis of a series of amphiphilic statistical and block copolymers has been reported based on poly(N-vinyl pyrrolidone), PNVP, as the water-soluble block and various polymethacrylates and poly(vinyl ethers) as the water insoluble blocks and their micellization behavior was examined both in organic solvents and in aqueous solutions [10,61–69]. In the frame of this project, block copolymers consisting of PNVP and poly(vinyl esters), PVEs, with alkyl side groups were synthesized and thoroughly characterized [70]. More specifically, the synthesis of block copolymers PNVP-*b*-PVEs, having poly(vinyl butyrate), PVBu, poly(vinyl decanoate), PVDc and poly(vinyl stearate), PVSt blocks was reported employing Reversible Addition Fragmentation Chain Transfer, RAFT, approaches.

Previous efforts have been documented for the synthesis of statistical and block copolymers of various PVEs. Most of them were based on poly(vinyl acetate), PVAc [71–73]. However, other VEs monomers have been employed as well, including vinyl pivalate, vinyl benzoate and vinyl octanoate [74–78]. The most frequently mentioned system in the literature is that of PNVP-b-PVAc block copolymers. The main target of these works was the study of the self-assembly behavior of the copolymers in aqueous solutions and their ability to act as drug delivery systems. On the other hand, very limited work has been reported with the synthesis of block copolymers of NVP with other VEs and in addition no effort was given to study the micellization behavior of these block copolymers in organic solvents that are selective for the PVEs blocks.

In order to fill this gap in the literature, the self-assembly behavior of PNVP-*b*-PVBu, PNVP-*b*-PVDc and PNVP-*b*-PVSt was studied in tetrahydrofuran, THF, which is a selective solvent for the PVEs blocks and a non-solvent for the PNVP blocks [79].

2. Materials and Methods

Refractive index increments, dn/dc at 25 °C were determined using a Chromatix KMX-16 refractometer (Milton Roy, LDC Division, Riviera Beach, FL, USA) operating at 633 nm and calibrated with aqueous sodium chloride solutions.

Dynamic light scattering, DLS, experiments were carried out on a BI-200SM goniometer system (Brookhaven Instruments, Holtsville, NY, USA) equipped with a 40 mW laser at a wavelength of 640 nm. Correlation functions were analyzed using both the cumulant method and the CONTIN software package (Brookhaven Instruments, Holtsville, NY, USA) [80]. Data were collected at scattering angles of 45°, 90°, and 135° at a temperature of 25 °C.

In all micellar systems studied, the angular dependence of the ratio Γ/q^2—where Γ is the decay rate of the correlation function and q is the scattering vector—was negligible. Therefore, apparent translational diffusion coefficients at infinite dilution, $D_{o,app}$, were extracted using the linear concentration dependence described by Equation (1):

$$D_{app}=D_{0,\,app}(1+kDc) \quad (1)$$

The corresponding apparent hydrodynamic radii, R_h, were calculated using the Stokes–Einstein relation (Equation 2):

$$R_h=kT/6\pi\eta_s D_0,\ app \quad (2)$$

doi:10.20944/preprints202508.0138.v1

where k is Boltzmann's constant, T is the absolute temperature, and η_s denotes the viscosity of the solvent.

Static light scattering, SLS, experiments were conducted on the same BI-200SM system used for DLS, and data were processed using the Zimm plot module of the Particle Explorer software (v1.2.0.6868, Brookhaven Instruments, Holtsville, NY, USA). The measurements were conducted at 25 °C at the following scattering angles of 45°, 60°, 75°, 90°, 105°, 120°, and 135°.

For all the measurements stock solutions were prepared by direct dissolution of the samples in THF, which has been previously dried over sodium and distilled just prior its use. The stock solutions were allowed to stand overnight at room temperature and then were gently heated in an oven at 40°C for at least 3 hours in order to facilitate the dissolution of the polymers and to obtain equilibrium micellar structures. The stock solutions were further diluted with dry THF to obtain solutions with lower concentrations. All the solutions were filtered using 0.22 μm pore size hydrophobic PTFE filters (Millex-LCR from Millipore) and directly introduced into the scattering cell prior the measurements.

3. Results and Discussion

3.1. Synthesis of the Block Copolymers of NVP and VEs

The synthesis of the PNVP-b-PVEs was described in detail in a previous publication [70]. Very briefly, NVP was polymerized first using O-ethyl S-(phthalimidylmethyl) xanthate as the CTA. The produced polymer was isolated, purified, characterized and further employed as macro-CTA for the subsequent polymerization of the respective VE monomer, leading to well-defined block copolymers. The molecular characteristics of these blocks are given in Table 1.

3.2. Self-Assembly Behavior of the PNVP-b-PVEs Block Copolymers in THF Solutions by Static Light Scattering

The SLS data from the PNVP-b-PVEs block copolymers in THF are given in Table 2, whereas characteristic Zimm plots from these measurements are provided in Figures 1-3.

Table 1. Molecular characteristics of the block copolymers.

	Macro CTA (PNVP) [a]		Block Copolymers [a]		NVP	Vinyl Ester
Sample	M_n 10^3 (Daltons)	Đ	M_n 10^3 (Daltons)	Đ	% mol[b]	% mol[b]
PNVP-b-PVBu #1	8.5	1.30	16.0	1.90	22	78
PNVP-b-PVBu #2	28.0	1.27	32.0	1.32	84	16
PNVP-b-PVBu #3	8.9	1.35	17.5	1.40	57	43
PNVP-b-PVBu #4	8.9	1.35	15.5	1.54	48	52
PNVP-b-PVDc #1	8.5	1.30	12.5	1.31	63	37
PNVP-b-PVDc #2	5.5	1.47	12.5	1.60	38	62
PNVP-b-PVDc #3	8.5	1.30	11.0	1.45	56	44
PNVP-b-PVDc #4	9.5	1.36	10.5	1.36	93	7
PNVP-b-PVSt #1	8.5	1.30	10.5	1.44	78	22
PNVP-b-PVSt #2	7.5	1.30	10.4	1.51	61	39
PNVP-b-PVSt #3	8.1	1.30	10.9	1.37	85	15
PNVP-b-PVSt #4	8.1	1.30	12.5	1.22	83	17

a. By SEC in $CHCl_3$. b. By ^1H-NMR.

Table 2. SLS data from the PNVP-b-PVEs block copolymers in THF.

Sample	M_w x10^{-4}	N_w	A_2 x 10^4 (cm^{3}mol/g^2)
PNVP-*b*-PVBu #1	15.9	9.94	1.40
PNVP-*b*-PVBu #2	5.69	1.78	0.69
PNVP-*b*-PVBu #3	3.62	2.07	3.86
PNVP-*b*-PVBu #4	3.22	2.08	4.39
PNVP-*b*-PVDc #1	10.5	8.40	3.50
PNVP-*b*-PVDc #2	6.35	5.08	2.07
PNVP-*b*-PVDc #3	3.35	3.05	2.50
PNVP-*b*-PVDc #4	3.59	3.42	5.16
PNVP-*b*-PVSt #1	3.82	3.64	1.48
PNVP-*b*-PVSt #2	7.13	6.86	2.78
PNVP-*b*-PVSt #3	4.44	4.07	1.30
PNVP-*b*-PVSt #4	18.6	14.88	1.90

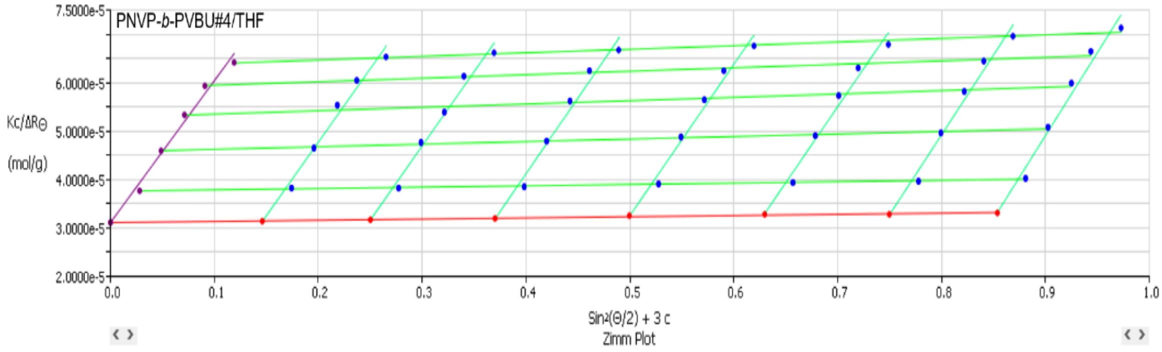

Figure 1. Zimm plot of the sample PNVP-b-PVBu #4 in THF.

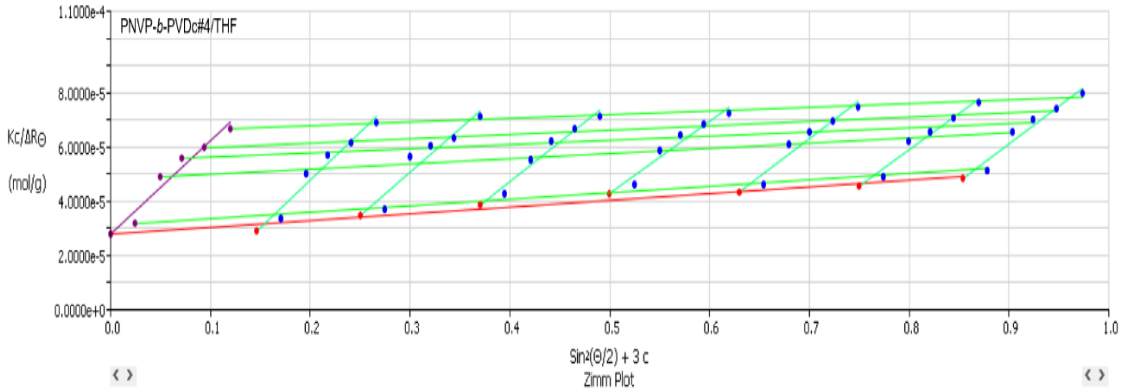

Figure 2. Zimm plot of the sample PNVP-b-PVDc #4 in THF.

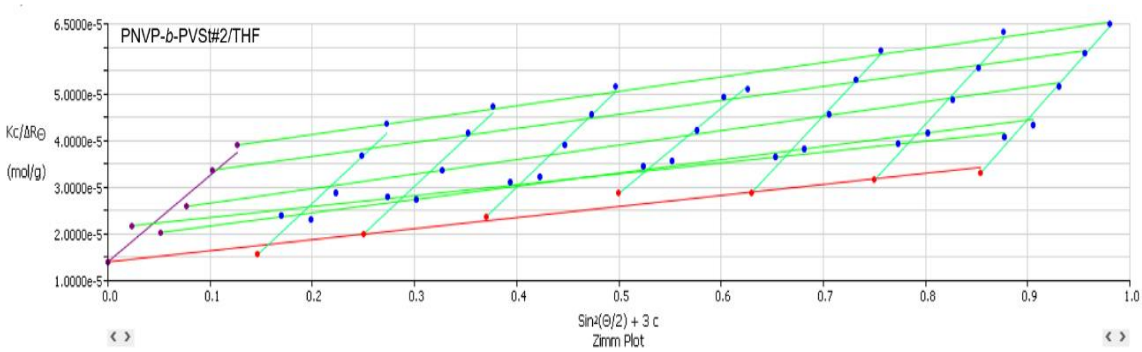

Figure 3. Zimm plot of the sample PNVP-b-PVSt #2 in THF.

In previous studies examining the self-assembly properties of statistical and block copolymers of PNVP with polymethacrylates it was concluded that THF is not able to promote the formation of large multimolecular micelles [61,68]. The degrees of association, N_w, were higher in the case of the block copolymers [62]. Nevertheless, even in this case the Nw values were not very high ($N_w<10$). These results look reasonable for the statistical copolymers, due to the specific distribution of the different monomer units along the polymer backbone. However, for the block copolymers having two distinct constituent chains connected with a covalent bond it would be expected that a more pronounced association behavior should be feasible. The main conclusion from the previous systems is that mainly unimolecular micelles are formed from the statistical copolymers, whereas from the block copolymers compact micelles of low aggregation number are formed in THF solutions.

This behavior was more or less confirmed in the present study concerning the self-assembly process of the PNVP-b-PVEs block copolymers in THF. The experimental data from the SLS measurements revealed low aggregation numbers in almost all cases. This can be attributed to the relatively low molecular weights of the samples. However, the main reason is correlated with the low ability of THF to promote the formation of large aggregates. Slightly higher N_w values were measured for the PNV-b-PVSt copolymers, indicating that the long alkyl side chain of the corona forming block, PVSt, through their hydrophobic interactions further stabilize the corona of the supramolecular structures or even facilitate intermicellar interactions leading to more complex patterns of association.

It has to be mentioned that the copolymers with the highest PNVP content have slightly lower N_w values, meaning that compact star-like micelles prevail in THF solutions. In addition, the low second virial coefficient values, A_2, from SLS measurements in THF solutions verify the formation of unimolecular or low aggregation number micelles.

3.3. Self-Assembly Behavior of the PNVP-b-PVEs Block Copolymers in THF Solutions by Dynamic Light Scattering

The conclusions derived from the SLS measurements were further confirmed and elucidated by the DLS results. CONTIN analysis is able to offer distribution analysis of the various populations that may be present in the selective solvent. Therefore, DLS data provide a deeper insight to the micellization process. The data are included in Table 3, whereas characteristic DLS plots from the different families of copolymers are displayed in Figures 4-6.

Table 3. DLS results of the block copolymers in THF.

Sample	Do (cm²/s)	K_d	R_{ho} A (nm)	R_{ho} B (nm)
PNVP-*b*-PVBu #1	11.2405	2.04	4.22	48.45
PNVP-*b*-PVBu #2	9.19953	-2.98	5.16	96.31
PNVP-*b*-PVBu #3	9.9667	8.58	4.76	170.06
PNVP-*b*-PVBu #4	10.4839	4.63	4.53	32.97

PNVP-*b*-PVDc #1	15.1746	-1.11	3.13	15.58
PNVP-*b*-PVDc #2	14.2491	0.96	3.33	35.82
PNVP-*b*-PVDc #3	11.6172	5.81	4.08	76.10
PNVP-*b*-PVDc #4	14.0547	0.29	3.38	85.11
PNVP-*b*-PVSt #1	12.2076	3.09	3.89	71.94
PNVP-*b*-PVSt #2	13.2195	1.37	3.59	81.37
PNVP-*b*-PVSt #3	14.3697	0.32	3.30	84.08
PNVP-*b*-PVSt #4	13.8421	1.40	3.43	94.93

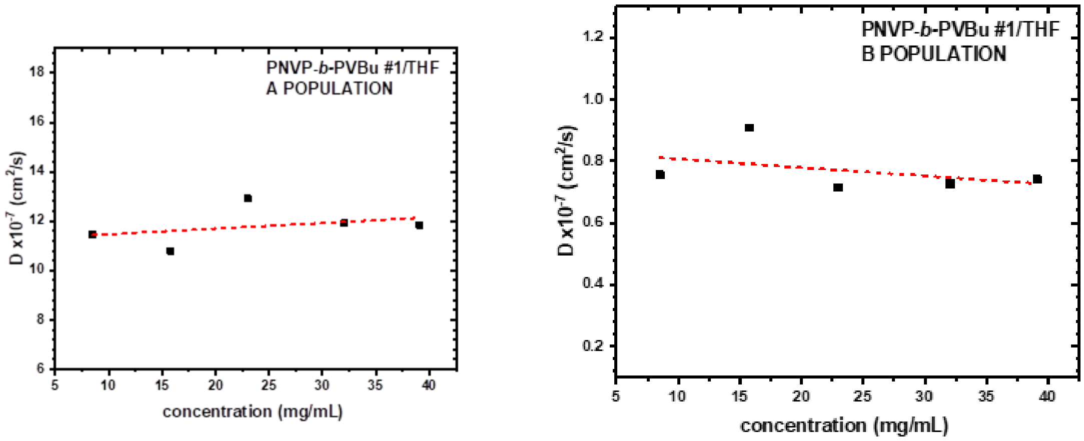

Figure 4. D vs c plots of the PNVP-b-PVBu #1 in THF.

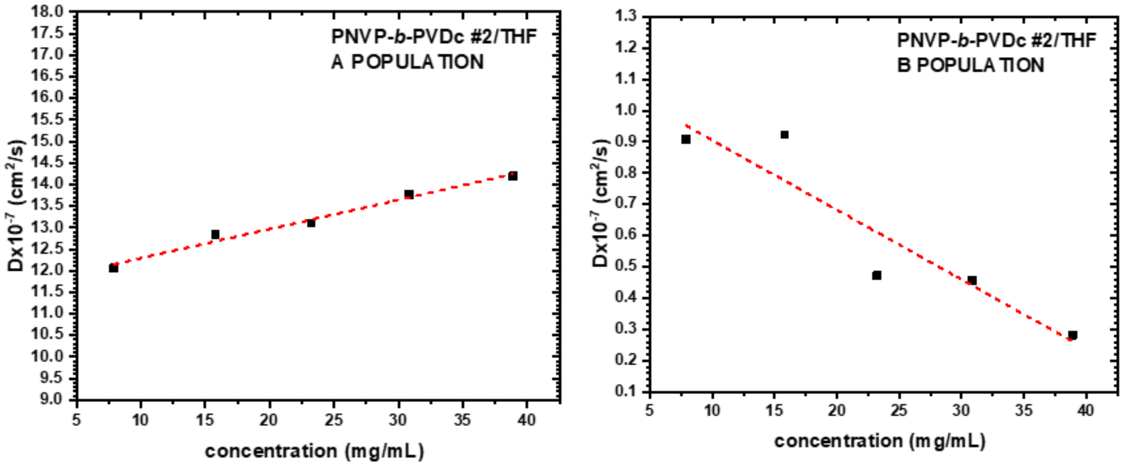

Figure 5. D vs c plots of the PNVP-b-PVDc #2 in THF.

As expected, the DLS measurements confirm and further fortify the corresponding SLS data. In the case of the PNVP-b-PVBu CONTIN analysis revealed that two different populations exist in the THF solutions. Characteristic CONTIN plots for the sample PNVP-b-PVBu #3 are given in Figure 7. Judging from their relative size it can be concluded that there is equilibrium between unimilecular and typical core-shell multimolecular micelles. The unimolecular micelles dominate in the selective solvent, since the high R_h value population range between 25 and 50% in all concentrations and for all samples. Taking into account that larger particles provide higher scattering intensity values than the small ones it can be derived that the contribution of the multimolecular micelles is much less than 20% in the solution. This result is in agreement with the low degrees of association measured by SLS measurements.

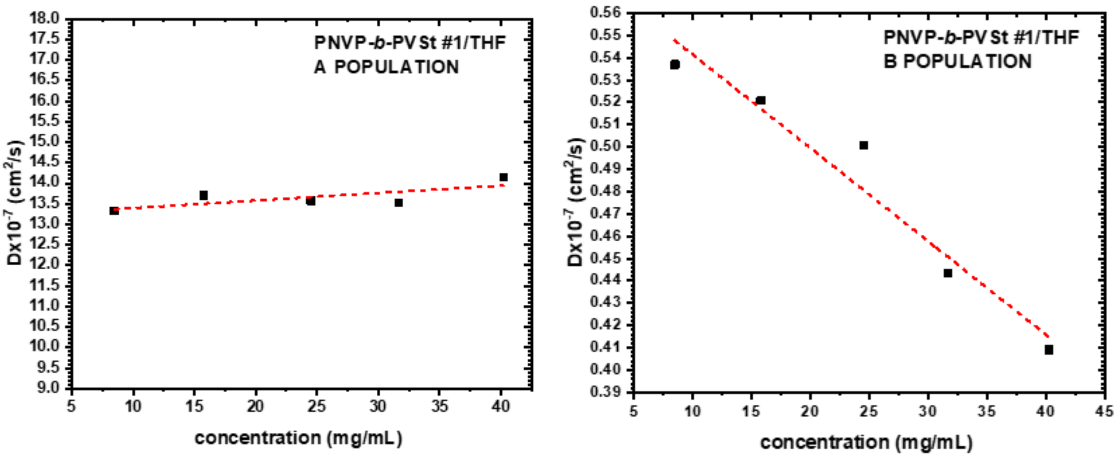

Figure 6. D vs c plots of the PNVP-b-PVSt #1 in THF.

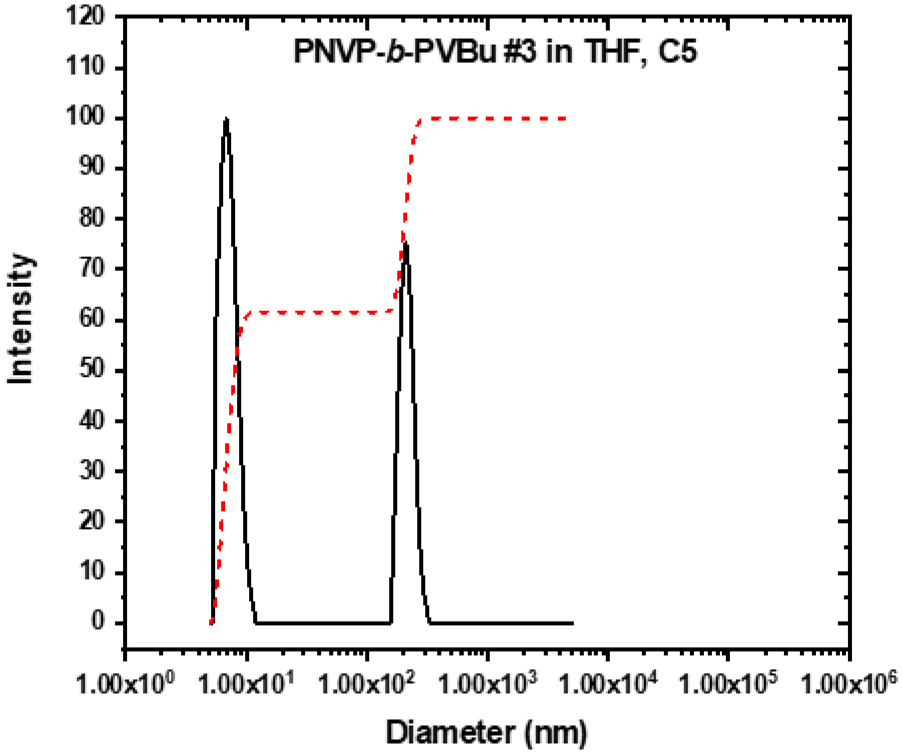

Figure 7. CONTIN plots for the sample PNVP-b-PVBu #3 (c=3.953x10^{-2} g/ml).

The k_D values in THF were low, as was expected from the low A_2 values from the SLS data. This result is reasonable, due to the existed relationship between k_D and A_2, described by the following equation:

$$k_D=2A_2M+k_f–u \qquad (3)$$

In this equation M is the molecular weight, k_f the coefficient of the concentration dependence of the friction coefficient and u the partial specific volume of the polymer.

In addition to these observations, no angular dependence was obtained from the DLS measurements confirming the formation of spherical structures. These structures were relatively polydisperse, judging from the values of the polydispersity factor μ_2/Γ^2, μ_2 being the second moment of the cumulant analysis and Γ the decay rate of the correlation function. These values were higher than 0.1 for all samples.

The DLS data for the PNVP-b-PVDc block copolymers were comparable to those previously presented for the PNVP-b-PVBu samples. CONTIN plots verified the presence of equilibrium between unimolecular and multimolecular micelles. A characteristic example is given in Figure 8. The population of the core-shell micelles is in the same order as in the previous case (ranging betweem 20 to 50%), however the R_h values of these structures are relatively lower compared to the multomilecular micelles coming from the PNVP-b-PVBu copolymers. This result indicates that the micelles having the corona from PVDc chains are more compact, due to the stronger hydrophobic interactions of the side alkyl groups of the PVDc chains. Otherwise, shperical, relatively polydisperse staructures were obtained in this case as well.

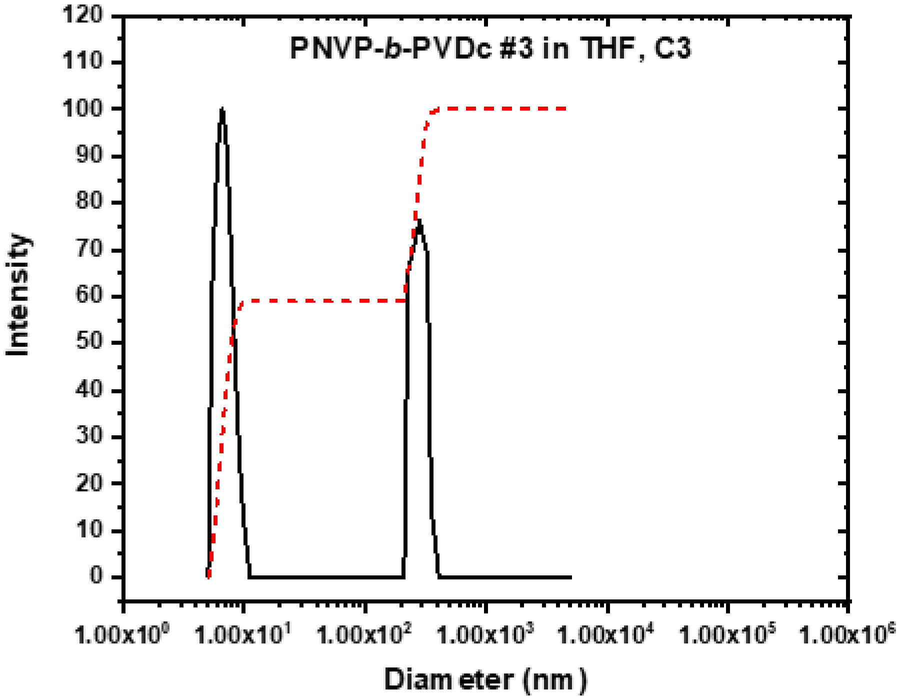

Figure 8. CONTIN plots for the sample PNVP-b-PVDc #3 (c=2.436x10^{-2} g/ml).

The situation was slightly differentiated in the case of the PNVP-b-PVSt block copolymers. From the SLS data it was concluded that the degrees of association were relatively higher compared to the other two families of copolymers. The DLS measurements and especially the CONTIN analysis showed that the equilibrium is shifted in this case towards the micellar structures. Their population is typically more than 50% and up to 70% for specific copolymers and at higher concentrations. Of course, the real population, as explained earlier is much lower, nevertheless much higher than for the other two types of block copolymers. The ability of stronger interactions between the PVSt chains, due to side chain crystallization, is responsible for this observation. Characteristic CONTIN plots are given in Figure 9. The second population is not only more pronounced in the overall content in the solution but has considerably higher R_h values. This is attributed to the high VSt content and the stronger hydrophobic interactions between the poly(vinyl ester) chains, which stabilizes the multimolecular structures. Very low or even negative k_d values were measured in all cases in agreement with the corresponding low A_2 values from the SLS measurements and the more extended association phenomena reported for this copolymerization system.

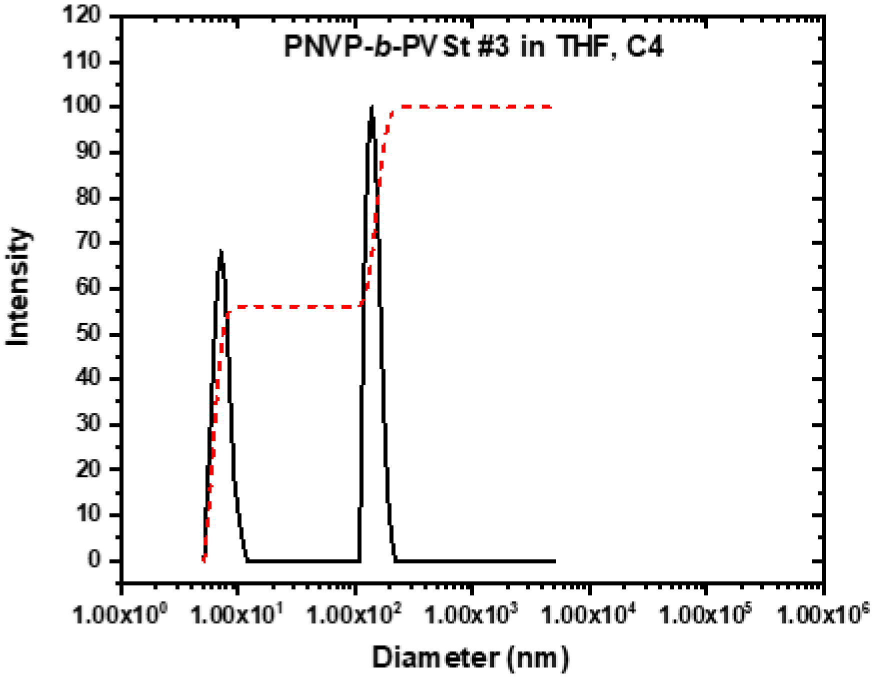

Figure 9. CONTIN plots for the sample PNVP-b-PVSt #3 (c=3.184x10^{-2} g/ml).

Comparison of the self-assembly behaviour with other statistical and block copolymers of PNVP with polymethacrylates in the same selective solvent THF revealed similarities and differences. The degrees of associations are higher than those of the statistical copolymers where almost exclusively unimolecular micelles dominate. However, compared to the respective block copolymers the association behaviour is more pronounced, especially in the case of the PNVP-b-PVSt copolymers, where a higher tendency for the formation of multimolecular micelles was obtained. The polymethacrylates, as solvophilic blocks provide small and compact micelles, as srevealed by CONTIN analysis without having equilibrium with unimolecular micelles. Therefore, the nature of the solvophilic block dramatically affects the self-assembly process.

This work will be further expanded with the study of the micellar properties of these block copolymers in aqueous solutions.

4. Conclusions

The self-assembly properties of amphiphilic block copolymers bearing hydrophilic poly(N-vinyl pyrrolidone), PNVP, block and various hydrophobic poly(vinyl esters), PVEs, blocks PNVP-*b*-PVEs, including poly(vinyl butyrate), PVBu, poly(vinyl decanoate), PVDc, and poly(vinyl stearate), PVSt, were explored in tetrahydrofuran, THF, which is a selective solvent for the PVEs blocks. The studies were based on static, SLS, and dynamic light scattering, DLS, measurements. Rather low degrees of aggregation were found by SLS data, indicating the presence of unimolecular or small micelles in THF. More details concerning the association equilibria in THF solutions were traced by the DLS techniques and the CONTIN analysis. In all cases equilibrium between unimolecular and compact and spherical multimolecular micelles is established in THF solutions. Upon increasing the size of the alkyl side group of the PVEs blocks the equilibrium is shifted towards the multimolecular structures. In all cases the supramolecular structures are relatively polydisperse. These experimental results are in agreement with previous studies reporting the micellization properties of block copolymers of PNVP with polymethacrylates in the same selective solvent. However, in the present system the trend towards the formation of multimolecular micelles is more pronounced, as revealed by CONTIN analysis.

Author Contributions: Conceptualization, Marinos Pitsikalis; Investigation, Nikoletta Roka, Vasilios Skiadas, Areti Kolovou and Theodosia Papazoglou; Methodology, Nikoletta Roka; Supervision, Marinos Pitsikalis; Validation, Marinos Pitsikalis; Visualization, Nikoletta Roka; Writing – original draft, Nikoletta Roka; Writing – review & editing, Marinos Pitsikalis.

Acknowledgments: This research is co-financed by Greece and the European Union (European Social Fund-ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning» in the context of the project “Strengthening Human Resources Research Potential via Doctorate Research” (MIS-5000432), implemented by the State Scholarships Foundation (IKY).

Conflicts of Interest: The authors declare no conflict of interest.

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