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Thermal Cloud Point Fractionation of Poly(vinyl alcohol-*co*-vinyl acetate): Partition of Nanogels in the Fractions

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Abstract: Poly(vinyl acetate-*co*-vinyl alcohol) (PVA), well-known as emulsion stabilizers, are obtained by partial hydrolysis of poly(vinyl acetate) (PVAc). Their thermal cloud point fractionation was performed in aqueous medium between 40 and 75 °C. This fractionation was carried out in order to get an insight in the partition of the initially present nanogels in the different fractions. All the fractions were characterized by size exclusion chromatography (SEC), NMR and dynamic light scattering (DLS) giving access to average degree of polymerization $\overline{DP_w}$, average degree of hydrolysis \overline{DH} , average sequence lengths of vinyl acetate n_0^{VAc} , volume fraction and average size diameter (D_v) of nanogels and “free PVA chains”. The polydispersity of the samples in $\overline{DP_w}$, \overline{DH} and n_0^{VAc} could be confirmed. The nanogels characterized by the highest values of volume fraction and D_v , in the range of 40–43 nm, were separated in the first coacervate fraction, whereas the most soluble fraction with low VAc content does not contain nanogels but only “free chains” of a D_v value of around 7–8 nm. The nanogels in the various fractions could further be disaggregated into “free chains” by complex formation with sodium dodecyl sulfate (SDS).

Keywords: thermal cloud point fractionation; poly(vinyl acetate-*co*-vinyl alcohol) (PVA); nanogels; sodium dodecyl sulfate; complex formation; particle size determination

1. Introduction

Poly(vinyl alcohol-*co*-vinyl acetate) copolymers, currently referred as PVA, that are obtained by partial hydrolysis of poly(vinyl acetate) PVAc, are well known as stabilizers for the emulsion and suspension polymerization processes of various vinyl monomers such as styrene, vinyl acetate or vinyl chloride [1,2]. The molecular characteristics of PVA's, mainly their polymerization degrees \overline{DP}_n , \overline{DP}_w and the average degree of hydrolysis \overline{DH} , in general in the range of 70 to 90 mol%, have a major influence on the monomer droplet size, the dispersion stability and on the properties of the final PVC resins [3,4].

An additional feature is that small colloidal particles, so-called nano- or microgels or "pseudo-micelles", which are generally present in PVA's may have an influence on their emulsifying and stabilizing efficiency. As shown by different authors [5-8] these PVA nano- or microgels are formed by intermolecular hydrophobe-hydrophobe interactions for PVA's having \overline{DH} values around 70–90 mol%. Furthermore, it should be mentioned that PVA's, used in industrial practice, are polydisperse in molar mass and in composition. For instance, Dawkins *et al.* [9] have clearly demonstrated by reversed phase liquid chromatography, that commercial PVA samples with an average \overline{DH} value of 72 mol% contain in fact PVA chains with \overline{DH} values ranging from 65 to 85 mol%. Zilberman *et al.* [10] came to a similar conclusion by cloud point fractionation, e.g., by temperature induced phase separation, of an aqueous PVA solution ($\overline{DH} = 72.5$ mol%). According to these authors it turned out that the average sequence distribution of vinyl acetate (VAc) and vinyl alcohol (VOH) monomer units, usually designated by "blockiness", has a major influence on the thermal phase separation and its compatibility with other water-soluble polymers. A typical example is that of hydroxypropyl methylcellulose, which is used in combination with PVA's in emulsifier formulations.

Another aspect of the PVA nanogels is their possibility to be disaggregated by complex formation with anionic surfactants; such as sodium dodecyl sulfate (SDS), as shown by Lewis and Robinson [6], Aladjoff *et al.* [11] and by Meehan *et al.* [12].

The aim of the present study was to take advantage of the cloud point fractionation technique, a process which does not need any additional solvent or precipitant, in order to check the "blockiness" index and the partition of the nanogels, especially their size and their relative volume fraction, in a fractioned PVA. In order to confirm the presence of nanogels in the different PVA fractions, this study will be completed by checking the influence of PVA/SDS complex formation on the disaggregation of these nanogels. These characteristics could be of interest for the optimization of the emulsifying efficiency of PVA's, by adjusting the saponification conditions of PVAc precursors.

2. Experimental Section

2.1. Materials

The PVAs examined in this study were supplied by Nippon Gohsei and Synthomer under the trade names KP08 and B72 respectively. These samples, hereafter used without further purification, are identified by their average \overline{DH} and \overline{DP}_w , as for instance PVA-73-650 and PVA-73-685 for sample B72 and KP08 respectively. The main characteristics of the PVA's, determined by ^1H NMR and SEC, are summarized in Table 1.

Table 1. Molecular characteristics of the poly(vinyl acetate-co-vinyl alcohol) (PVA) samples.

PVA's	DH (mol%)	\overline{M}_w (g mol ⁻¹)	\overline{M}_n (g mol ⁻¹)	\overline{DP}_w	PI	$\overline{n}_0^{\text{VAc}}$	CP* (°C)
PVA-73-650	73.2	36,400	15,100	650 ± 20	2.41 ± 0.05	3.6 ± 0.1	28.5 ± 0.5
PVA-73-685	72.5	37,700	18,400	685 ± 35	2.05 ± 0.03	4.3 ± 0.1	27.5 ± 0.5

* Cloud Point.

The average hydrolysis degree, \overline{DH} with a precision of ±0.5 mol%, was determined using ¹H NMR (Bruker AC-400F operating at 400 MHz) in dimethylsulfoxide (DMSO)-d₆ at 70 °C according to Van der Velden and Beulen [13]. These characteristics were confirmed by ¹³C NMR spectroscopy of the polymers solubilized in a 50/50 (v/v) D₂O and deuterated acetone mixture. This technique gives in addition access to the average sequence lengths of vinyl acetate $\overline{n}_0^{\text{VAc}}$ defined by Moritani and Fujiwara [14]. It may be noticed that sample PVA-73-685 has the highest VAc sequence length $\overline{n}_0^{\text{VAc}}$.

The SEC measurements were carried out with a Shimadzu LC-20AD liquid chromatograph equipped with two Varian PL gel 5 μm MIXED-C columns (column, injection and refractometer temperature: 30 °C; injection volume: 100 μL; solvent: tetrahydrofuran at 1 mL min⁻¹) and a refractive index detector (Shimadzu RID-10A). The PVA samples were at first reacylated as recommended by Bugada and Rudin [15] and the “universal calibration technique” with polystyrene standards was applied for the calculation of \overline{M}_n , \overline{M}_w and the polydispersity index $PI = \overline{M}_w / \overline{M}_n$.

Sodium dodecyl sulfate (SDS), obtained from Acros Organics with a purity of 99%, was used without any further purification.

2.2. Procedure for the Thermal Cloud Point Fractionation

The PVA solutions of 7.5 wt% were prepared by dissolving under agitation 7.50 g PVA powder in 92.50 g triple distilled and filtered (0.22 μm Millipore filter) water at room temperature for 24 hours. The obtained solutions were poured into a separating funnel and thermostated for 24 hours, the time required to reach an equilibrium situation corresponding to a constant fraction of phase separated coacervate at different fractionation temperatures. At the first fractionation temperature, 41 °C, two fractions were separated, a coacervate F₁ and a completely transparent supernatant layer F₁'. The coacervate F₁ was removed from the funnel and the remaining supernatant layer F₁' was used for a second fractionation step at 50 °C to give fractions F₂ and F₂'. The last two fractions, F₃ and F₄, were separated from the supernatant fraction F₂' at 75 °C.

Each isolated fraction was characterized by NMR, SEC and DLS.

2.3. Sample Preparation

The PVA solutions of 1 wt%, for the DLS measurements, were prepared by diluting under agitation the required amounts of each separated fraction in triple distilled and filtered (0.22 μm Millipore filter) water at room temperature for 24 hours.

The SDS solutions were prepared by dilution of a 1 wt % “stock solution”. To avoid the hydrolysis of SDS, all surfactant solutions were used within 24 hours.

For the preparation of PVA/SDS solutions, each PVA fraction was directly diluted in the aqueous SDS solution at the required concentration under agitation for 24 hours at room temperature.

Before use, all solutions have been filtrated over 0.45 μm Chromafil Xtra MV-45/25 filter.

2.4. Dynamic Light Scattering

DLS measurements were carried out on a Malvern Nano-ZS6 Zetasizer equipped with a 4 mW He-Ne laser operating at a wavelength of 532 nm. The measurements were made at a scattering angle $\theta = 173^\circ$ at a fixed temperature of 20 $^\circ\text{C}$. Quartz cuvettes were used for all the experiments. Data (Dv and volume fraction) were acquired with the Malvern's Dispersion Technology Software version 4.20.

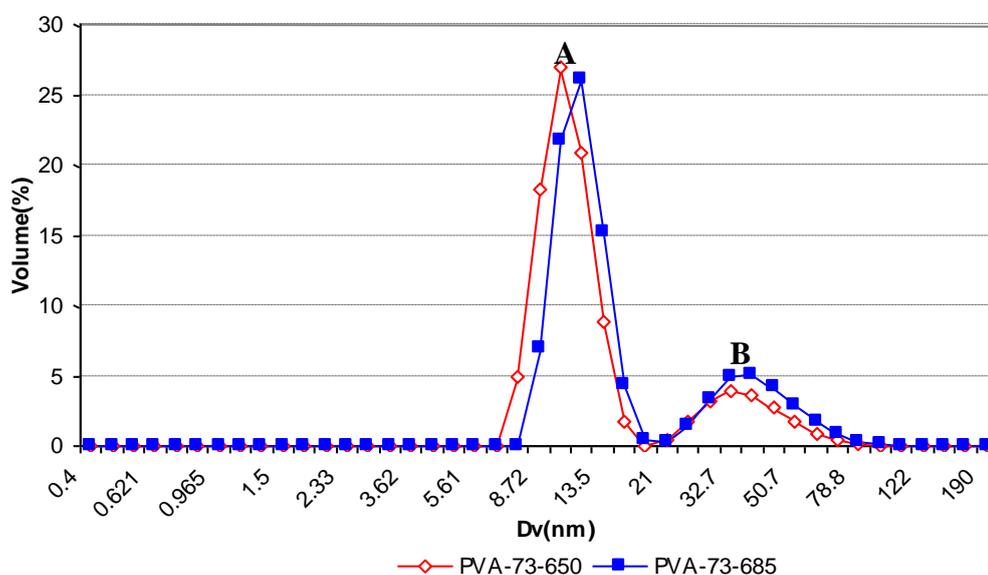
To determine the diameter of the particles, the data were collected in automatic mode, typically requiring a measurement duration of 70 seconds. The "data quality report" incorporated in the software indicated "good quality" for all the obtained data. For each experiment at a given temperature, the average of 5 consecutive measurements is indicated in the tables and figures.

3. Results and Discussion

These two PVA samples, PVA-73-650 and PVA-73-685, having very similar characteristics, such as \overline{DH} , \overline{DPw} but different n_0^{VAc} values, as shown in Table 1, were selected for our study in order to check that the "blockiness", e.g., the average VAc sequence length, could have an influence on the nanogel characteristics.

This aspect appears clearly in Figure 1, showing the particle size distribution of the initial PVA's at a concentration of 1 wt% in aqueous solution at 20 $^\circ\text{C}$.

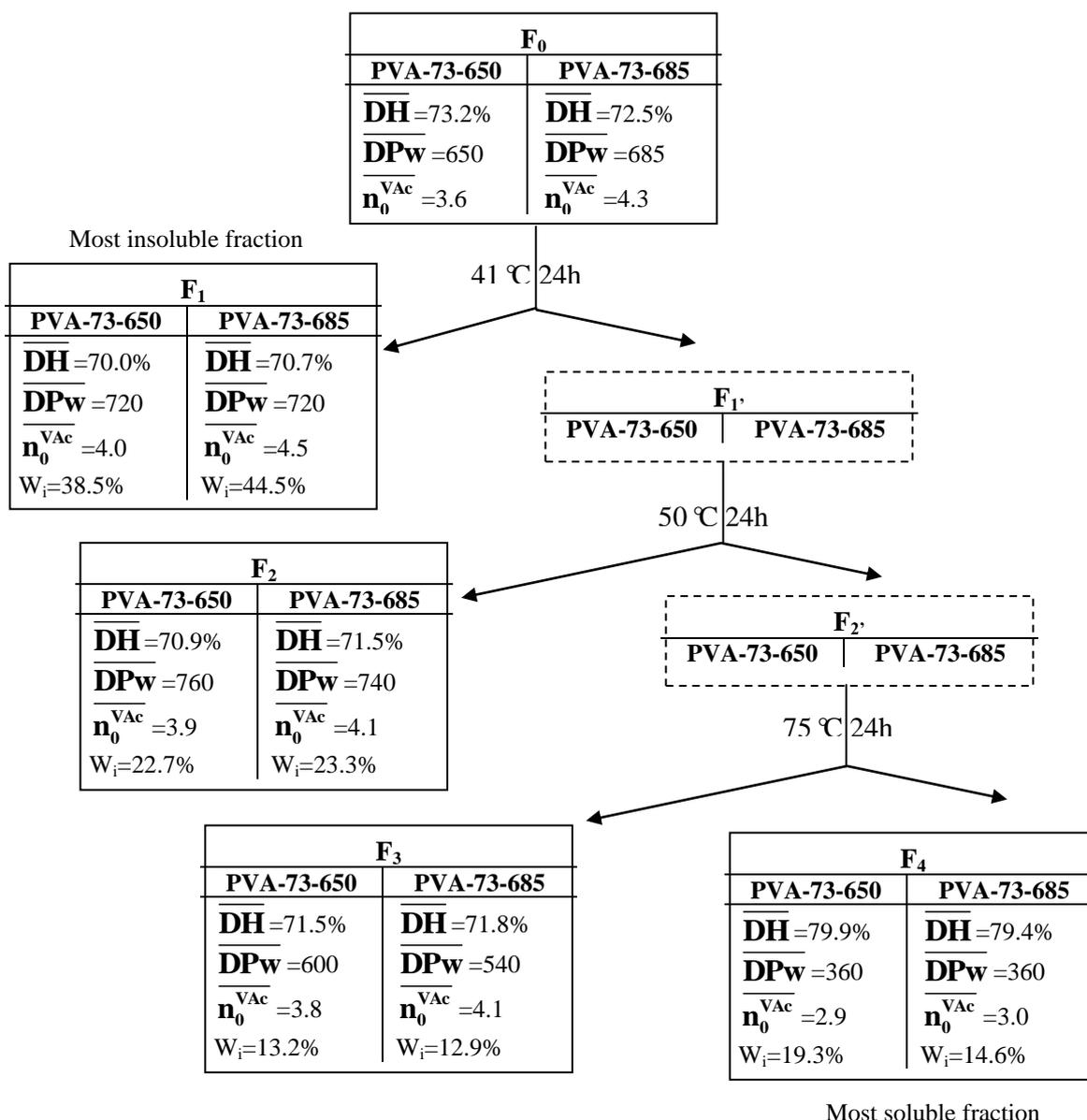
Figure 1. DLS-size distributions: Dv for the non-fractionated samples PVA-73-650 and PVA-73-685. A representing the "free chains" and B the nanogels peaks.



As previously shown, peak 1 and peak 2 correspond to “free PVA chains” and to nanogels respectively [8]. These so-called nanogels are formed by hydrophobic interactions between PVAc sequences as demonstrated by Lewis and Robinson [6] and by Aladjoff *et al.* [7].

The thermal cloud point fractionation process is schematically outlined in Figure 2:

Figure 2. Schematic representation of the different fractionation steps. Molecular characteristics of the phases in equilibrium for sample PVA-73-650 and PVA-73-685 with \overline{DH} -average degree of hydrolysis, \overline{DPw} -weight average degree of polymerization, n_0^{VAc} -average sequence length of vinyl acetate and W_i -weight %.



Three temperature steps above the cloud point are involved in this process. A first separation is carried out at 41 °C. After separation of this fraction F1, the temperature of the supernatant fraction F1' is increased to 50 °C. This operation leads to a coacervate F2 and a supernatant phase F2' which is further fractionated at 75 °C. The final fractions are F3 and F4 respectively.

The different fractions were characterized by NMR, SEC and by gravimetry. For a given PVA sample, PVA-73-650 and PVA-73-685 respectively, it can be noticed that:

- the \overline{DH} values of F_1 , F_2 and F_3 are lower than that of F_0 , the initial PVA sample; this is a direct evidence of a *fractionation in composition*; as expected, the VAc rich species, with a lower solubility, are predominant in the coacervate,
- the \overline{DH} values of F_4 , the most soluble fraction, are coming close to 80 mol%,
- the \overline{DPw} values of F_1 and F_2 are higher than that of F_0 , with afterwards a decrease for F_3 and F_4 ; this is indicative of a *fractionation in molar mass*,
- the average VAc sequence length $\overline{n_0^{VAc}}$ has a tendency to decrease from F_1 to F_4 ,
- F_4 corresponds not only to fractions with lowest VAc content, but also to that of lower \overline{DPw} and $\overline{n_0^{VAc}}$ respectively.

By taking into account the W_i values of the fraction, given as the weight % with respect to F_0 , it is of interest to notice that the mass balance of the complete fractions process are of 93.7 and 95.3, for PVA-73-650 and PVA-73-685 respectively. A similar observation could be made for \overline{DH} , \overline{DPw} and $\overline{n_0^{VAc}}$ balances.

In agreement with Zilberman *et al.* [10] and with Lerner and Alon [16] these results, obtained by thermal cloud point fractionation, are a direct evidence that the fractionation is influenced simultaneously by the polydispersity in composition, molar mass and sequence distribution of the VAc monomer units.

For a given PVA sample, the major differences in their characteristics, \overline{DH} , \overline{DPw} and $\overline{n_0^{VAc}}$, which can be noticed between F_1 , the most insoluble fraction, and F_4 , the most soluble one, has a direct influence on their cloud points. In fact for sample PVA-73-650 the cloud point is shifted from 26.5 °C for fraction F_1 to 70.5 °C for fraction F_4 . For sample PVA-73-685 the corresponding shift is from 26.5 °C to 70.5 °C. Furthermore, for the fractions F_1 it is worth noting the 6% increase of W_i for the sample PVA-73-685 with respect to PVA-73-650 with the $\overline{n_0^{VAc}}$ values of 4.5 and 4.0 respectively.

The next step consisted in the determination by DLS of the particle size distributions and the volume fractions of the nanogels and the “free chains”. An illustration of the bimodal size distribution of the non-fractionated sample PVA-73-650 (F_0) is given by Figure 3. This figure shows in addition the size distribution of the corresponding fractions F_1 and F_4 .

For F_1 it appears clearly, as compared to F_0 , a size shift from 11.4 to 13.0 nm for the “free chains”, which is in agreement with the \overline{DPw} increase from 650 to 720. A similar trend is observed and for the nanogels, their size increase from 38.0 to 42.8 nm, with corresponding volume fraction of 18.0 and 24.2%. For fraction F_4 an almost monomodal size distribution curve can be noticed with an average particle size $D_v = 8.1$ nm. This decrease in size can directly be correlated to the low \overline{DPw} of this fraction, e.g., 360 as compared to 720 for F_1 . If “free chains” are definitely predominant in fraction F_4 , a close inspection of the size distribution shows the presence of a small “tail” which might correspond to a minor residual amount of aggregates.

The detailed characteristics of the different fractions are given in Tables 2 and 3 for the sample PVA-73-650 and PVA-73-685 respectively.

Figure 3. DLS-size distributions: D_v for fractions F_0 , F_1 and F_4 of sample PVA-73-650 (1 wt% solution at 20 °C); F_0 being the non-fractionated sample.

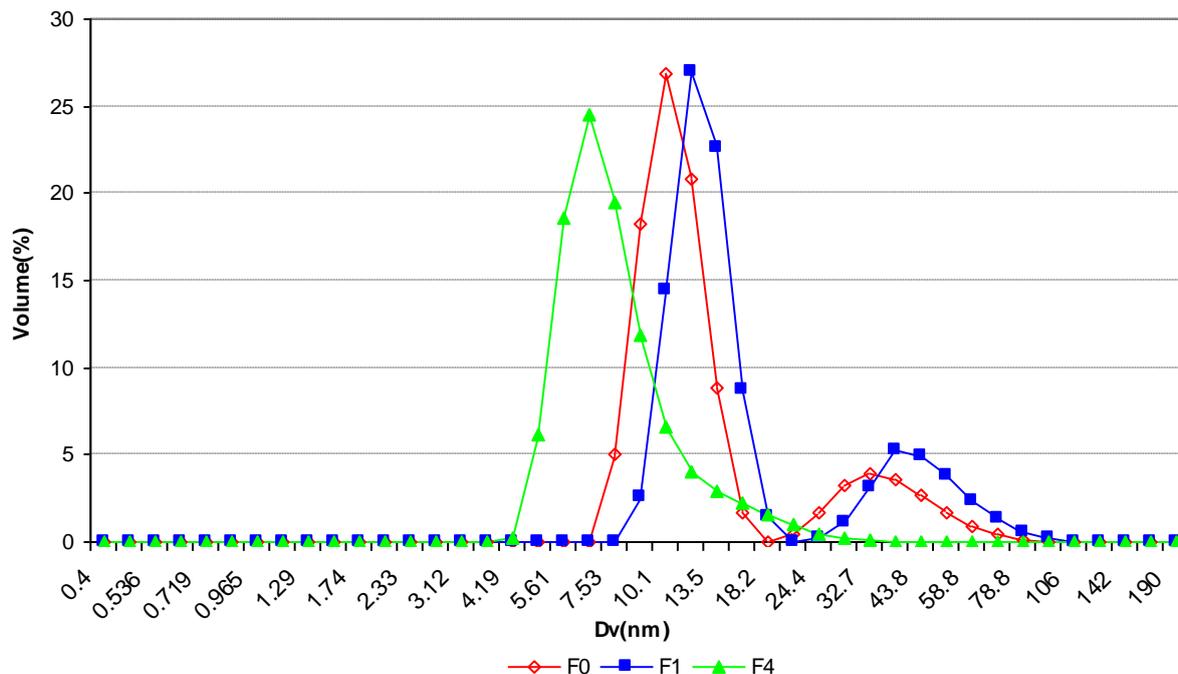


Table 2. Volume fraction and size average (D_v) of nanogels and “free chains” of different PVA-73-650 fractions at a concentration of a 1 wt%.

PVA-73-650	Nanogels		Free-chains	
	Volume fraction (%)	D_v (nm)	Volume fraction (%)	D_v (nm)
F_0	18.0	38.0	82.0	11.4
F_1^*	24.2	42.8	75.8	13.0
F_1^{**}	15.5	32.4	84.5	9.7
F_2^*	23.1	41.2	76.9	14.2
F_2^{**}	10.1	27.9	89.9	9.1
F_3^*	20.9	32.7	79.1	9.1
F_4^{**}	-	-	100	8.1

* coacervate phase. **supernatant phase.

Table 3. Volume fraction and size average (D_v) of nanogels and “free chains” of different PVA-73-685 fractions at a concentration of a 1 wt%.

PVA-73-685	Nanogels		Free-chains	
	Volume fraction (%)	D_v (nm)	Volume fraction (%)	D_v (nm)
F_0	22.9	39.8	77.1	14.2
F_1^*	29.5	40.7	70.5	11.6
F_1^{**}	15.8	36.1	84.2	12.3
F_2^*	26.7	39.2	73.3	12.1
F_2^{**}	20.2	22.1	79.8	7.5
F_3^*	27.0	32.3	73.0	10.7
F_4^{**}	-	-	100	9.0

* coacervate phase. **supernatant phase.

As a general observation for both PVA samples it can be noticed that for the nanogels the values of the volume fraction and Dv corresponding to a coacervate phase (F_1, F_2, F_3) are systematically higher than those present in the supernatant phase (F_1', F_2' and F_3'). This is a clear indication that the nanogels are preferentially located in the coacervate phase. Furthermore it appears that the volume fractions of nanogels in all coacervate phases are higher than the corresponding value of the starting PVA. Moreover, it is of interest to notice that for both PVA samples the size of nanogels present in the most insoluble fraction F_1 is increased with respect to those existing in the initial fraction F_0 .

On the opposite, the most soluble fraction F_4 contains only “free chains” with a monomodal size distribution (see Figure 3). The corresponding Dv values of 8–9 nm are typical of the hydrodynamic diameter of “free PVA chains” having a $\overline{DP_w}$ of 360 [8].

From these fractionations tests, it turns finally out that the coacervate fraction F_1 contains nanogels characterized by the highest size and volume fraction whereas in the fraction F_4 , the most soluble one, only “free chains” are present.

At this point, the proof has to be given that the nanogels initially present in F_0 , the starting PVA's, are in fact those distributed in the resulting fractions. In other words, the demonstration has to be provided that no additional nanogels might have been generated in the fractionation process operated at temperatures above the cloud point temperature. Moreover one has to take into account the fact that the characterization by DLS of the different fractions is carried out at 20 °C for PVA concentration of 1 wt%. In this respect, the thermo-reversibility of the PVA solutions at a concentration of 1 wt% could be assessed by different heating cycles at temperatures above the cloud point such as 41 °C and 50 °C, followed by subsequent cooling back to 20 °C. Within the experimental error limits no variations in size and volume fraction were observed with respect to the initial characteristics of the solution. Furthermore, it could be demonstrated that neither the volume fraction nor Dv of the PVA solutions are influenced by the dilution process [8].

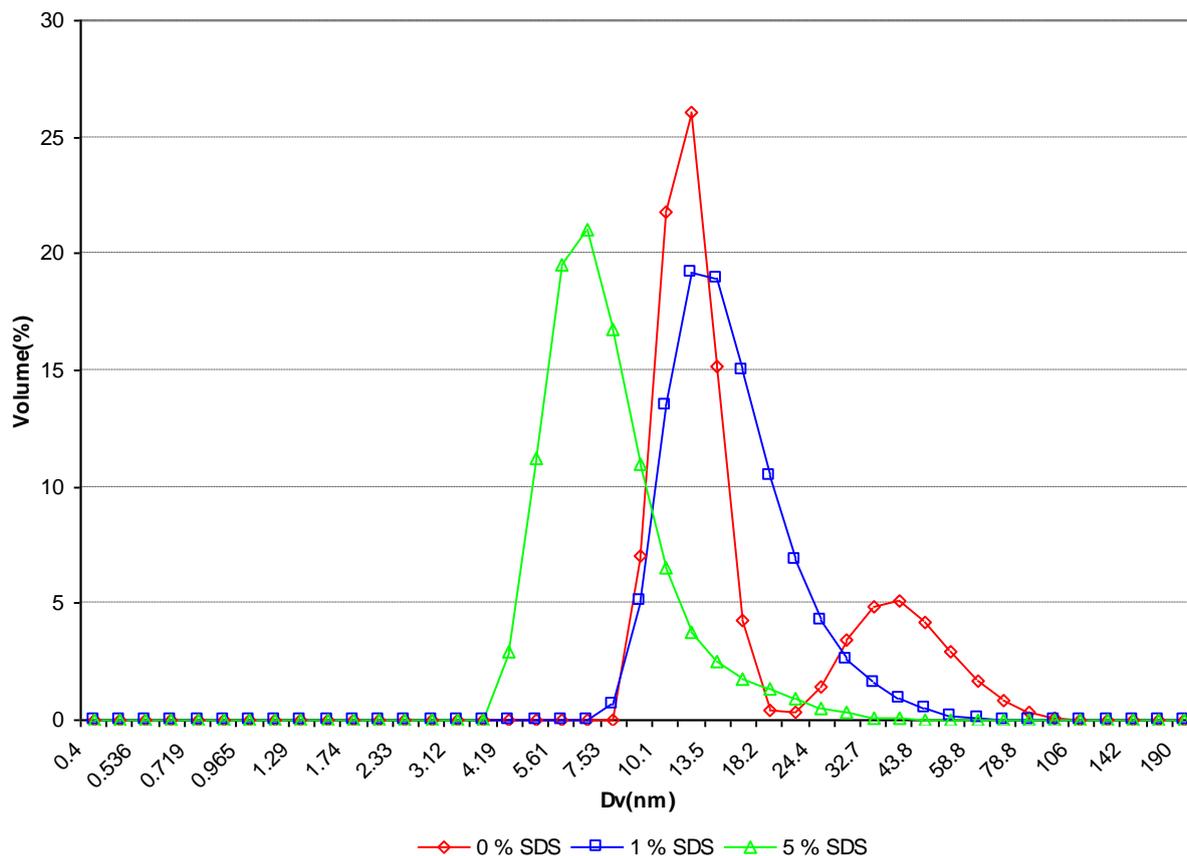
A further proof that no additional nanogels have been generated in the fractionation process can be given by the size balance of nanogels by taking into account the weight % W_i of the different PVA fractions. In a first approximation this balance is such as $\Sigma Dv = \Sigma W_i Dv_i / \Sigma W_i$. For PVA-73-650 this type of calculation leads to ΣDv of 40.5 nm, in fair agreement with the Dv of 39.6 nm corresponding to the non-fractionated PVA sample. A similar agreement was obtained for sample PVA-73-685 with ΣDv of 38.9 nm as compared with to initial Dv of 39.8 nm.

With the well-characterized PVA samples obtained by thermal cloud point fractionation process, it was of interest to study their behavior in presence of SDS. In fact, anionic surfactants, such as SDS, are known to form complexes with PVA, inducing the disaggregation of nanogels, as reported by different authors [6,8,11,12,17].

A typical example of the disaggregation effect of nanogels is displayed in Figure 4 for the fraction F_1 of sample PVA-73-685:

From this figure, showing the size distribution of the fraction F_1 of PVA-73-685 at two SDS concentrations, it can be noticed that by addition of SDS at a concentration of 1 wt% with respect to PVA, the peak attributed to nanogels has partially disappeared. The monomodal peak obtained at this SDS concentration shows a remaining “tail” attributed to a minor fraction of nanogels that are still present, however of lower size as the initial ones.

Figure 4. DLS-size distributions: Dv for fraction F₁ of sample PVA-73-685 (1 wt% solution at 20 °C) at different SDS concentrations indicated with respect to PVA.



On further addition of SDS, such as a concentration of 5 wt%, the whole distribution curve is shifted to lower size values, corresponding to the “free chains”/SDS complex. For this fraction it can be admitted from DLS distribution curves that the nanogels are disaggregated at a SDS concentration around 5 wt% with respect to PVA.

The size characteristic of the different fractions of PVA-73-650 and PVA-73-685 at SDS concentrations of 1 and 5 wt% with respect to PVA are summarized in Table 4:

Table 4. The evolution of the size average (Dv) of different fractions of samples PVA-73-650 and PVA-73-685 at a SDS concentration of 1 and 5 wt% respectively with respect to PVA.

Fractions	Dv (nm)			
	PVA-73-650		PVA-73-685	
	1% SDS	5% SDS	1% SDS	5% SDS
F ₁	19.3 ± 0.9	7.6 ± 0.7	16.6 ± 0.3	7.1 ± 0.5
F ₂	16.2 ± 0.7	7.4 ± 0.5	13.8 ± 0.7	6.9 ± 0.6
F ₃	14.7 ± 0.4	6.9 ± 0.3	14.1 ± 0.7	7.7 ± 0.3
F ₄	8.3 ± 0.3	7.8 ± 0.3	9.3 ± 0.2	7.6 ± 0.3

From this table it is worth noting that for both PVA samples at a SDS concentration of 1 wt% with respect to PVA, the D_v values are decreasing from fraction F_1 to fraction F_4 . For these fractions, this tendency can be correlated to the corresponding decrease of vinyl acetate content and of $\overline{n_0^{VAc}}$.

However, it can be noticed that a SDS concentration of 1 wt% with respect to PVA is not sufficient to disaggregate completely the nanogels present in fractions F_1 , F_2 and F_3 . A complete disaggregation is only reached at higher SDS concentrations, such as 5 wt%, with a possible formation of “free chains”/SDS complex having a D_v value of around 7 nm.

A particular behavior can be observed for the most soluble fraction F_4 of lower $\overline{DP_w}$ and VAc content. Moreover, this fraction does not contain nanogels, as shown in Tables 2 and 3, and the monomodal distribution can be considered as “free chains” with a D_v values between 8–9 nm. As no size change is observed in the presence of a SDS concentration of 1 wt% with respect to PVA, it can be concluded that the possible complex formation with SDS has no major influence on their size.

Further work is in progress in order to investigate the direct thermal cloud point fractionation of PVA/SDS complexes and preliminary tests have already shown that the cloud point of such systems are shifted to higher temperatures by addition of SDS. As a consequence the fractionation of “nanogels-free” systems would have to be performed at temperatures of around 80–85 °C.

4. Conclusions

In addition to various fractionation techniques, such as SEC and HPLC published up to now for PVA's, it could be confirmed that the thermal cloud point fractionation is a valuable alternative procedure to give an insight in the polydispersity characteristics of this type of polymer.

Two PVA samples, with same overall $\overline{DP_w}$ and \overline{DH} values but having different average sequence lengths of vinyl acetate $\overline{n_0^{VAc}}$, were fractionated in three temperature steps between 40 and 75 °C.

The nanogels with highest values of volume fraction and D_v were separated in the most insoluble fraction F_1 whereas the most soluble fraction F_4 no longer contains nanogels, only “free chains”.

In the presence of an SDS concentration of 1 wt% with respect to PVA a partial disaggregation of nanogels present in fractions F_1 , F_2 and F_3 was noticed. A complete disaggregation is only reached at higher SDS concentrations, such as 5 wt%, with formation of “free chains”/SDS complex having a D_v value of around 7 nm. In the presence of SDS, no size change is observed for the fraction F_4 with higher \overline{DH} values and lower “blockiness”.

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