

Dynamic Light Scattering Study of the Ultrasonication of P(VDF-TrFE) : A New Model

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Abstract

The purpose of this paper is to understand the mechanisms occurring during the ultrasonication of the copolymer P(VDF-TrFE). In these experimental conditions, the polymer adopts a core-shell structure and its hydrodynamic diameter is measured by dynamic light scattering (DLS). The results show that, without covalent bonds breakage, the hydrodynamic diameter decreases with ultrasonication time and a smaller size population appears. This evolution is reversible in a matter of days. A new two-step mechanism is proposed to describe this phenomenon: firstly the erosion of a core-shell structure and secondly the contraction of the core. Beyond shedding a new light on the phenomena occurring during the sonication of polymers used in nanocomposites elaboration, this work also strongly questions the traditional techniques used to study the degradation of polymers, which uses the hydrodynamic diameter measurement to determine the molecular weight.

Keywords: poly(vinylidene difluoride-trifluoroethylene), ultrasonication, dispersion, dynamic light scattering, hydrodynamic diameter.

Abbreviations

P(VDF-TrFE): poly(vinylidene difluoride-trifluoroethylene)

NP: nanoparticle

MEK: methyl ethyl ketone

PVDF: polyvinylidene difluoride

SEC: size-exclusion chromatography

DMF: dimethylformamide
DLS: dynamic light scattering
SLS: static light scattering
CAC: critical aggregation concentration
NZS: Zetasizer Nano ZS

Introduction

During the past few years, the copolymer poly(vinylidene difluoride-trifluoroethylene) P(VDF-TrFE) has attracted a growing interest, mainly because of its ferroelectric, pyroelectric and dielectric properties. Indeed, its high dielectric constant is useful in a large range of capacitor applications [1]. To improve the dielectric constant and thus the capacitance, or its ferroelectric properties, extensive research on P(VDF-TrFE) was carried out as it is but also as a matrix for nanocomposites [2]. These nanocomposites were prepared by incorporating various nanoparticles (NPs) in P(VDF-TrFE) in order to obtain reinforced materials with better mechanical properties or to add new properties to the matrix such as piezoelectric or nonlinear optical properties [3–6]. In these materials, the ultrasonication step is crucial. A good dispersion of nanoparticles is necessary to strengthen mechanical properties of the material, such as the elastic constant. This was observed for various polymers and even in oligomers [3–6]. The goal of the dispersion, performed by ultrasonication, is generally to break the agglomerates of NPs, and, in the process, to decrease their hydrodynamic volume, which is the apparent volume occupied by a spherical (organic or inorganic) particle or agglomerate in a solvent.

In this work, we solely focus our efforts on the other component of the nanocomposite, i.e. the polymer (here P(VDF-TrFE)), with the goal of understanding the processes occurring during its ultrasonication. Our primary motivation is the following: to obtain nanocomposites with homogeneous properties, it is necessary to improve the quality of nanoparticles dispersion within the polymer. For a constant number of molecules, the higher the hydrodynamic volume of the polymer molecule in the solvent is, the more “unfolded” the molecule is, and the easier the filling with nanoscopic fillers will be. Because the nanofillers are usually dispersed by ultrasonication, it is of great importance to know if the ultrasonication may modify the hydrodynamic volume of the polymer.

This paper is organized as follows: first we describe the structural and behavioral hypotheses related to the ultrasonication of P(VDF-TrFE) dissolved in a solvent, then we depict the experimental study based on Dynamic Light Scattering (DLS) measurements of the hydrodynamic diameter. A new mechanism related to the behavior of the P(VDF-TrFE) exposed to ultrasounds is proposed to explain the results. The well-established use of the hydrodynamic diameter to measure the molecular weight of polymers is severely questioned by our findings.

Hypotheses of this study

Structure of the polymer in a solvent

According to Park *et al.* [7], the polymer poly(vinylidene difluoride) (PVDF) has different structures in function of its dilution in an organic solvent. The polymer chains are extended and individualized only in very diluted solutions, i.e. with a concentration of 10^{-6} g/mL, called Critical Aggregation Concentration (CAC). Just above the CAC, the polymer chains form a hard sphere of uniform density. With the increase of the concentration, this last structure is transformed in core-shell structure, with

the polymer chain aggregating around the hard sphere [7–9]. These different structures of the polymer are illustrated in figure 1. In this paper, we assume that P(VDF-TrFE) has the same behaviour and forms a core shell-structure for standard concentrations used in the nanocomposite preparation process, in our case 130 mg/mL. In this context, the measured hydrodynamic diameter corresponds to the size of the core-shell structure.

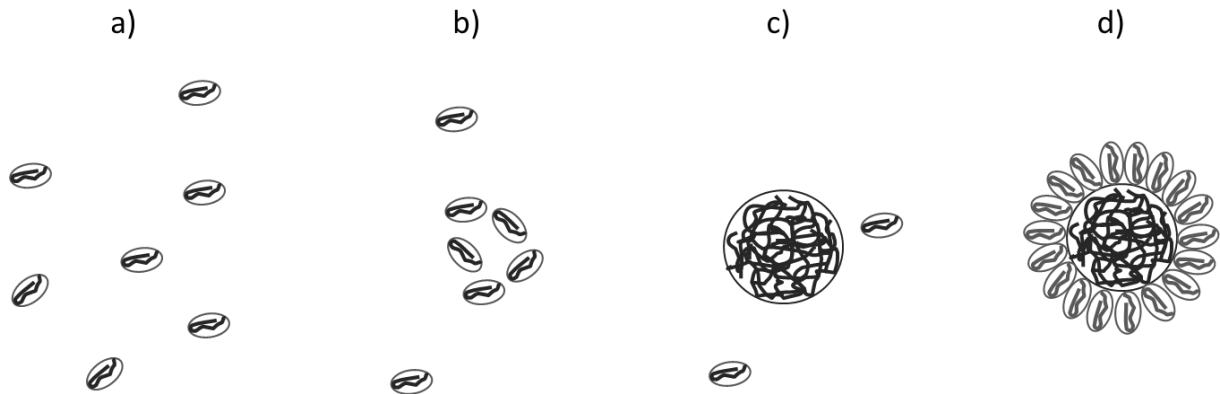


Figure 1: Schematic representation of the different structures of the PVDF in a solvent depending on its concentration a) below the CAC at very low concentration, b) below CAC with a higher concentration c) just above the CAC and d) far above the CAC.

Nature of the bonds affected by ultrasonication

We also focus our discussion on the weak bonds, since we believe the creation/breakage of covalent bonds to be rather negligible in the conditions of our experiments. This has already been demonstrated by studying the thermal properties of our copolymer with regard to the ultrasonication time in a previous study [10]. Indeed, we observed no shift of the Curie and melting temperatures between a film made of sonicated P(VDF-TrFE) and a film made of P(VDF-TrFE) without sonication, which can only happen if there is no rupture of the covalent bonds and the molecular weight is unchanged.

Molecular weight determination using the hydrodynamic volume: a major issue?

If the different processes of agglomeration and deagglomeration of inorganic nanoparticles in suspension are well studied and modeled in terms of agglomerate size [11,12], there is no equivalent work for the agglomerates of polymer molecules under ultrasonication. Assuming that no covalent bonds are broken during this process, there is no study to our knowledge that deals with the effect of ultrasonication on the weak bonds and the subsequent changes on the shape and the size of the hydrodynamic volume.

The studies we found in the literature dealing with the effects of the ultrasonication on polymer solutions were investigated by size-exclusion chromatography (SEC) or static light scattering (SLS) but only to determine if this process could break molecules (thus covalent bonds) and subsequently modify the molecular weight of the polymers [13–18]. However, these techniques rely on the measurement of the hydrodynamic diameter to determine the molecular weight.

This way of proceeding may pose a major problem: if the sonication changes the hydrodynamic volume without breaking the molecular chains, the molecular weight is then unchanged. The

dependence between the two would be dubious and the results obtained by these techniques could be biased.

Materials and Methods

We characterize the hydrodynamic diameter of P(VDF-TrFE) molecules with the ultrasonication time using DLS. The experiments are realized in two solvents with different dipolar moments in order to observe the influence of the solvent quality on the hydrodynamic diameter.

Preparation of the solutions

Two experiments are carried out to analyze the effect of the ultrasonication on the hydrodynamic diameter of the P(VDF-TrFE). The protocol is the same for the both experiments: only the solvent has been changed. The two selected solvents are methyl ethyl ketone (or MEK, Sigma Aldrich) and dimethylformamide (or DMF, Sigma Aldrich) because they are known to be good solvents for the P(VDF-TrFE)[10][19] and they have different dipolar moment. MEK is better solvent than DMF because of its lower dipolar moment (see Table 1). This will give us an interesting comparison of the copolymer behavior under ultrasonication, since we can expect that it is easier for the polymer coil to expand in a better solvent (or shrink in a less good solvent).

Solvents	Dipolarmoment
methyl ethyl ketone	2.78
dimethylformamide	3.82

Table 1: Properties of different solvents (McMaster University, Canada, Website).

The copolymer P(VDF-TrFE) (70/30 %, $M_w = 350\,000\text{ g}\cdot\text{mol}^{-1}$, Piezotech S.A.S, France) is dissolved in MEK (at 80-85°C) or in DMF (at 95-100°C) for 2.5 hours with magnetic stirring in order to obtain a 3 wt.% solution (concentration $C = 2.47 \cdot 10^{-2}\text{ g/mL}$). Then, the solutions are filtered with a 2.7 μm glass microfiber template (Whatman).

Ultrasonication of solutions

The solution is sonicated with a Transducer Digital Sonifier Moder 450 (Brandson Ultrasonics Corporation, USA) with a frequency of 20 kHz and a maximum power of 400 W. 10 mL of solution are taken, cooled in ice water to prevent evaporation of the solvent and sonicated at 30% power (i.e. 120W) with a pulse on/off 0.1/0.1 (s/s) with a duration from 5 seconds to 300 seconds.

Dynamic light scattering (DLS)

The hydrodynamic diameter of the polymer is measured by DLS (like in [20]), with a Zetasizer Nano ZS (NZS, Malvern Instruments), right after ultrasonication. The viscosity and the refractive index of the solutions required for hydrodynamic diameter measurements by DLS are determined by rheometry (RheolabQC, Anton-Paar) and refractometry (Abbemat WR, Anton Paar).

The main difficulty that we overcame is the dispersion of the average hydrodynamic diameters calculated by the NZS for a single-sized population. This phenomenon may be the result of the presence of large clusters in suspension, which pass in front of the laser beam randomly and distort the average hydrodynamic diameter measurements. To obtain reproducible measurements, we defined a new protocol by varying the number of runs per measurement. Each measurement includes 150 to 400

runs of 10 seconds. We found out that the numbers of runs per measurement had to be increased with the ultrasonication time to maintain reproducibility. The given hydrodynamic diameters for each solution are calculated by the average of three measurements.

Results and discussion

P(VDF-TrFE) hydrodynamic diameter in MEK and DMF after ultrasonication

Figure 2 depicts the evolution of the hydrodynamic diameter of a single population, centered initially (i.e. without ultrasonication) at about 207 nm, versus the ultrasonication time. The hydrodynamic diameter of P(VDF-TrFE) clearly decreases with the ultrasonication time until it reaches a threshold limit. After 300s, the size is about 90 nm, and approximately the same after 780 sec. The shape of the curve indicates that the polymer molecule is not broken.

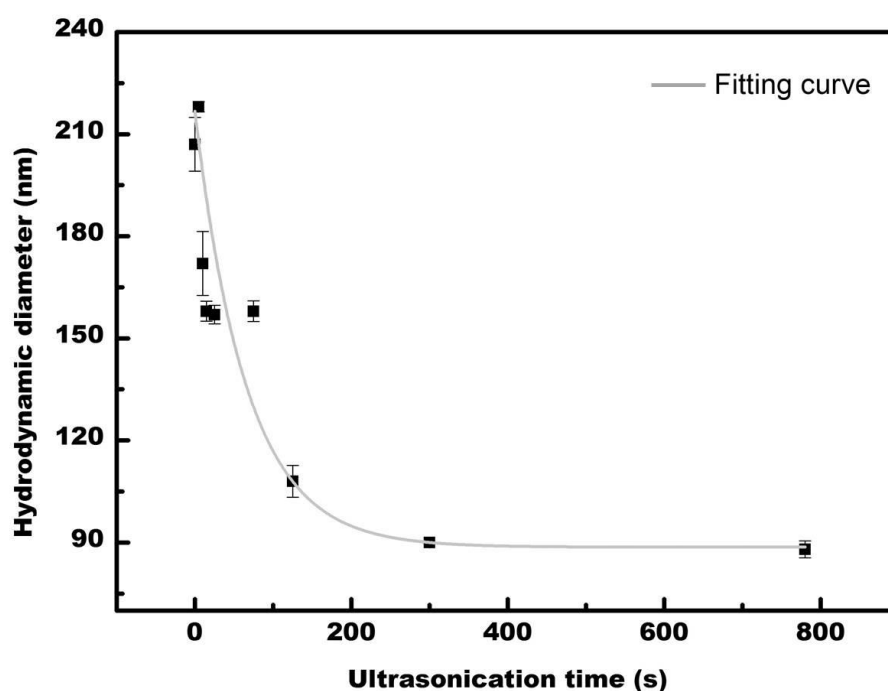


Figure 2: P(VDF-TrFE) hydrodynamic diameter versus ultrasonication time, in MEK. The error bar corresponds to the standard error between the three measurements. The fitting curve is in gray.

Figure 3 shows that the hydrodynamic diameter evolves in the same manner in DMF as in MEK. Again, the hydrodynamic diameter decreases gradually. Although DMF is a less good solvent than MEK, we found out the copolymer coil is swollen similarly in DMF and MEK with no sonication: the diameter is about 200nm. After 300 s of ultrasonication, the hydrodynamic diameter is about 120 nm, which is larger than in MEK.

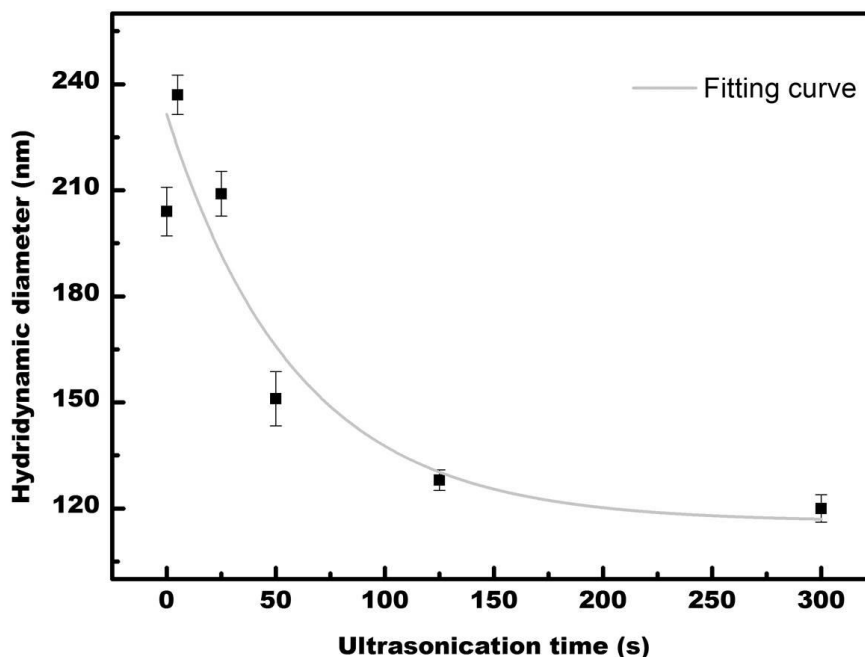


Figure 3: P(VDF-TrFE) hydrodynamic diameter versus ultrasonication time, in DMF. The error bar corresponds to the standard error between the three measurements.

Long term evolution of the hydrodynamic diameter without additional ultrasonication

To validate that there is no chain scission, the evolution of the hydrodynamic diameter after ultrasonication is investigated in MEK. The figure 4 shows that the polymer recovers its original size six days after ultrasound exposure. The reversibility of the evolution of the hydrodynamic polymer definitely proves that no covalent bond breaks during ultrasonication, thus confirming our initial hypothesis.

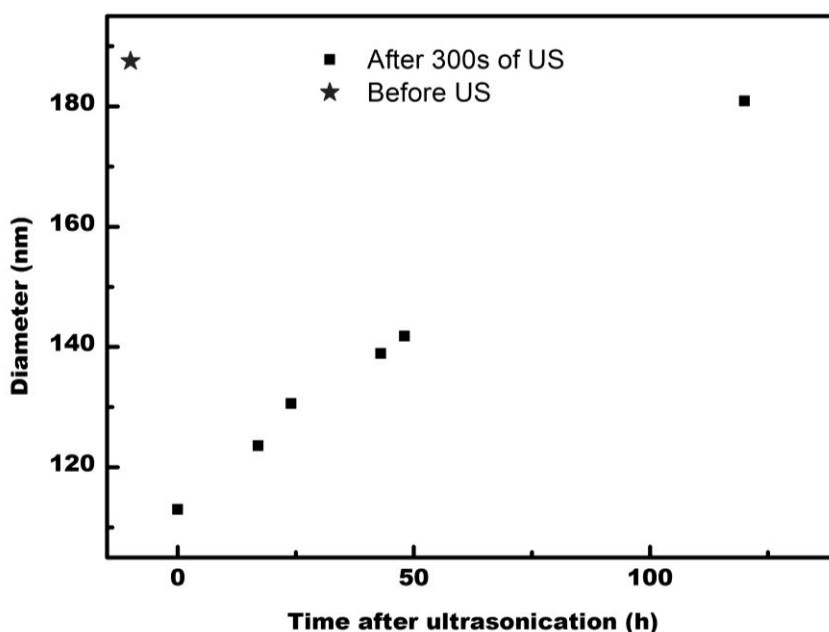


Figure 4: Evolution of the P(VDF-TrFE) hydrodynamic diameter in MEK days after ultrasonication

Observation of the appearance of new populations of size

Figure 5 and 6 depict the intensity of the light scattered by the polymer versus the hydrodynamic diameter for different ultrasonication times.

In figure 5, we show that, in addition to the initial population centered on 207 nm, a new population appears after 300s of ultrasonication, with hydrodynamic diameters over 300 nm. Our interpretation is that after a certain time, enough charges are created at the surface of several polymer core-shell structures to bond it efficiently, by electrostatic effect, very similar to what happens with inorganic particles [11], thus leading to a new population with a larger hydrodynamic diameter.

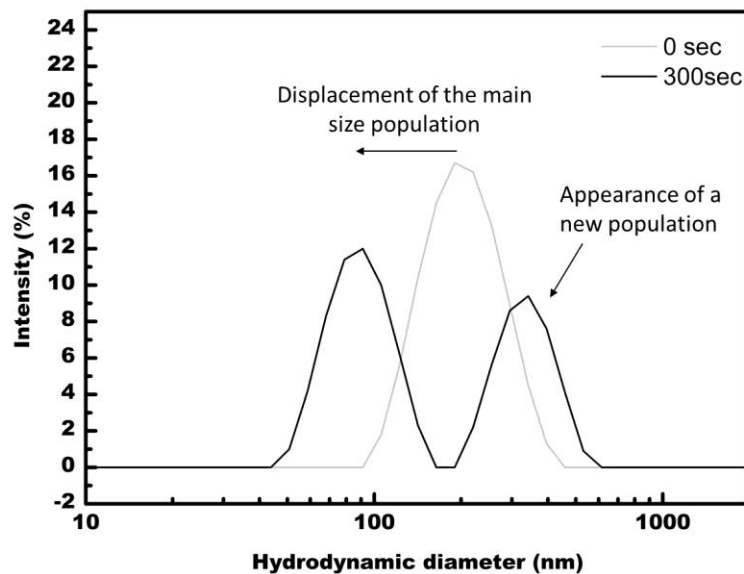


Figure 5: DLS curves representing the appearance of a larger hydrodynamic diameter population after 300s of ultrasonication, in MEK. The main size population is centered about 207 nm and 90 nm without and after 300s of sonication, respectively. The new size population is centered about 368 nm.

In some cases, (see Fig.6) smaller populations (about 30 nm) are observed after a few dozens of seconds (here 65 sec). We believe that it denotes the presence of individualized polymer chains because 30 nm matches the size of single polymer chains appearing in highly diluted solutions [7].

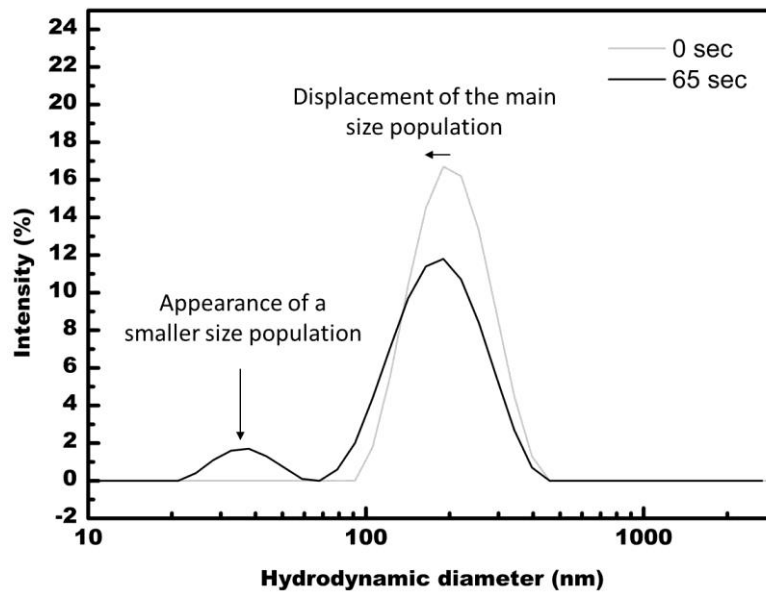


Figure 6: DLS curve representing the appearance of a smaller hydrodynamic diameter population after 65s of ultrasonication. The main size population is centered about 207 nm and 163 nm without and after 65s of sonication, respectively. The new size population is centered about 32 nm.

To confirm this last interpretation, the solutions are diluted at different concentrations in an effort to create individualized polymers chains. DLS measurements are performed without ultrasonication. We expect that the lower the concentration of the polymer is, the easier the formation of individualized chains will be and the more the population about 30 nm will be detected. These results are gathered in Table 2.

Concentration (g/mL)	In MEK		In DMF	
	Diameter (nm)	Intensity (%)	Diameter (nm)	Intensity (%)
$3 \cdot 10^{-2}$	26	3.1	-	-
$3 \cdot 10^{-3}$	-	-	28	75.3
$3 \cdot 10^{-4}$	62	8.6	59	64.8

Table 2: Hydrodynamic diameters sizes as a function as copolymer concentration in MEK and DMF.

In MEK and in DMF, small hydrodynamic diameters of about 30 nm are observed at concentrations of $3 \cdot 10^{-2}$ g/mL and $3 \cdot 10^{-3}$ g/mL, respectively. The peak intensity and the population size increases (about 60 nm) with dilution. This confirms that the individualized particles are present and swells when the copolymer concentration decreases, as described in the work of Park *et al.* [7]. Thereby, this confirms that the new population observed about 30 nm in the previous experiment after the ultrasonication is related to individualized copolymer molecules.

Mechanisms occurring during the ultrasonication of P(VDF-TrFE): a new model

To explain the decrease of the hydrodynamic diameter and the apparition of a new population at 30 nm, we propose a mechanism consisting in two steps: the shell erosion and then the core's contraction. As explained above, similarly to Park *et al.* in comparable conditions [7], we assume that the polymer is in a core-shell structure. The shell is composed of partially solvated, weakly entangled

molecules bonded to the core molecules. The core is composed of highly entangled and badly solvated molecule.

First step: The shell erosion (Fig.7)

The ultrasonication starts with the destruction of the shell by breaking the Van der Waals bonds between the partially solvated molecules of the shell and the core. The molecules constituting the shell break away from the core continuously with the ultrasonication time. When the complete destruction of the shell is achieved, the copolymer does not form a core-shell structure with a smaller diameter but rather a hard sphere (former core) and some individualized well solvated molecules. This proposed mechanism is very similar to the erosion mechanism commonly accepted for agglomerates of inorganic nanoparticles in suspension subjected to ultrasounds.

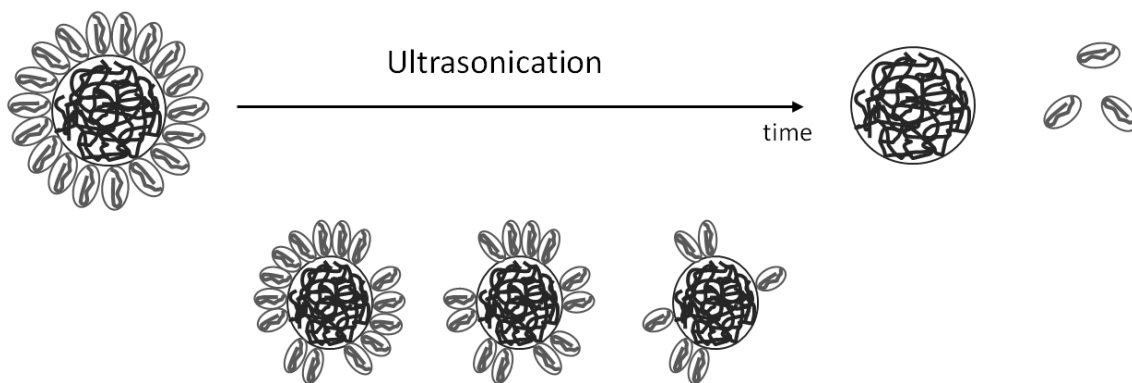


Figure 7: Schematic representation of the erosion mechanism of P(VDF-TrFE) submitted to ultrasonication

Second step: The core contraction

A previous study [21] has reported that, near the collapse of a bubble during the cavitation process, the end of a polymer chain is attracted by the locally created vacuum. The tension resulting from the opposite forces, *i.e.* the attraction forces reaction coming from the entangled chains, induces the breakage of the polymer chain. More precisely, the authors explain that for a hydrodynamic volume containing only one molecule, the chain is extended and breaks, non-randomly, at 15% of its center. In our case, several entangled molecules constitute the core, preventing a sufficient deployment of the chains to break them. The proposed mechanism is the following: instead of untying, the chains are tightened further together, leading to a shrinking of the hydrodynamic volume (Fig. 8).

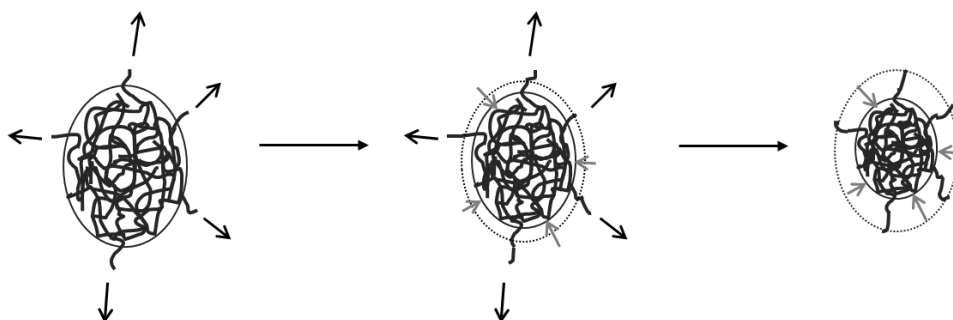


Figure 8: Schematic representation of the polymer contraction.

Additional discussion

Why is the final threshold hydrodynamic diameter different in MEK and DMF ?

In figure 5 and 6, we observed that the threshold value for the hydrodynamic diameter after a few minutes of ultrasonication was 90 nm in MEK and 120 nm in DMF. We can now explain this considering the erosion mechanism of the core-shell described here above, and the difference of dipolar moments between the two solvents.

Since its dipolar moment is lower, the MEK is a better solvent than the DMF and the molecules forming the shell are more solvated. Thus, the thickness of the shell in MEK is larger than in DMF. As the initial hydrodynamic diameters measured are similar in both solvents, the diameter of the core in MEK is smaller than in DMF. Once eroded, only the cores remain and the final diameter is larger in the DMF than in the MEK (Fig. 9).

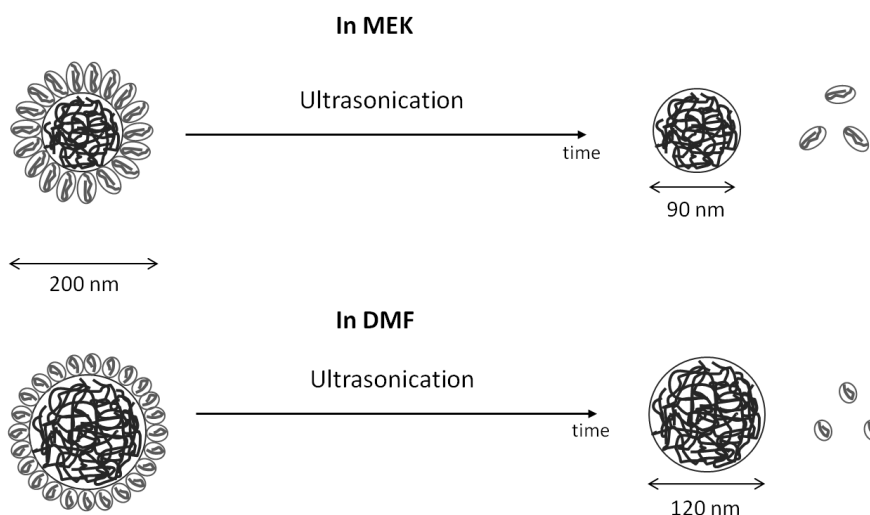


Figure 9: Schematic representation of P(VDF-TrFE) behavior in two solvents.

SLS and SEC measurements of the molecular weight of sonicated polymers: questioning the link between molecular weight and hydrodynamic volume

Our work questions the use of techniques such as Static Light Scattering (SLS) or SEC to study the chain degradation of polymer after ultrasonication ([13],[15],[16–18]), since they use the

hydrodynamic volume to determine the molecular weight. In the case of the SEC, the equations related to the conventional and universal calibrations, respectively (1) and (2), are given below:

$$(1) V_h = C_1 - C_2 \log(M_w)$$

$$(2) V_h = C_3 - C_4 \log(M_w \cdot [\eta])$$

With $[\eta]$ the viscosity, V_h the hydrodynamic volume, M_w the molecular weight and C_i the equation constants.

In SLS, the molecular weight depends on the hydrodynamic volume, through the intensity of the light scattering (3). The higher the hydrodynamic volume is, the higher the intensity of light scattering and the higher the molecular weight will be.

$$(3) \frac{KC}{R_\theta} = \left(\frac{1}{M_w} + 2A_2C \right) P(\theta)$$

With R_θ the Rayleigh ratio (the ratio of the intensity of scattered light to the intensity of the incident light of the sample), A_2 the 2nd virial coefficient, C the concentration, $P(\theta)$ the angular dependence of the sample scattering intensity and K the optical constant. Here, the term $\frac{KC}{R_\theta}$ is linked to the intensity of the light scattered.

In short, for both techniques, if the hydrodynamic volume decreases without degradation under ultrasonication, which we proved to be the case here for P(VDF-TrFE), the results could be biased because it is possible to have two different volumes for the same molecular weight.

To determine the molecular weight with such techniques, a study of the evolution of the hydrodynamic diameter of the polymer with the ultrasonication time should be performed to ensure that it is not modified without chain scission.

Conclusion and perspectives

P(VDF-TrFE) is dissolved in solvents at concentrations for which it adopts a core-shell structure. The results show that hydrodynamic diameter of the core-shell, measured by DLS, decreases with ultrasonication time. The complete reversibility of this evolution cleared proves that there is no covalent bonds breakage and that only weak bonds are involved.

The appearance of a smaller size population, related to individualized chains, leads us to propose a new two-step mechanism: first, the erosion of the core-shell structure occurs, creating a smaller size population. Then, the extremities of the copolymer chains are attracted by the vacuum created by collapsing bubbles generated by cavitation, leading to a mechanical shrinking. The linkage between the molecular weight and the hydrodynamic diameter used by techniques such as SEC or SLS is questioned, since we proved that the hydrodynamic diameter can evolve without modifying the molecular weight.

In the future, our better understanding of the phenomena occurring during the ultrasonication of P(VDF-TrFE) will help us to have deeper understanding of the P(VDF-TrFE) nanocomposites with optimized nanoparticles dispersion, and consequently enhanced properties.

Compliance with Ethical Standards:

Funding: This work was partly funded by the French Ministry for Education and Research (C.T. PhD grant). The authors declare that they have no conflict of interest.

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