

# Influence of a Density Mismatch on TMPTMA Shells Nonconcentricity

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**ABSTRACT:** Some laser target designs require low-density organic foam shells to study fusion on the French high-power laser laser mega joule. Low-density trimethylolpropane trimethacrylate foam shells composed of C, H, and O, 2 mm diameter, 100- $\mu\text{m}$  wall thickness, and 250  $\text{mg cm}^{-3}$  density are synthesized by a microencapsulation technique using a droplet generator. These shells have to reach a sphericity higher than 99.9% and a nonconcentricity (NC) lower than 1%. The wall thickness variation is one of the most difficult specifications to meet. An important factor in reducing this defect is the density matching

between the three phases of the emulsion at polymerization temperature. The influence of a density mismatch between the internal water phase and the organic phase on the NC of TMPTMA foam shells was studied. The best NC results and yields of shells are obtained with a density gap between the internal water phase and the organic phase of 0.078  $\text{g cm}^{-3}$  at 60°C, with an average NC around 2%. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4882–4888, 2012

**Key words:** density; microencapsulation; dispersion; shell; trimethylolpropane trimethacrylate

## INTRODUCTION

To achieve ignition on the French high-power laser LMJ (laser mega joule), different target designs are being developed. Low gain targets made of low-density organic foam shells can be used to study fusion. The aim is to produce low density foam shells composed of C, H, and O satisfying strict specifications. The criteria to fulfill are the following: diameter ranging from 1.7 to 2.3 mm, wall thickness about 100  $\mu\text{m}$ , 250  $\text{mg cm}^{-3}$  density, sphericity > 99.9%, and nonconcentricity (NC) < 1%.

The foam shells are made by microencapsulation of an aqueous phase inside an organic phase with a triple orifice droplet generator. The double emulsion water-in-oil-in-water is first shaped, and then the organic phase is polymerized. After solvent exchanges, a wet foam shell is obtained. The issue is to hit all the specifications at the same time. During the last 5 years, many developments have been achieved on a droplet generator system allowing to meet main requirements (diameter, density, and

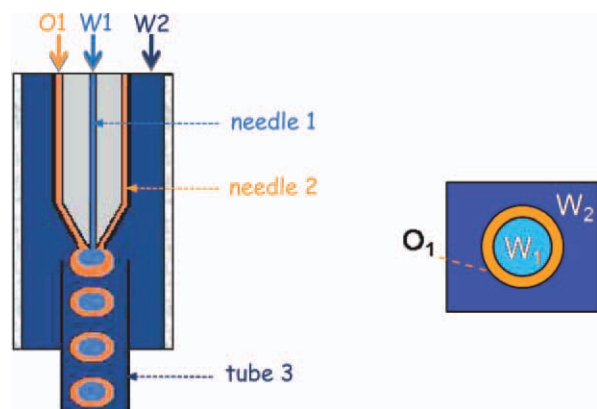
thickness). Nevertheless, it remains difficult to reach the sphericity and NC demands. The wall thickness variation is the hardest specification to fulfil. A lot of parameters have an influence on the NC specification: density, kinetics, deformation, interfacial tension, and viscosity.

According to the literature, density is a key factor to meet the NC specification. From 1991 to 2003,<sup>1–4</sup> the following concept can be found in the literature: the density of the internal water phase has to be equal to the density of the organic phase in order to obtain more concentric shells, and the density-matching temperature is the polymerization temperature at which the shell shape is set. Moreover,<sup>3–5</sup> to eliminate shell sagging caused by gravity and to keep the shells suspended in solution during polymerization, the density of the aqueous bath must be equal or slightly less than the density of the shell formed.

In 2003, Streit et al.<sup>6</sup> studied the effect of density matching on the NC of divinyl benzene (DVB) foam shells. It appeared that “the percent of NC will be minimized with a room temperature density mismatch between 0.008 and 0.009  $\text{g cm}^{-3}$ .” They also emphasize that other production process variables scatter the data in this range, making it difficult to determine the effect of the density difference. Thus, in 2005, Streit et al.<sup>7</sup> concluded that “matching density beyond a rough match has not had a clear effect on NC.” However, in 2005 and 2006, Paguio et al.<sup>8,9</sup>

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**Figure 1** Triple orifice droplet generator. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

explained that a slight density mismatch of the internal organic phase and the water phase ( $0.01 \text{ g/cm}^3$  at  $70^\circ\text{C}$ ) was one of the two factors that helped produce resorcinol–formaldehyde (RF) shells with good wall uniformity.

Our study is based on trimethylolpropane trimethacrylate (TMPTMA) foam shells. Thus, starting from all this different points of view in the literature about density matching improving or not the NC of RF or DVB shells, we decided to check the influence of density gaps between the organic and aqueous phases, on the NC of TMPTMA foam shells. In this aim, the evolution of density of the different phases with temperature will be initially presented. Then, the effect of growing density gaps on the NC of TMPTMA foam shells will be discussed. A short discussion concerning the yields of the syntheses and the reproducibility will also be presented.

## EXPERIMENTAL

### Microencapsulated droplet generation

The shells are produced by a microencapsulation technique using a triple orifice droplet generator as illustrated in Figure 1. The internal water phase (W1) is delivered by the needle 1 and is surrounded by the needle 2, which delivers the organic phase (O1). The encapsulated drop of water surrounded by the organic solution is then stripped off from the triple orifice droplet generator to the tube 3 by the external water phase (W2). The diameter of the shell is controlled by the W2 flow, and the wall thickness is determined by the ratio of the W1 and O1 flow rates.

Shells travel through the tube 3 and then pass through a tube with areas of constriction before being collected into an agitated horizontal flask. This flask is placed into a heated water bath at  $60^\circ\text{C}$  and under nitrogen flow of  $60 \text{ mL/min}$ . The shells start to polymerize once collected into the flask. After

polymerization, they undergo several water washes to clean the surface. The last step consists in replacing W1 with ethanol.

### Materials

The external water phase is a solution of 5% poly(vinyl alcohol) in water. The organic solution is composed of a monomer (TMPTMA), a mixture of two solvents [dibutyl phthalate (DBP) and ethylbenzene], a surfactant (Span<sup>®</sup> 80: sorbitane monooleate), and an initiator (azobisisobutyronitrile). The internal water phase solution is a mixture of water and deuterated water. The amount of deuterated water to introduce is calculated for each synthesis as a function of the density of the organic solution prepared and the density aimed. A typical composition is described in Table I.

### Densitometer

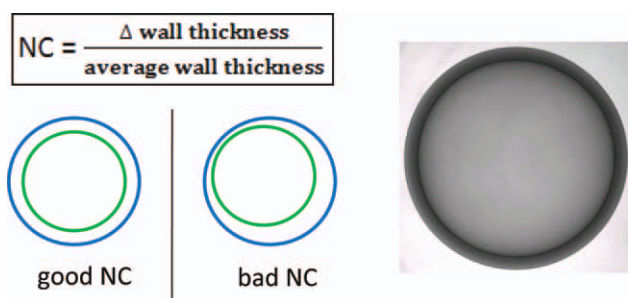
The evolution of density with temperature was measured precisely on a densitometer (Anton Paar<sup>®</sup>, DMA 5000) from  $20$  to  $80^\circ\text{C}$  for each solution. The densitometer accuracy is  $10^{-6} \text{ g cm}^{-3}$  for density measurement and  $0.001^\circ\text{C}$  for temperature measurement. The evolution of the organic phase density with temperature is measured without the initiator in order to avoid polymerization inside the densitometer tube.

### NC measurements

Characterization of the foam shells is carried out using a telecentric optical microscope (Optique Peter<sup>®</sup>, Melles Griot). Because these foam shells are transparent while they are in liquid, several parameters can be measured: the inner and outer diameter, the sphericity, and the wall uniformity. The telecentric optical microscope gives for each shell a curve of the wall thickness variation. Thus, NC is equal to the peak to peak amplitude of the curve divided by the average wall thickness as illustrated in Figure 2.

**TABLE I**  
Composition of the Three Different Phases

		Conc. (wt %)
W2	H <sub>2</sub> O	95
	PVA	5
O1	AIBN	1.3
	DBP	74
	Ethylbenzene	9.1
	TMPTMA	13.1
	Span 80	2.5
W1	H <sub>2</sub> O	From 100 to 0
	D <sub>2</sub> O	From 0 to 100



**Figure 2** NC definition and picture of a humid shell seen with a telecentric optical microscope. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

In each bottle, 35 foam shells are picked up randomly and characterized among the 50–250 shells synthesized.

## RESULTS AND DISCUSSION

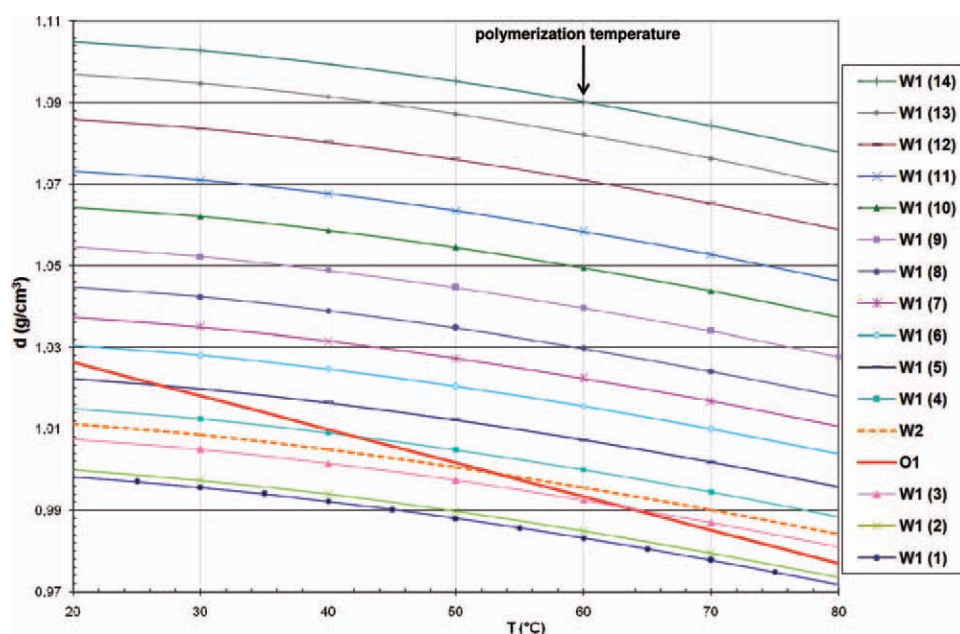
To study the influence of density on NC, TMPTMA foam shells were synthesized with varying density mismatch between the W1 and O1 phases. The composition of O1 and W2 is always the same to hold their density constant. Therefore, several internal water phases (W1) are used with different densities to find out which gap will lead to the lowest NC. Moreover, the density of W1 will be either higher or lower than the density of O1 at polymerization temperature in order to study the effect of a density mismatch between W2 and the shell (O1/W1). The density of the internal water phases can vary from

the density of pure water [W1 (1)] to the density of pure deuterated water [W1 (14)]. Thus, the density of the internal water phase can be up to 10% of the density of the organic phase.

The results of the evolution of density with temperature for O1, W1, and W2 are illustrated in Figure 3. As expected, when temperature increases, the density of the organic phase decreases with a linear pattern, whereas the densities of the water phases decrease with a slight curve pattern. At polymerization temperature (60°C), the density of W2 is almost equal to the density of O1 (difference of 0.0024 g cm<sup>-3</sup>). The density of W1 (1), pure water, is lower than the density of O1 at 60°C. If the amount of deuterated water in the internal water phase increases, the density of W1 will increase and become eventually higher than the density of the organic phase [W1(4)–W1(14)].

The density difference between the aqueous bath (W2) and the average density of the shell formed (O1/W1) can also be interpreted from Figure 3. It is easy to see that the internal water phases W1(1) and W1(2) will lead to an average shell density lower than the density of the aqueous bath. The internal water phases, from W1(4) to W1(14), will lead to an average shell density higher than the aqueous bath. And the W1(3) phase should lead to an average shell density almost equal, maybe slightly less, than the one of the aqueous bath.

Thus, 14 internal water phases have been used to synthesize TMPTMA foam shells, and their compositions are described in Table II. The compositions of the external water phase and the organic phase are



**Figure 3** Evolution of density with temperature of the 14 internal water phases (W1) compared to the organic phase (O1) and the external water phase (W2). Results are presented in the order of the density growing with W1 (1) at the bottom and W1 (14) at the top. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

TABLE II  
Composition of the 14 Internal Water Phases and the Density Difference Between W1 and O1 at 20 and 60°C

	Concentration (wt %)		Measured density at 20°C (g cm <sup>-3</sup> )	Density difference at 20°C: dW1—dO1 (g cm <sup>-3</sup> )	Density difference at 60°C: dW1—dO1 (g cm <sup>-3</sup> )
	H <sub>2</sub> O	D <sub>2</sub> O			
W1 (14)	0	100	1.104937	0.078	0.097
W1 (13)	6.6	93.4	1.096912	0.070	0.089
W1 (12)	16.2	83.8	1.085824	0.059	0.078
W1 (11)	27.5	72.5	1.073265	0.047	0.065
W1 (10)	35.8	64.2	1.064347	0.038	0.056
W1 (9)	44.6	55.4	1.054543	0.028	0.046
W1 (8)	53.8	46.2	1.044687	0.018	0.036
W1 (7)	61	39	1.037248	0.011	0.029
W1 (6)	67.5	32.5	1.030546	0.004	0.022
W1 (5)	75.6	24.4	1.022287	-0.004	0.014
W1 (4)	83.1	16.9	1.014978	-0.011	0.007
W1 (3)	90.6	9.4	1.007433	-0.019	-0.001
W1 (2)	98.2	1.8	0.999932	-0.027	-0.008
W1 (1)	100	0	0.998210	-0.028	-0.01

described in Table I. During one experiment, a maximum of six bottles of shells are collected. For each bottle, only one internal water phase has been used, from W1(1) to W1(14). Table II gives the density difference between W1 and O1 at 20 and 60°C for each internal water phase.

To study different density gaps between W1 and O1, 29 bottles of shells were collected from several sets of experiment. Figure 4 illustrates the average NC of the shells as a function of the density gap between W1 and O1 at polymerization temperature for the 29 bottles collected.

The results obtained do not show a straight line evolution of the average NC with the density mismatch between W1 and O1. At first, when the density gap increases from -0.01 to -0.001, the average NC increases from 7.5 to 11.3%. Second, when the density gap increases from -0.001 to 0.089, the average NC decreases down to 2%. Then, a further

increase of the density gap from 0.089 to 0.097 increases the average NC value to 3.9%. Thus, the best NC results are obtained with both internal water phases W1(12) (dW1—dO1 = 0.078 at 60°C) and W1(13) (dW1—dO1 = 0.089 at 60°C) with an average NC around 2%.

In a second time, we focused on the amount of shells showing the best NC values with a criterion of NC lower than 4%. The percentage of shells with NC < 4% as a function of the gap density between the internal water phase and the organic phase at 60°C is illustrated on Figure 5. The evolution of these results can be directly related to the one presented on Figure 4. At first, when the density gap increases from -0.01 to -0.001, the percentage of shells with NC < 4% decreases from 29% to 12%. Second, when the density gap increases from -0.001 to 0.089, the percentage of shells with NC < 4% increases up to 94%. Then, a further increase of the

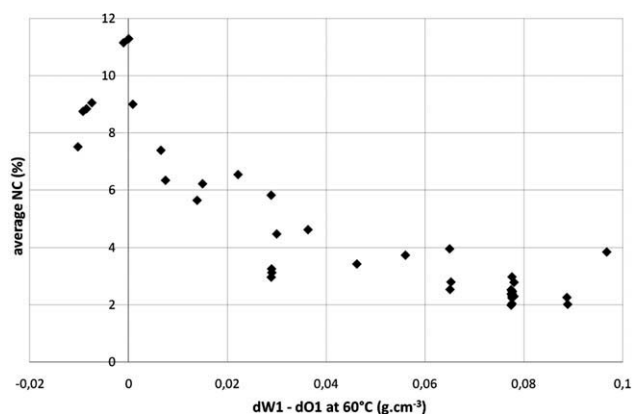


Figure 4 Average shells NC as a function of the density gap between the internal water phase and the organic phase at 60°C for the 29 bottles collected.

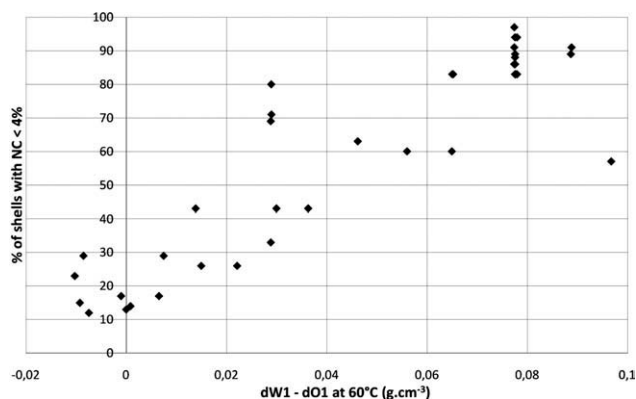
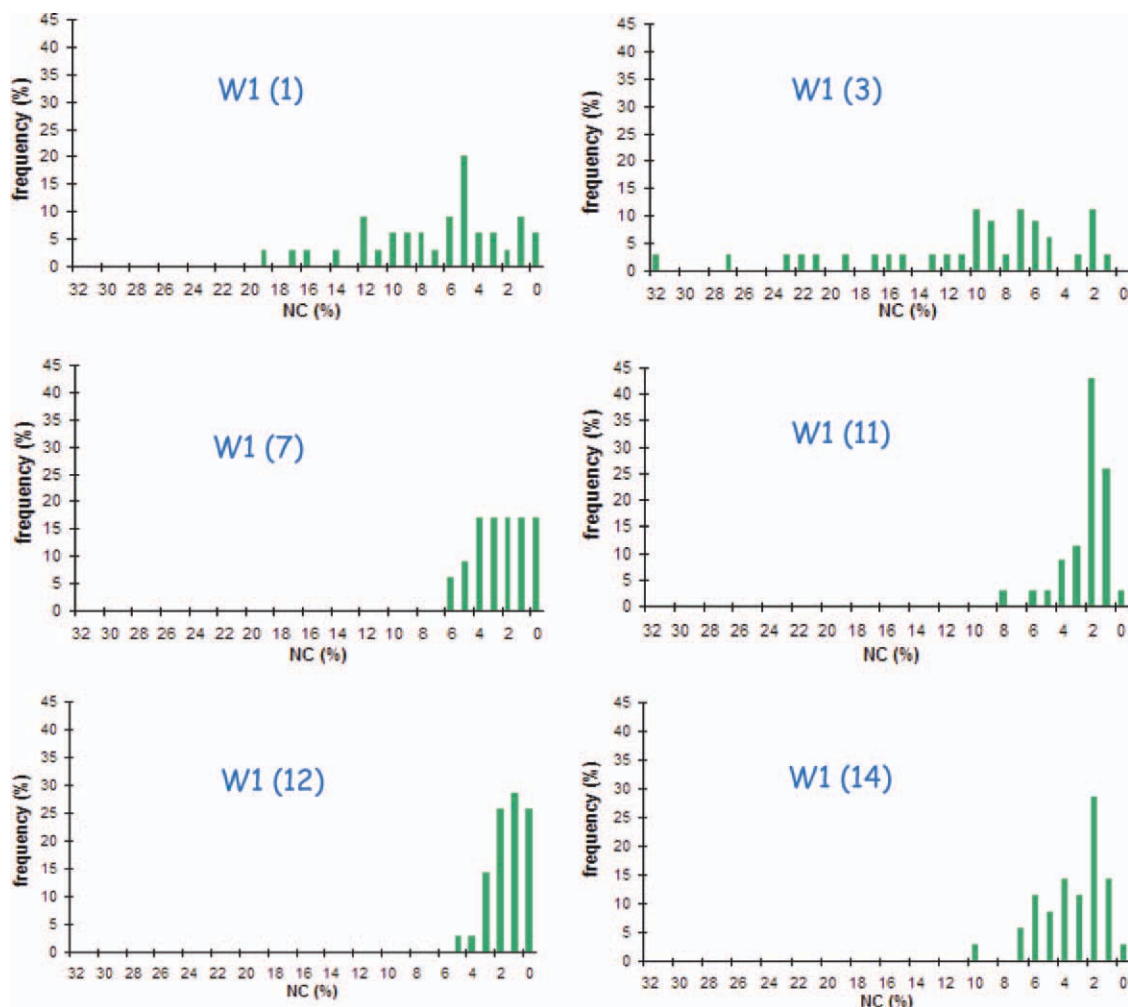


Figure 5 Percentage of shells with NC < 4% as a function of the density gap between the internal water phase and the organic phase at 60°C for the 29 bottles collected.





**Figure 6** Representation of the repartition of shells NC for six internal aqueous phases. Each graph represents the frequency of shells in percent versus the shells NC. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

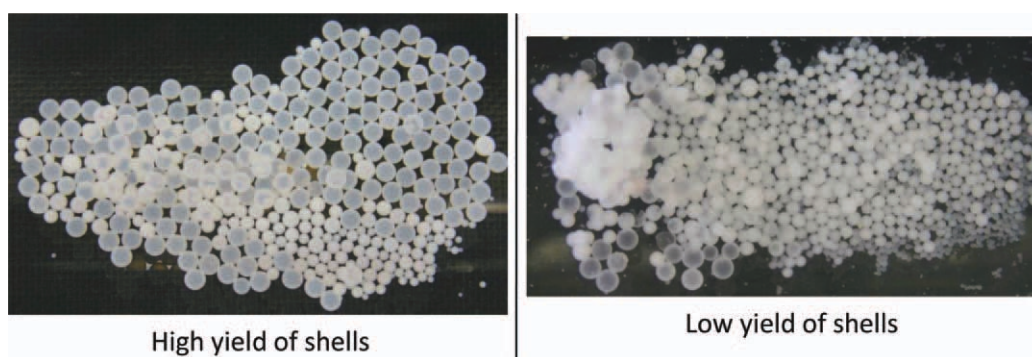
density gap from 0.089 to 0.097 results in decreasing the percentage of shells with  $NC < 4\%$  to a final value of 57%.

The results described in Figures 4 and 5 show that widening the density gap up to 0.089 [W1(13)] will enhance the average NC and the percentage of shells with  $NC < 4\%$ . With a further increase, from 0.089 to 0.097, lower results are obtained. Figure 6, showing the repartition of shells NC, supports this interpretation of the results. Thus, the repartition of shells NC is really wide for W1(1) and W1(3) and becomes narrower with W1(7), (11), (12), and (14). The narrowest repartition is obtained with W1(12), that is, to say with a density difference between W1 and O1 equal to 0.078 at 60°C. All the results obtained also show that better NC results are obtained when the density of the shell is higher than the density of W2 at polymerization temperature.

In addition to the NC study, the yields of the various syntheses were investigated. In each bottle of collected shells, coalescence and phase inversion occurred leading to the formation of beads instead

of shells. Figure 7 shows the difference between two collected bottles, one with a high yield of shells and one with a very low yield of shells.

The yield has been calculated with the number of shells obtained in each bottle at the end of the syntheses, after the alcohol exchanges, compared to 250 shells (the maximum of shells that can be obtained with an untroubled experiment). The yield of shells described in Figure 8 is an average of the yield obtained with each bottle for the same density gap. Overall, the curve shows a bell-shaped profile with yield values higher than 50% for a density gap between  $-0.008$  and  $0.078$  [from W1(2) to W1(12)]. However, the yields are very low for extreme values of the density gap:  $-0.01$ ,  $0.089$ , and  $0.097$  [W1(1), (13), and (14)]. As mentioned before, the best NC results are obtained for both a density gap of  $0.078$  and  $0.089$ . However, the yield of shells for a density gap of  $0.078$  is 50%, whereas it falls to 27% for a density gap of  $0.089$ . A compromise has thus to be made between good NC results and a high yield of shells. This is the reason why the internal water

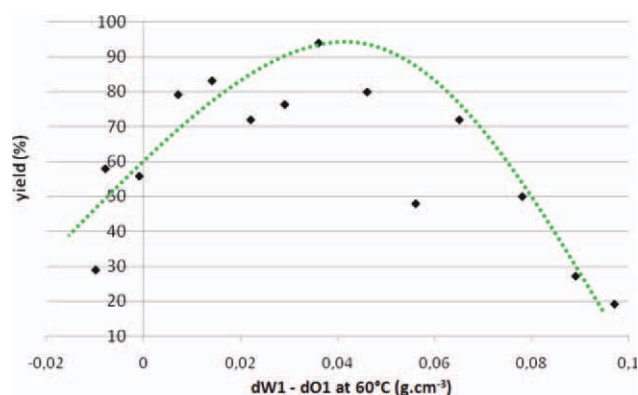


**Figure 7** Pictures of the final products obtained within two different bottles with different experimental parameters. On the left picture, you can see a descent amount of shells with few beads. On the right picture, you can see just a few shells, a lot of beads and an agglomerate of beads. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

phases W1(12) ( $dW1 - dO1 = 0.078$  at  $60^\circ\text{C}$ ) will be used for further experiments.

To check the reproducibility of the process, the first set of experiments [from W1(1) to W1(7)] has been replicated. The results obtained for these two experiments are presented in Figure 9.

As expected, for density gaps inferior to  $-0.001$ , the average NC increases in both experiments. Then, for density gaps higher than  $-0.001$ , the average NC decreases as the density gap between W1 and O1 grows. Both sets of experiment show the same trend meaning that the experiment could be considered as reproducible even if the replicated experiment (second set) shows better results than the first one especially for density gaps higher than  $0.014$ . This means that foam shells NC depend not only on density but also on other process parameters. Density of the shells was controlled for but the one parameter that could not be controlled for is the centering of the needle 1 inside the center of the needle 2, which may have lead to the differences in results between the two sets of experiment. The centering of the capillaries is the only parameter set manually while the others is all set automatically.

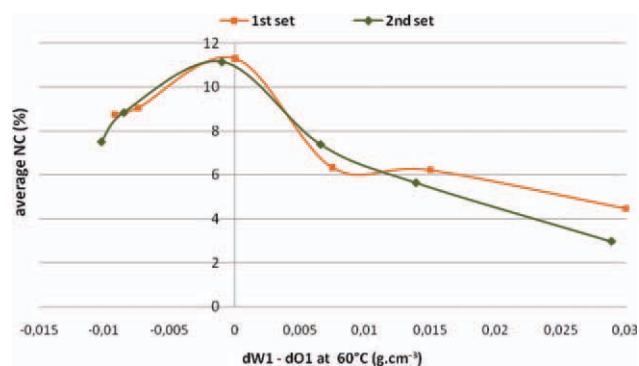


**Figure 8** Yield of shells obtained as a function of the density gap between the internal water phase and the organic phase at  $60^\circ\text{C}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Because the centering of the needle 1 within the needle 2 cannot be perfect, the internal water phase has to center itself within the organic phase to obtain shells with a good NC. Thus, (9), a density mismatch may be beneficial as it allows the internal water phase to move and center inside the organic phase. This could explain why better results of NC are obtained with important density mismatch for TMPTMA foam shells.

## CONCLUSION

The influence of density gaps between the different organic and aqueous phases on the NC of TMPTMA foam shells has been studied. The results show that the density of W1 has to be higher than the density of O1, and the shell density has to be higher than the density of W2 to get shells with a good NC. The best results have been obtained with the internal water phase W1(12), which lead to a density gap of  $0.078$  between O1 and W1 at  $60^\circ\text{C}$ . With W1(12), 94% of the shells have a NC  $< 4\%$  and an average NC of 2% is reached. The replication of an experiment gives the same trend line in the results but the value of the results obtained also depends on other



**Figure 9** Average shells NC as a function of the density gap between the internal water phase and the organic phase at  $60^\circ\text{C}$  for both sets of experiment. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

parameters such as the centering of the needle 1 within the needle 2 inside the droplet generator. Because density is not the only parameter having an influence on NC, deformations, interfacial tensions, and kinetics of polymerization will also be investigated in a further work.

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