# Investigation of flow through P[NIPAM/MMA] copolymer coated glass capillary tubes, and glass copolymer adhesion improvements with hydrofluoric acid etching

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**Abstract**

This study aims to display the retention of the thermo-responsive properties of the copolymer poly(N-isopropyl acrylamide-methyl methacrylate) [P(NIPAM/MMA)] when coated on the inner diameter of a glass capillary tube, and to prove the stability of the copolymer coating when subjected to pressure driven fluid flow. The study shows that the fluid flow through such a capillary tube follows Hagen-Poiseuille flow. Furthermore, this study examines methods of improving polymer adhesion to glass by hydrofluoric acid etching. Such a coated tube system is applicable in drug delivery, self cleaning tubes, and MEMS.

**Introduction**

Copolymers of poly(N-isopropyl acrylamide) [PNIPAM] and poly(methyl methacrylate) [PMMA] have been shown to exhibit thermo-reversible volume phase transition in aqueous surroundings with very small amounts of dissolution.[1] This study proposes coating glass capillary tubes with such a copolymer to observe the effects of the volume phase transition on fluid flow. It was predicted that when the copolymer swells in an aqueous environment the diameter of the tube would decrease. Once heated to the lower critical solution temperature (LCST), the copolymer was expected to shrink and return to its original thickness, thus increasing the diameter of the tube.

For this study, pressure driven flow though a cylindrical pipe was assumed to follow the Hagen-Poiseuille law, which can be described by the relation:

$$Q = \frac{\pi r^4}{8\mu}\left|\frac{\mathrm{d}P}{\mathrm{d}x}\right|$$

where $Q$ represents the volumetric flow rate, $r$ represents the radius of the cylindrical pipe, $\mu$ the viscosity of the fluid traveling through the cylindrical pipe, and $dP/dx$ representing the pressure drop across the pipe. The high dependency of the flow rate on the cylindrical radius reveals that any small change in tube diameter due to the copolymer volume phase transition can have dramatic effects on volumetric flow rate.

One experimental procedure in this study takes advantage of gravity driven flow, which follows the simplified form of Bernoulli's principle:

$$P = \rho g h$$

Where $P$ is the pressure due to a column of liquid, $\rho$ is the density of the fluid, $g$ is the acceleration due to gravity, and $h$ is the height of the liquid column. The experimental procedure utilized a constant liquid height, causing the pressure due to the liquid is constant (assuming the density was constant). This allowed for a constant, steady state pressure drop term in the Hagen-Poiseuille equation.

Adhesion improvement of P(NIPAM/MMA) to glass capillary walls can be achieved by multiple methods, including modification of the chemistry of the glass surface[2,3] and bombardment with nanoparticles. However, a simpler and less material intensive method was desired. It is known that roughening a surface improves mechanical adhesion due to an increase in surface area.[4] To roughen the surface of glass etching by hydrofluoric acid was considered. The chemical reaction between silicon oxide (the main component of glass) and hydrofluoric acid is given by:

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$$

The etching properties of hydrofluoric acid on a glass surface has been well studied in G. Spierings[5].

**Procedure**

The materials used to observe this flow were as follows: for the radical copolymerization, N-isopropyl acrylamide (NIPAM), methyl methacrylate (MMA), 2-methyl-propionitrile (AIBN), pure ethanol, pure hexane, and dimethyl formamide (DMF) were used; to create glass tube tips, Precision Glide hypodermic needles, epoxy, and 1 mm glass capillary tubes were used; for the pressure driven flow setup described in Figure 1, a Omegalynx HPP-2023 pressure gauge was used, as well as standard disposable syringes and tubing.

A 0.25% wt solution of poly(methyl methacrylate/N-isopropyl acrylamide) [P(MMA/NIPAM)] copolymer was prepared via radical copolymerization according to the procedure described by Y. Zhang et al.[1] Glass capillary tubes were placed under ultraviolet light for an hour, then immersed in the copolymer solution for a 20 h period while heated to 60 ° C. The glass tubes were removed from solution, cut in half, and heated until dried. Hypodermic needles were removed from their plastic casing and the dry, coated glass tubes were placed into the plastic holder and sealed with epoxy. After 24 h., the epoxy was set completely, and what will be referred to as a 'glass tube tip' was produced. Two pressure driven flow systems were set up as described by Figure 1 and Figure 2, hereby referred to as Setup 1 and Setup 2, respectively.

*Flow Experiment 1*

Setup 1 used an air filled syringe to drive water through Segment 2, based upon an experimental setup described by S. Sinah Ray et al.[6] A Cole Palmer syringe pump (Cat. No. 780210C) was used to achieve a constant flow rate and the pressure was measured using the pressure gauge. An experimental run began with a measurement of the inner diameter of the a coated glass capillary tube under a microscope at 10x. After closing Stopcock 1 (in Figure 1), the pressure of Segment 1 was raised to approximately 10 millibar. Segment 2 was then filled with water. Stopcock 1 and 2 were opened and the syringe pump was turned, causing the water to flow. Pressure was measured every five seconds as time progressed. Using a coated tube with a wetted room temperature inner diameter of 270 μm, the system was run at three flow rates: 0.5, 1.0, and 2.0 mL/min; and at two temperatures: room temperature and 40°C.

*Flow Experiment 2*

Setup 2 involved a container of water kept at a constant level through the use of a reservoir with an outlet for the glass tube tip at the bottom. The flow rate into the container (from the reservoir) was kept equal than the flow rate out of the container through the glass tube tip to ensure a constant height. An experimental run for this setup involved placing a weighed Petri dish under the container, opening the stopcock and collecting water while timing the interval. The water-containing Petri dish was weighed and the weight of the collected water was determined. Assuming a density for water, the volume of water expelled into the Petri dish over the time period could be calculated, and from this volume and time a flow rate out of the system was calculated. The pressure caused by the liquid column above the tube was calibrated so a liquid jet was maintained out of the capillary tube so that any surface tension effects could be neglected.

*Hydrofluoric Acid Etching*

The P(NIPAM/MMA) adhesion to an HF etched glass surface was examined experimentally. One set of glass capillary tubes received no treatment, one set was placed under UV light a distance of approximately 40 cm from the light source for three hours, and three sets were filled with 2% hydrofluoric acid by capillary action and allowed to sit for 2 minutes, 4 minutes, and 8 minutes. All of these capillary tubes were then coated with the a solution of 0.25% wt copolymer as described by the method above. (The HF treated tubes were safely evacuated by low air flow and rinsed thoroughly with water before coating with the copolymer.) All of these coated tubes were made into glass tube tips (as described above) and were subjected to fluid flow using Setup 2. The pressure in the system was increased until the copolymer coating 'slipped' out of the glass capillary tube. The pressure at which this occurred was deemed the 'fail pressure' and was recorded.

**Results and Discussion**

From the experimental results of a coated glass tube with an inner diameter of 270 μm at a temperature below the LCST, there was a linear correlation between pressure and flowrate observed for both room temperature and elevated temperature. The results are described by Figure 5. The differing slopes are an attribute to the temperature dependence of viscosity of water. However, upon using the experimental flow rate and pressure with the Hagen-Poiseuille relation, the percent error of the calculated radius (with respect to the radius measured under a microscope) was unreasonably high, as shown by the percent error column in Figure 5. This may be attributed to a single or number of systematic errors. Sources of error could include, but are not limited to: an improperly calibrated syringe pump, resulting in an assumed flow rate that may differ from the actual flow rate; an incorrect negligence of the surface tension of the water out of the glass tube; or a misinterpretation of the pressure gauge reading. Furthermore, the data is not complete; more data points must be taken and evaluated, and more glass tubes must be examined.

The results of Setup 2 are described in Figure 6. The percent error of the calculated radius for all three tests are very small, however the copolymer did not achieve volume phase transition as indicated by similar measured radii. The failure of volume phase transition could be due to copolymer crystal degradation prior to preparing the copolymer solution, as the copolymer crystals were prepared many months prior to the experiment.

Thus, a new copolymer solution was made, and new tubes were prepared and tested in a the same manner. The result of a test at room temperature is described at the bottom of Figure 6. Unfortunately the diameter of the tube continued to decrease as the experiment progressed until the water flowed out of the capillary tube in droplets rather than jet flow, suggesting that the copolymer water absorption threshold had not been met prior to the experiment. This was attributed to a large thickness of polymer coated caused by too large of a concentration.

To decrease the coating thickness, a new copolymer solution with a 0.17% wt concentration was made. After 4 experimental runs, it was noted that the copolymer suffered damage due to the flow (which is seen in Figure 7), thus affecting results. It is speculated that a decrease in concentration caused a weak copolymer structure.

The preliminary results of the HF etching experiment are described in Figure 8. While more data points need to be taken, the general trend appears to be that as the time allowed for HF to react with the glass increases, the fail pressure increases. It is also notable that half of the coating still visibly remained for the 8 minute HF treated tube, suggesting high adhesion to glass.

## Conclusion

In this study, two systems were considered to observe flow through a copolymer coated glass capillary tube. Setup 1 shows promise through the linear correlation displayed by the data, but errors must be dealt with before this becomes a reliable method. Thus, the system as is is not a recommended method to observe fluid flow of this type. Setup 2 was very precise, which can be shown by the small standard deviation of the radius calculations. It has also been proven to be accurate, exhibited by the relatively low percent error. Thus, this method may be best to conduct such a study. Finally, P(NIPAM/MMA) copolymer adhesion to the inside of glass capillary tubes is increased as the time allowed to react increases for the range of two to eight minutes.

Suggestions for future work include: further investigating the hydrofluoric acid etching treatment; comparing the hydrofluoric acid treatment to saline treatments examined previously and to a novel process of nanoparticle powder bombardment; further calibrating the copolymer concentration to optimize the coating thickness to maintain jet flow within the Setup 2; and to attempt to cross link copolymer to improve structural rigidity.

## Acknowledgments

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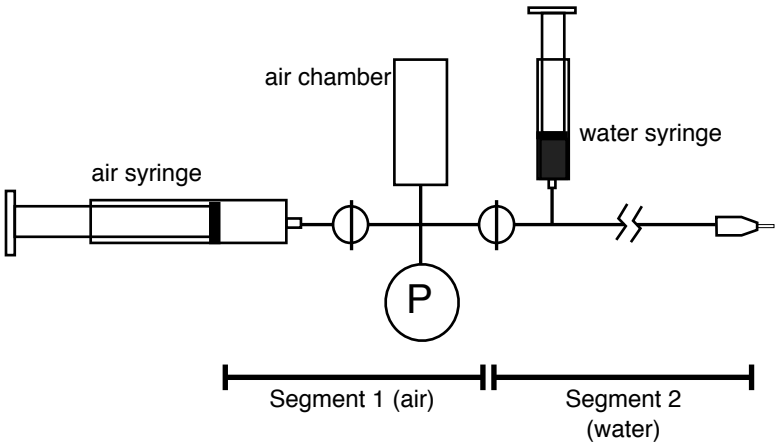



**Figure 1** Schematic of the first experimental setup, utilizing a constant flow rate. The syringe pump, not represented in this diagram, was used on the left-most syringe to drive air into Segment 1. This supplied the pressure for the the water flow in Segment 2.

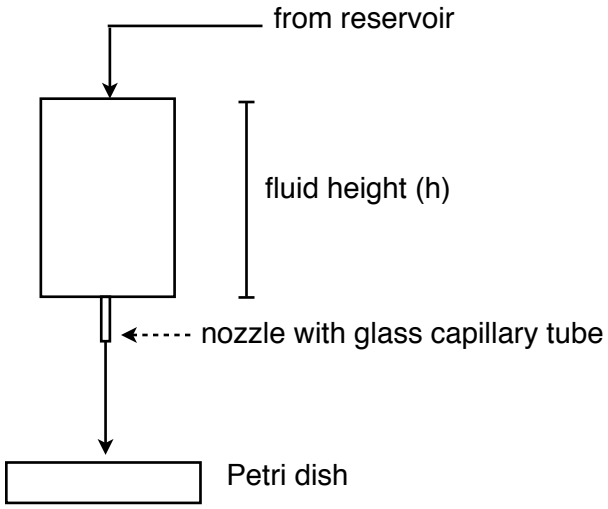
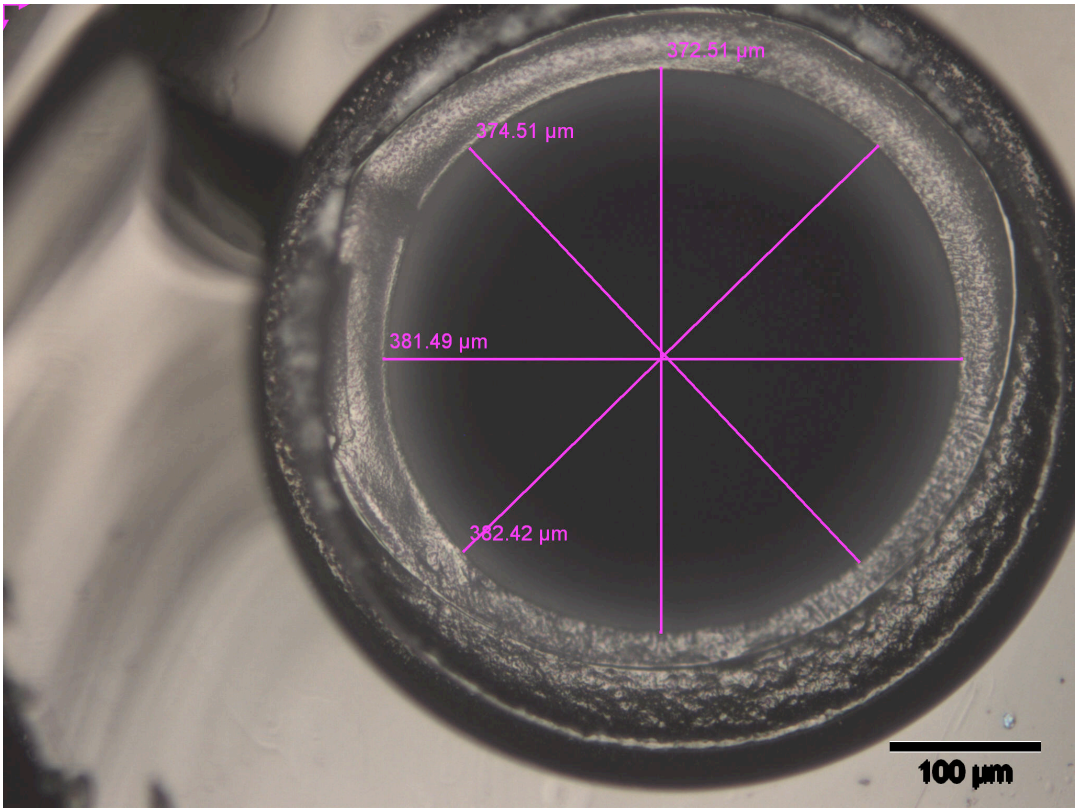



**Figure 2** Schematic of the second experimental setup. Gravity drives water flow through the glass tip into the Petri dish, and is weighed to find the volume of water expelled over a period of time.


372.51 µm
374.51 µm
381.49 µm
382.42 µm
100 µm

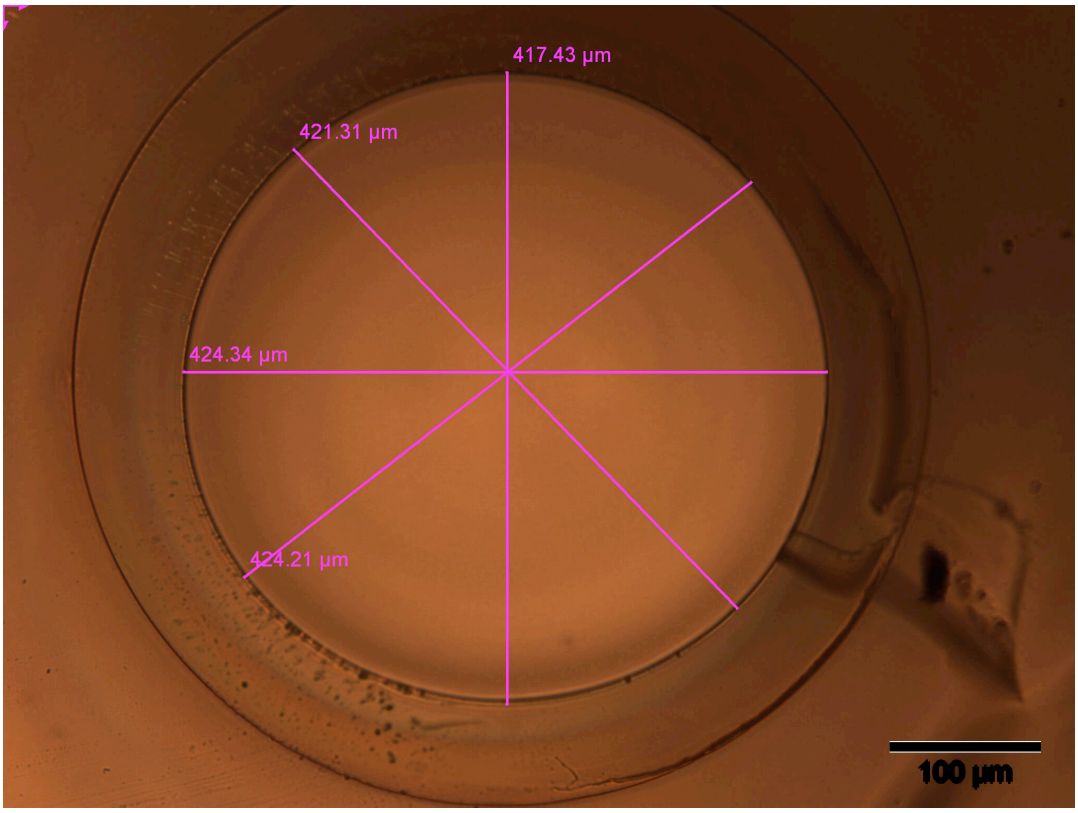

417.43 µm
421.31 µm
424.34 µm
424.21 µm
100 µm

**Figure 3** Tube cross sections viewed under a microscope at 10X exhibiting the swelling of the copolymer coating ***Left*** A coated tube heated at 50 ºC, thus in its 'shrunk' state. ***Right*** A tube that has been submerged in water for 5 minutes at room temperature. Note the decrease in diameter when cooled in an aqueous environment.

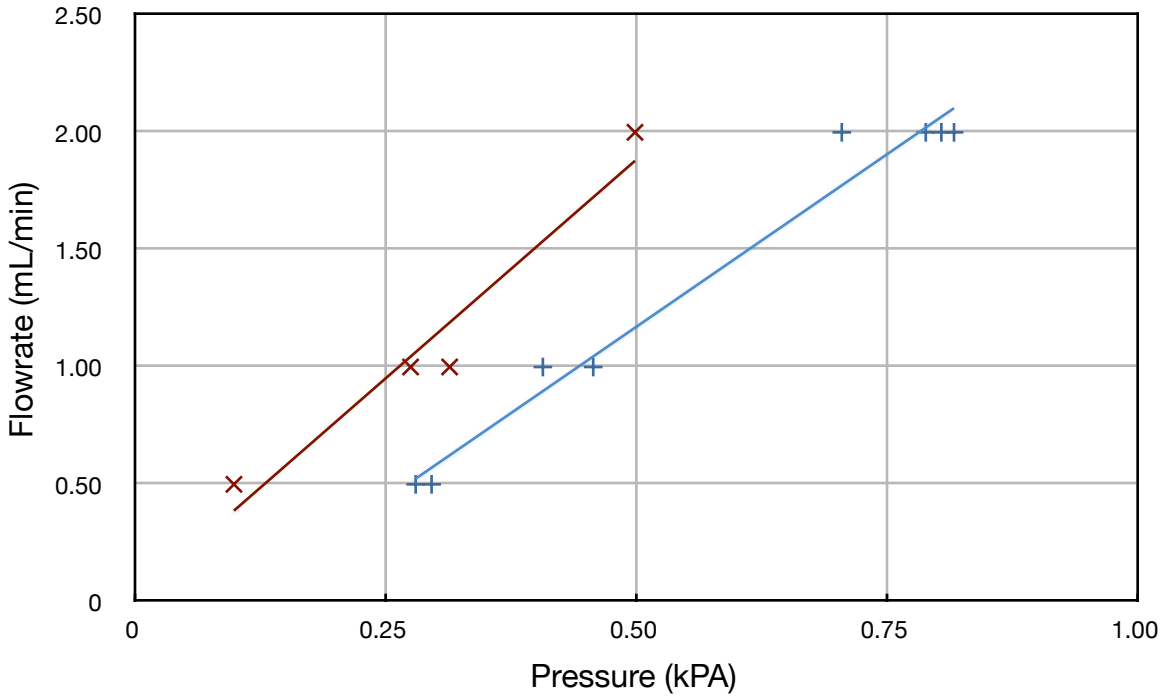



**Figure 4** The flow rate versus average pressure for the first experimental setup. The 'x' marks represent the room temperature trials, whereas the '+' marks represent the elevated temperature trials.

| Temperature (K) | Flow rate ($cm^3sec^{-1}$) | Calculated radius (μm) | Radius error (%) |
|---|---|---|---|
| 296.85 | 0.0083 | 453 | 236 |
| 296.65 | 0.0167 | 488 | 261 |
| 296.725 | 0.0333 | 500 | 271 |
| 313.15 | 0.0083 | 463 | 243 |
| 313.15 | 0.0167 | 492 | 264 |
| 313.15 | 0.0333 | 513 | 280 |

**Figure 5** The radius as calculated by the Hagen-Poiseuille equation using experimental pressure and flowrate for Setup 1.

| | Optically Measured Radius (μm) | Average Calculated Radius (μm) | Radius Standard Deviation (μm) | Radius error (%) |
|---|---|---|---|---|
| **Non-Coated Tube** | 282.5 | 249.5 | 0.11 | 11.7 |
| **Coated Tube 1 at Room Temp.** | 233.1 | 227.8 | 0.04 | 2.27 |
| **Coated Tube 1 at 50 C** | 229.1 | 204.4 | 0.25 | 10.8 |
| | | | | |
| **Coated Tube 2 at Room Temp.** | -- | 215.6 | 0.73 | -- |
| | | | | |

**Figure 6** The radius as calculated by the Hagen-Poiseuille equation using the experimental flowrate for Setup 2.

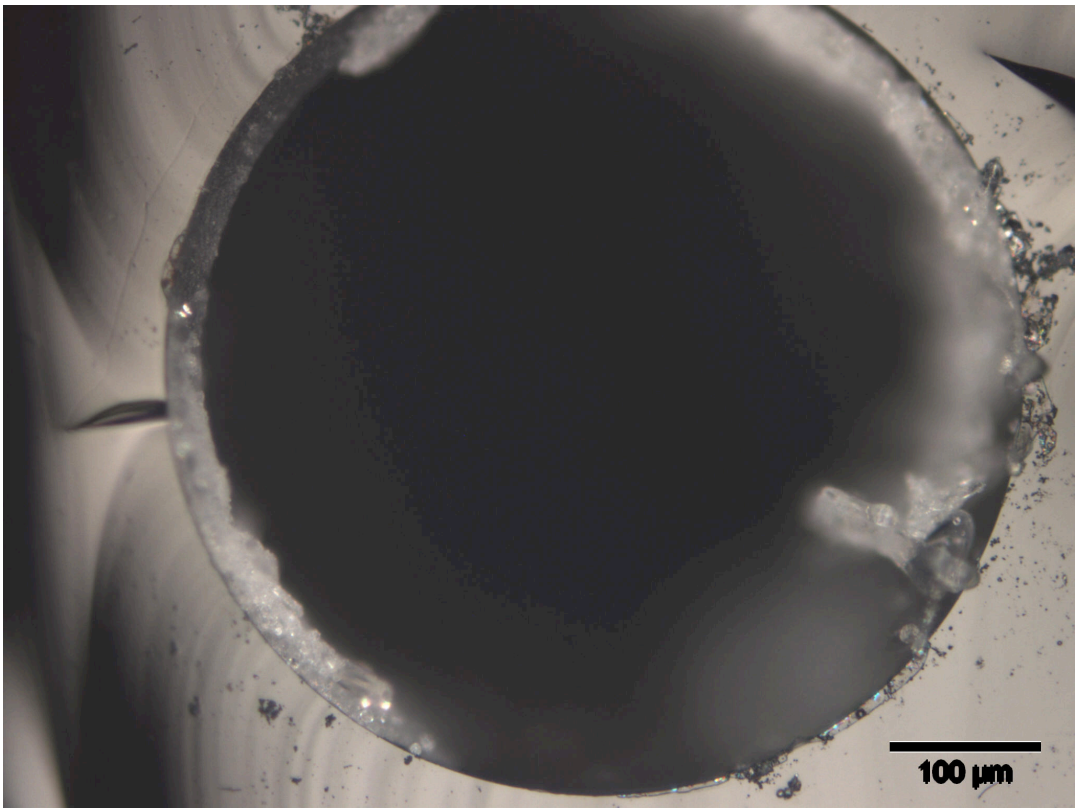



**Figure 7** The structural damage after 4 runs with a 0.17% wt P[NIPAM/MMA] copolymer.

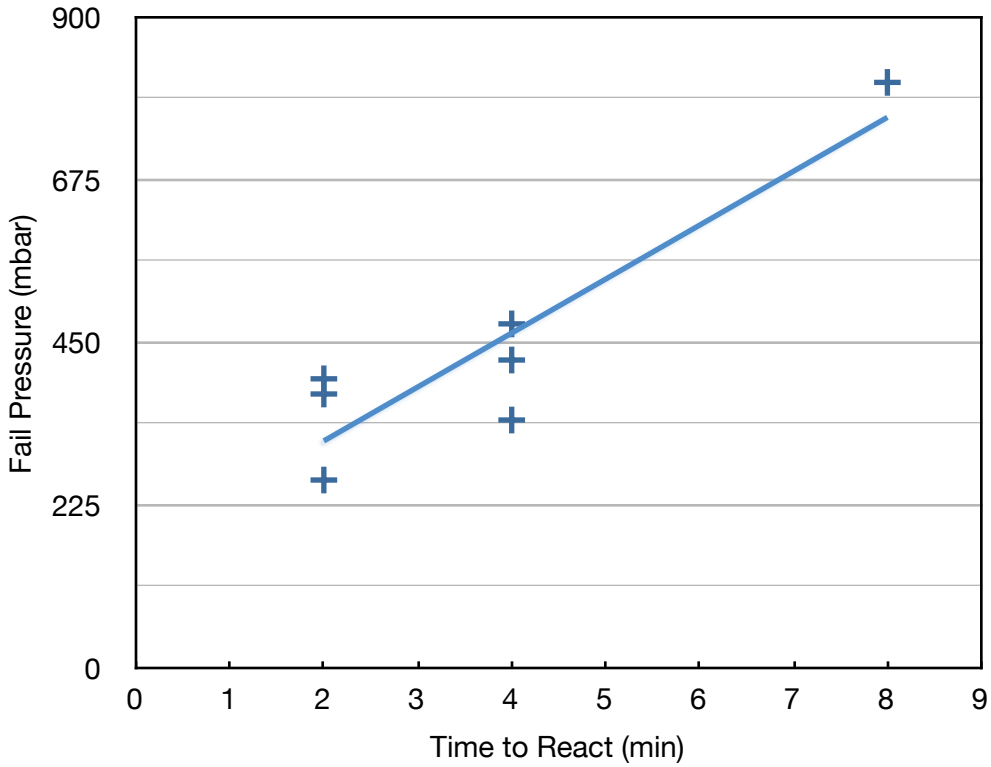



**Figure 8** The fail pressure versus time for the hydrofluoric acid etching experiment.