



NE 335 Macromolecular Science 2

University of Waterloo
Nanotechnology Engineering

DEPARTMENT OF CHEMISTRY

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1. Introduction

Objective

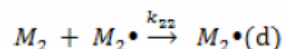
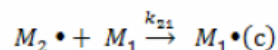
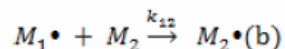
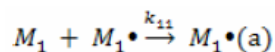
The main objective of this experiment is to perform the radical copolymerization of styrene and methyl methacrylate, and to study the effects of various free styrene mole fraction in the mixture on the styrene mole fraction in the resulting copolymer. The reactivity ratios of styrene and MMA (r_{sty} and r_{MMA} respectively) are also calculated using non-linear least squares and the Finemann Ross methods.

Background

Homopolymers are polymers that contain one type of repeating unit throughout their entire chain. There are many applications associated with homopolymers, including plexiglass and natural rubber [1]. Although sometimes the properties of one single monomer are sufficient to achieve desired properties within a material, there are sometimes drawbacks as well. Researchers have hence combined various homopolymer mixtures to form new types of polymers that exploit the desired properties of more than one type of monomer [2]. These polymers are known as block copolymers.

Many methods of copolymerization are available, such as condensation polymerization, radical polymerization, and ionic polymerization [1]. With the myriad of monomers available and the range of polymerization methods listed below, there are literally hundreds of types of copolymers that can be formed via different choices of monomers and technique. In a typical copolymerization reaction, the initial mole fractions of each monomer determine the mole fraction of the resultant copolymer at any given time. Different initial concentrations will thus yield copolymers of different compositions, which is an important implication of the structure of the copolymer.

Taking a look at the reaction kinetics, it is assumed that the growth of the polymer is only affected by the nature of the ends of the growing chain and that of the monomers involved in the reaction [1]. The following four rate equations show the possible reaction mechanisms that happens during copolymerization:



In the above expressions, M_1 and M_2 correspond to monomers 1 and 2, and $M_1 \cdot$ and $M_2 \cdot$ are the radical chain ends. k_{11} , k_{12} , k_{21} , k_{22} are the kinetic rate constants, where the first number in the constant refers to the monomer present at the radical chain end and the second number represents the monomer to be added. Another variable, the reactivity ratio, is introduced. The respective reactivity ratios of monomer 1 and monomer 2 can be defined as follows:

$$r_1 = k_{11}/k_{12} \quad \text{Eq (1)}$$

$$r_2 = k_{22}/k_{21} \quad \text{Eq (2)}$$

To determine the reactivity ratios of the monomers in a reaction, a series of experiments must be performed at various initial monomer concentrations. It is important to relate the mole fraction of free monomer in a mixture to the mole fraction of the monomer in the growing copolymer chain at any given value. The equation describing such relationship is given as follows:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \quad \text{Eq (3)}$$

In Eq (3), F_1 is the mole fraction of monomer 1 in the growing copolymer. r_1 and r_2 are the reactivity ratios of monomers 1 and 2 respectively as described in Eq (1) and (2). f_1 and f_2 corresponds to the mole fraction of free monomer 1 and 2, respectively, in a mixture of monomers 1 and 2.

Eq (3) can be solved using various numerical methods. In the end, the azeotrope compositions of the copolymer can be determined. An azeotropic feed is the point in the reaction where F_1 is equal to f_1 , meaning that the compositions of the reaction mixture and the growing copolymer are exactly the same. To solve Eq (3), two methods investigated in this lab are non-linear least squares and Finemann Ross methods. Non-linear least-squares makes use of the sum of the square errors of an estimated F_1 value compared to the actual experimental value. By minimizing the sum of square errors, it is possible to solve for the constants r_1 and r_2 . The Finemann Ross method is achieved by substituting:

$$x = [M_1] / [M_2], \quad y = d[M_1] / d[M_2]$$

where $[M_1]$ and $[M_2]$ are the concentrations of monomers 1 and 2 respectively and $d[M_1]$ divided by $d[M_2]$ is the molar ratio of the two monomers in the copolymer. Having done this, the values of x and y are fitted such that:

$$y = x \frac{1 + r_1 x}{r_2 + x} \quad \text{Eq (4)}$$

so that Eq (4) can be linearized as:

$$G = \frac{x(y-1)}{y} = r_1 F - r_2 \quad \text{Eq (5)}$$

where $F = x^2 / y$. Then the method of linear least squares can be used to fit Eq (5), where r_1 is the slope of the plot and r_2 is its y-intercept [1].

The reactivity ratios provide some insight on the behaviours of each monomer in the copolymerization. In general, if $r > 1$ for a given monomer, it means that this monomer prefers to add to its own species. Conversely, if $r < 1$ for a given monomer, it means that this monomer prefers to add to the other monomer that is involved in the reaction. The product of the reactivity ratios is also an important parameter to be considered. If both r_1 and r_2 are much less than 1, then the product $r_1 r_2$ would be close to zero, implying that alternating polymerization is favoured since both monomers 1 and 2 have the tendency to add to each other. In the case of $0 < r_1 r_2 < 1$, both reactivity ratios are still less than 1, and this is the most common case. In the situation where one monomer has an r value greater than 1, the copolymerization initially is dominated by this species, which is the more reactive monomer. Analyzing reactivity ratios and their products is hence a useful way of determining how a given monomer will react in copolymerization.

2. Experimental

The majority of the procedures were followed exactly as specified in the NE 335 lab manual [1]. The following minor changes were made:

- In step 1, four solutions were prepared instead of five (100% styrene was removed).
- In step 8, the solids were not air dried. Instead they were placed in a pump and dried for 20 minutes.
- For the procedures involving UV/Vis spectroscopy, spectra were recorded for each solution from 250 nm to 250 nm as opposed to 200 nm to 350 nm.

3. Results

Mole Fraction of Monomers

Sample calculation for vial #1.1:

Molar mass of Styrene (g/mol) = 104.15 g/mol

Molar mass of MMA (g/mol) = 100.12 g/mol

Moles of styrene = (Mass of styrene / Molar mass of Styrene) = (27.4826 g) / (104.15 g/mol) = 0.264 mol

Moles of MMA = (Mass of MMA / Molar mass of MMA) = (65.6560 g) / (100.12 g/mol) = 0.656 mol

Mole fraction of styrene = (Mol of styrene) / (Mol of styrene + Mol of MMA) = 0.264 / (0.264 + 0.656) = 0.287

Mole fraction of MMA = (1 – mol fraction of styrene) = 1 – 0.287 = 0.713

The results for the rest of the vials are tabulated below:

Mass of styrene (g)	Moles of styrene	Mol Fraction of Styrene	Mass of MMA (g)	Moles of MMA	Mol fraction of MMA
27.4826	0.26387518	0.2869	65.6560	0.655773072	0.7131
35.6704	0.342490639	0.3749	57.1810	0.57112465	0.6251
54.6650	0.524867979	0.5824	37.6830	0.376378346	0.4176
70.3052	0.675037926	0.7596	21.3920	0.213663604	0.2404

Mole Fraction of Copolymers*Sample calculation for vial #1.1:*

Mass of CHCl_3 = Mass of (Vial + Cap + Polystyrene + CHCl_3) – Mass (Vial + Cap + Polystyrene) = 31.3048 g – 16.4737 g = 14.8311 g

Volume of CHCl_3 = Mass of CHCl_3 / Density of CHCl_3 = (14.8311 g) / (1.492 g/mL) = 9.94 mL

Abs(269) of styrene = Abs(269.1) – Abs(350) = 0.443 – 0.00285 = 0.4423

Mole fraction of styrene in copolymer (using Eq. 6 in the manual):

$$\begin{aligned}
 x &= \frac{M_{MMA}}{\frac{m}{V} \frac{\epsilon_{sty}(270\text{nm})}{Abs(270\text{nm})} + M_{MMA} - M_{Sty}} \\
 &= \frac{100.12 \text{ g/mol}}{\frac{0.0099 \text{ g}}{0.00994 \text{ L}} \frac{169.2533 \text{ M}^{-1} \text{ cm}^{-1}}{0.4423 \text{ cm}^{-1}} + 100.12 \text{ g/mol} - 104.15 \text{ g/mol}} \\
 &= 0.2655
 \end{aligned}$$

Mole fraction of MMA in copolymer = (1 – mol. Fraction of styrene) = 1 – 0.2655 = 0.7345

The results for the rest of the vials are tabulated below:

Vial #	m (g)	Mass of CHCl ₃ (g)	CHCl ₃ Vol. (mL)	Abs(269) of styrene (cm ⁻¹)	Mol fraction of styrene	Mol fraction of MMA
1.1	0.0099	14.8311	9.940416	0.442302	0.2655	0.7345
1.2	0.0128	14.8542	9.955898	0.60806	0.2830	0.7170
2.1	0.0094	14.8326	9.941421	0.533489	0.3383	0.6617
2.2	0.0127	14.8157	9.930094	0.724399	0.3396	0.6604
3.1	0.0103	14.8137	9.928753	0.799738	0.4646	0.5354
3.2	0.0104	14.782	9.907507	0.791621	0.4543	0.5457
4.1	0.0097	14.857	9.957775	0.978255	0.6086	0.3914
4.2	0.0100	14.7953	9.916421	0.969464	0.5820	0.4180

4. Discussion

Proof of Eq (6)

Equation (6) states that:

$$x = \frac{M_{MMA}}{\frac{m \epsilon_{sty}(270nm)}{V Abs(270nm)} + M_{MMA} - M_{sty}}$$

Derivation:

$$x = \text{fraction styrene} = \frac{\text{mol (Sty)}}{\text{mol (Sty)} + \text{mol (MMA)}} \quad \begin{array}{l} m = \text{mass} \\ M = \text{molar mass} \end{array}$$

$$x = \frac{\frac{m_{sty}}{M_{sty}}}{\frac{m_{sty}}{M_{sty}} + \frac{m_{MMA}}{M_{MMA}}} = \frac{\frac{m_{sty}}{M_{sty}}}{\frac{m_{sty} M_{MMA} + m_{MMA} M_{sty}}{M_{sty} M_{MMA}}}$$

$$x = \frac{m_{sty} M_{MMA}}{m_{sty} M_{MMA} + m_{MMA} M_{sty}} = \frac{M_{MMA}}{M_{MMA} + \frac{m_{MMA} M_{sty}}{m_{sty}}}$$

$$m = \text{total mass of polymer}; \quad m_{MMA} = m - m_{sty}$$

$$x = \frac{M_{MMA}}{M_{MMA} + \frac{M_{sty}}{m_{sty}}(m - m_{sty})} = \frac{M_{MMA}}{M_{MMA} + \frac{M_{sty}}{m_{sty}}m - M_{sty}}$$

$$\text{Beer's Law (Styrene): } Abs(\lambda) = \epsilon(\lambda) CL$$

$$\text{Since } L=1, \quad Abs = \epsilon C \rightarrow C_{sty} = \frac{Abs}{\epsilon}$$

$$m_{sty} = M_{sty} \times C_{sty} \times V$$

$$m_{sty} = M_{sty} \times V \times \frac{Abs}{\epsilon}$$

$$x = \frac{M_{MMA}}{M_{MMA} + \frac{M_{sty}}{M_{sty}} \frac{\epsilon}{Abs} \frac{m}{V} - M_{sty}}$$

$$x = \frac{M_{MMA}}{\frac{m}{V} \frac{\epsilon_{sty}(270nm)}{Abs(270nm)} + M_{MMA} - M_{sty}} = \text{Eq. (6).}$$

Finemann-Ross Data Calculations

Sample Calculation for Vial #1.1:

$$x = \frac{[M_1]}{[M_2]} = \frac{\text{mol of styrene}}{\text{mol of MMA}} = \frac{0.2639}{0.6558} = 0.4023$$

$$y = \frac{d[M_1]}{d[M_2]} = \frac{\text{mol fraction of styrene in co-polymer}}{\text{mol fraction of MMA in co-polymer}} = \frac{0.2655}{0.7345} = 0.3615$$

$$G = \frac{x(y-1)}{x} = \frac{0.4023(0.3615-1)}{0.3615} = -0.7107$$

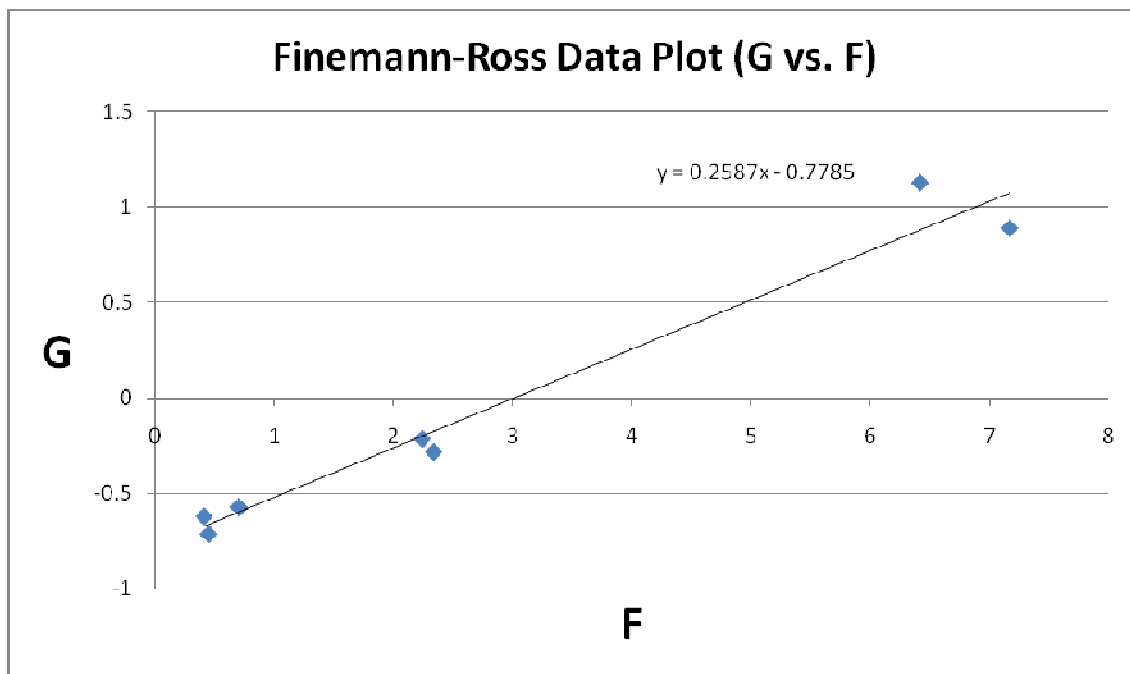
$$F = \frac{x^2}{y} = \frac{0.4023^2}{0.3615} = 0.4479$$

G and F values for the remaining vials are summarized below:

Vial #	x	y	G	F
1.1	0.402388	0.361498	-0.71072	0.447903
1.2	0.402388	0.394615	-0.61731	0.410314
2.1	0.599678	0.511262	-0.57326	0.703383
2.2	0.599678	0.514306	-0.56632	0.69922
3.1	1.394522	0.867597	-0.21282	2.24147
3.2	1.394522	0.832363	-0.28086	2.336352
4.1	3.159349	1.554979	1.127586	6.419048
4.2	3.159349	1.392376	0.890315	7.168673

Finemann-Ross Data Plot

Plotting G vs. F:

***Non-Linear Least Squares***

Non-linear least squares (NLLS) curve fitting was performed using Excel SOLVER. The mole fractions of free styrene and MMA in the mixture were plotted against the mole fraction of styrene in the copolymer using the following equation [1]:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}$$

Initial guesses of r_1 and r_2 of 0.5 and 0.5 were made, and F (calc) represents values obtained when the guesses were used as parameters in the above equation. The sum of square errors (SSE) was then calculated using actual values of F_1 and the calculated values of F_1 with the guesses. SOLVER then minimizes the SSE by changing the

parameters r_1 and r_2 . The following table shows the final results and the optimized values of r_1 and r_2 .

r (sty)	r (MMA)
0.2554	0.7713

Sample	F (sty)	f (sty)	f (MMA)	F (calc)	F (sty - calc)²
1.1	0.2655	0.2869	0.7131	0.2743	7.786E-05
1.2	0.283	0.2869	0.7131	0.2743	7.528E-05
2.1	0.3383	0.3749	0.6251	0.3353	9.028E-06
1.1	0.3396	0.3749	0.6251	0.3353	1.853E-05
3.1	0.4646	0.5824	0.4176	0.4662	2.421E-06
3.2	0.4543	0.5824	0.4176	0.4662	1.406E-04
4.1	0.6086	0.7596	0.2404	0.5922	2.681E-04
4.2	0.582	0.7596	0.2404	0.5922	1.046E-04
				SSE	6.963E-04

Reactivity Ratios

The reactivity ratios are the slope and intercepts of the Finemann-Ross (FR) data plot.

$$r_{sty} = 0.2587$$

$$r_{MMA} = 0.7785$$

$$r_{sty}r_{MMA} = 0.2014$$

The reactivity ratios obtained from NLLS are as follows.

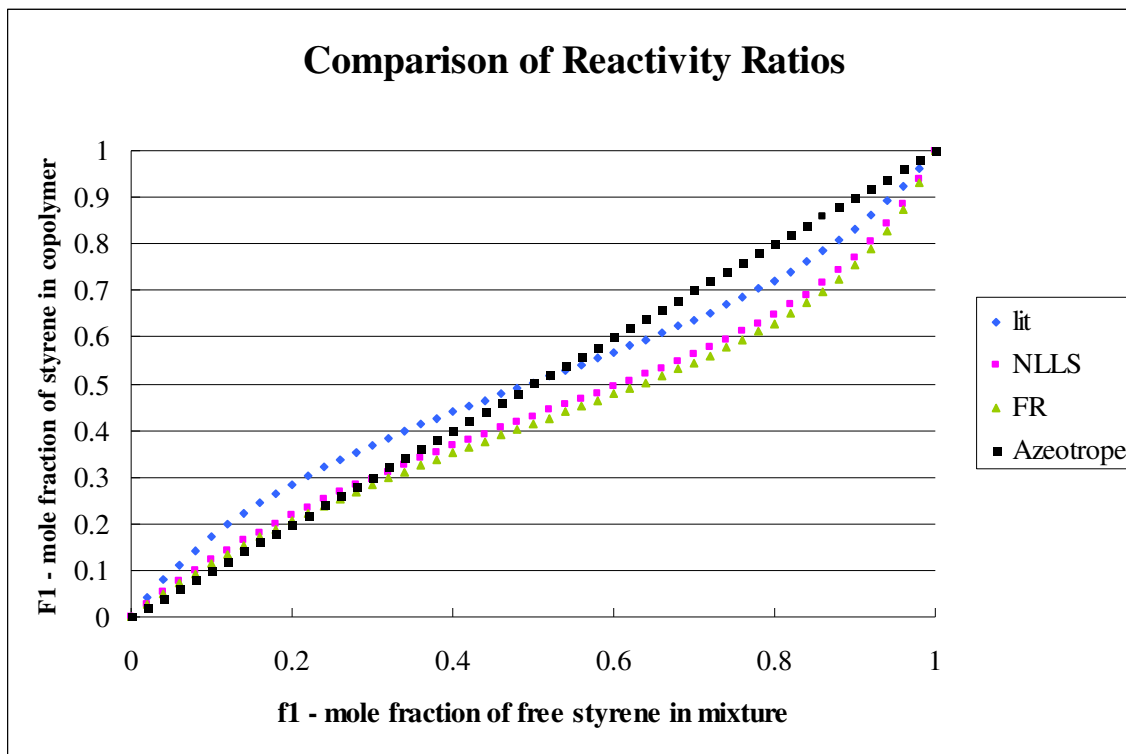
$$r_{sty} = 0.2554$$

$$r_{MMA} = 0.7713$$

$$r_{sty}r_{MMA} = 0.19696$$

ML Curves and Azeotropes

The expected curves for F_{sty} versus f_{sty} using all three sets of reactivity ratios – literature, NLLS, and FR – are shown below. The azeotrope curve, which is essentially nothing but $F_{\text{sty}} = f_{\text{sty}}$, is also displayed on the same plot.



Taking a look at the figure, all three plots exhibit a similar trend. Starting at the origin, the plots show an inverse S-shape configuration. F_{sty} increases rapidly at low f_{sty} values. Then it reaches a relatively linear region at around $f_{\text{sty}} = 0.3$ until f_{sty} reaches approximately 0.8 in which case F_{sty} increases rapidly until the end. The black straight line refers to an azeotropic feed in which case $F_{\text{sty}} = f_{\text{sty}}$ for all values of f_{sty} . Analyzing the plot of the azeotropic feed and comparing it with the other plot, one can determine the values of f_{sty} in which an azeotropic feed is achieved at different reactivity ratios.

Azeotropic Feeds

An azeotropic feed mixture refers to the point where copolymer composition matches the free monomer composition [1]. In the plot shown above, this refers to the points where the azeotrope line intersects with the three other lines, indicating that at those points, F_{sty} is equal to f_{sty} . Zooming in to the plot reveals the following azeotropic feeds for the r values obtained using the different methods.

Literature value: azeotropic feed occurs at $f_{sty} = 0.51$

NLLS method: azeotropic feed occurs at $f_{sty} = 0.33$

Finemann-Ross method: azeotropic feed occurs at $f_{sty} = 0.21$

Comparison of Reactivity Ratios

As mentioned in the introduction, the product of the reactivity ratios gives information on how the monomers will react in the copolymerization reaction. Going back to the previous calculation, it was shown that $r_{sty}r_{MMA}$ equals approximately 0.20 in both NLLS and FR. It is indicated that when two monomers have different reactivity ratios, the resulting copolymer will contain a higher fraction of the more reactive monomer, which is the one with the higher r value. In this case, r_{MMA} is 0.77 where r_{sty} is 0.25, which means that the copolymer will have a higher proportion of MMA. The results obtained in the earlier part of the report showing the mole fractions of MMA and styrene in the copolymer complement this observation.

Referring back to the plot of the comparison between the reactivity ratios obtained from different methods, there's a significant gap between them and the literature values. The pink and green data plots, corresponding to the NLLS method and FR methods respectively, are very close to each other. It is evident that the r_{sty} and r_{MMA} values outputted by the two analysis methods agree with each other to a high degree. However,

these values are much lower than obtained literature values, which are represented by the blue data plots.

The discrepancies can be explained in several ways. Many r_{sty} and r_{MMA} values from literature are unreliable due to the methods of calculation and analysis [1]. The accuracy of the reactivity ratios depends not only on the experimental techniques involved in the performance of the lab, but as well as the method of analysis. For instance, various numerical methods can be used to yield the results, but each method may give a slightly different answer.

Furthermore, many errors and uncertainties were incorporated with the experiment. The volatility of the solvent, chloroform, probably contributed to the inaccuracy in the data, as chloroform evaporates rapidly, causing the loss of mass and volume and thereby skewing the results. The handling of the samples may have also contributed to inaccuracy. Contamination may have occurred during steps such as the handling of quartz cuvettes and the transfer of samples into the solvent. Loss of mass was also possible during the polymerization steps as samples had to be poured several times from one apparatus to another. The earlier the uncertainties were incorporated the experiment, the more they affect the final results as the uncertainties carry through from step to step.

5. Questions

The answers to the questions 1 and 2 are attached as hand-written sheets.

3. If you start a reaction with a styrene MMA copolymerization mixture that is not an azeotropic feed composition, outline in general terms what will happen to the measured copolymer composition as monomer conversion goes from 0 to 100%.

The answer to this question can partially be found by looking back at the graph displaying the comparison between the different reactivity ratios. Evidently, an azeotropic solution would yield the straight line, $F_{\text{sty}} = f_{\text{sty}}$ since the mole fraction of free

styrene in mixture would be the same as the mole fraction of styrene in the copolymer at all times. However, non-azeotropic feeds give an inverse S-shape configuration. At $f_{\text{sty}} = 0$, $F_{\text{sty}} = 0$ naturally because there is no styrene monomer in the solution. At $f_{\text{sty}} = 100$, then clearly $F_{\text{sty}} = 100$ because the entire solution is composed of styrene.

Changing the reactivity ratios of styrene and MMA will change the shape of the curve. The relative magnitudes of the two values will determine the amount of contribution of styrene and MMA in the copolymerization. If r_{sty} is greater than r_{MMA} , then the copolymerization will be largely dominated by styrene. Conversely, if r_{MMA} is greater than r_{sty} , then the copolymerization will be largely dominated by MMA as the monomer conversion goes from 0 to 100%.

6. References

- [1] N. McManus, M. Tam, J. Duhamel, *Nanotechnology Engineering NE 335 Lab Manual*, University of Waterloo, Waterloo, pp. 2-1 to 2-12 (2008).
- [2] M. Tam, *Nanotechnology Engineering NE 335 Lecture Notes*, University of Waterloo, Waterloo, slide set 2 (2008)