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2026

Polymer techniques:
Book of laboratory reports and practical learnings

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Dados Internacionais de Catalogação na Publicação (CIP)
(Câmara Brasileira do Livro, SP, Brasil)

D155p Damásio, Renato Augusto Pereira.
Polymer Techniques [recurso eletrônico] : Book of Laboratory Reports and Practical Learnings / Renato Augusto Pereira Damásio. – São José dos Pinhais, PR: Editora Seven, 2026.
Dados eletrônicos (1 PDF).

ISBN 978-65-6109-390-3

1. Engenharia. 2. Polímeros. 3. Laboratório. 4. Processo. I. Título.

CDU 678.7

Bruna Heller - Bibliotecária - CRB10/2348

Índices para catálogo sistemático:

1 Polímeros 678.7

DOI: 10.56238/livrosindi202676-001

Seven Publications Company
CNPJ: 43.789.355/0001-14
editora@sevenevents.com.br
São José dos Pinhais/PR

AUTOR DO LIVRO

Hey! I am Renato Damásio!

You can call me Re!

This collection of laboratory reports are examples of the knowledge and skills I have developed through the Polymer techniques during the fall 2024.

PhD and researcher

Currently, I am a PhD student at SUNY College of Environmental Science and Forestry. I received Master's and License degree in Forestry Sciences from Lisbon University- Portugal. In 2015, I completed my master's degree in forestry sciences in 2015 from the Federal University of Viçosa and graduated with Forestry Engineering degree from the Federal University of Viçosa in 2013. I have contributed to journal publications and patents through collaborative work. I have participated as a Scientific Initiation Fellow in many projects. I have worked as a specialist research scientist at the company Klabin S/A for 7 years in the R&D sector. I have an expertise in the following areas: Agricultural Sciences, Engineering Sciences and Technologies, Materials Engineering with an emphasis in Pulp, Paper and Wood, Coatings, Films, Cosmetics, Biomedicine, and Nanotechnology.

Enjoy this personal and private book! It is free! As my science donation for you!

All this informations and results was produced in Baker laboratory at State University of New York College of Environmental Science and Forestry.

Thanks to Gitsov, Ivan PhD and Professor at the same University and the teaching assistant Marcellin Adjoumane.

All the experiments were carried out and interpreted by me and in some practices an small group was evolved.

SUMMARY

POLYMERS IN SOLUTION: VISCOSITY VS MOLECULAR MASS DETERMINATION

ABSTRACT

Viscosity is one of the parameters fast and easily measure for many types of susbtances. This patameter are consider an important characteristic to defining a portfolium of polymer aplication. To determine the kinematic viscosity ASTM D445[2] and their adaptations are most used in many types of industry. The objective of this report was use pure solutions of tetrahydrofuran (THF) and toluene as base solvent for poly(methyl methactylate) (PMMA) viscosity studies. Pure solutions of tetrahydrofuran (THF) and toluene was prepared contanied 15 ml of each reactant in a 50 ml flasks with 6 different concentrations (0; 0.005; 0.01; 0.015; 0.02 and 0.025 g/ml) of poly(methyl methactylate) (PMMA). Cannon-fenske capillary according according to ASTM D445[2] was used in this laboratory practice to determine the kinematic viscosity of the prepared solutions and the molecular mass (Mw) was calculated using the equation commonly known as the Mark-Houwink-Sakurada applying different values for constants K and α. THF based solution $\eta\, red$ shows a linear increase expressed by the equation coeficient R^2=0.99. $\eta\, red$ is an direct function of specific viscosity and relative viscosity, both direct related to *t*, that is demosntrated by the results with the linear increase. Toluene based solution $\eta\, red$ not expresse a clearly tendency, during the measurements of *t* and t_o, by the equation coeficient R^2=0.31. $\eta\, inh$ showed the same non-linear tendency. The average PMMA M_W (g/gmol) considering all solvent bases of THF and toluene was 1.2046 g/gmol and 9.485107x10^5 respectively. A higher interaction with PMMA and toluene are finded.

INTRODUCTION

Viscosity is one of the parameters fast and easily measure for many types of susbtances acording their classification. This patameter are consider an important characteristic to defining a big portfolium of polymer aplication.

To determine the kinematic viscosity ASTM D445[2] and their adaptations are most used in many types of industry. Considering this standard once the working solutions in this report are transparent, and by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer[2], the viscosity are determined. This test method is dependent upon the behavior of the sample and is intended for application to liquids for which primarily the shear stress and shear rates are proportional, called Newtonian flow behavior[2].

Considering the method discussed, the objective of this report was use pure solutions of tetrahydrofuran (THF) and toluene as base solvent for poly(methyl methactylate) (PMMA) viscosity studies.

EXPERIMENTAL

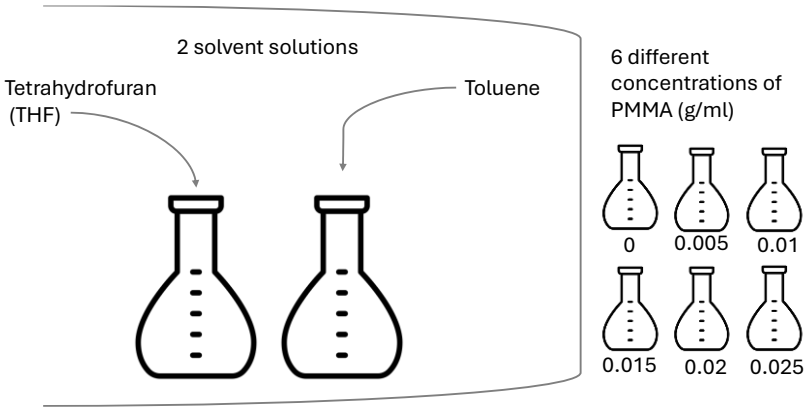
MATERIALS

For this experiment pure solutions of tetrahydrofuran (THF) and toluene was prepared contanied 15 ml of each reactant in a 50 ml flasks with 6 different concentrations of poly(methyl methactylate) (PMMA).

POLYMER SOLUTION PREPARATION

Fig. 1 shows PMMA was dissolved into 50 ml flasks with THF and toluene at 0; 0.005; 0.01; 0.015; 0.02 and 0.025 g/ml of PMMA.

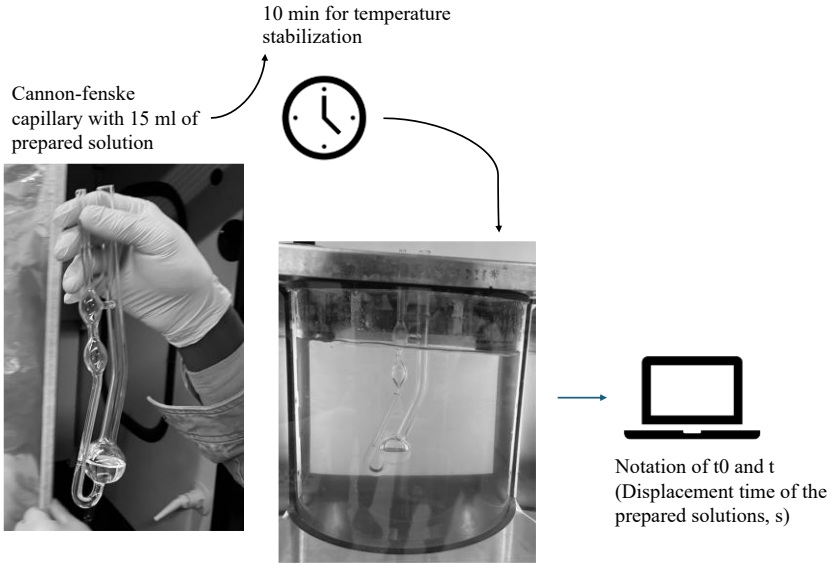
Figure 1 – PMMA solution preparation in THF and Toluene solvent base at different concentrations for viscosity determination.



VISCOSYMETER

Fig. 2 shows a cannon-fenske capillary according according to ASTM D445[2] was used in this laboratory practice to determine the kinematic viscosity of the prepared solutions. During the determination, adapatation in the standard was applied when was necessary.

Figure 2 – Procedure to determine kinematic viscosity of the prepared solutions using Cannon-fenske capillary.



VISCOSITY DETERMINATION

Viscosity and their calculations was determined according according to ASTM D445[2]. In this report Inherent viscosity ($\eta\ inh$) (Eq. 1) and Reduced viscosity ($\eta\ red$) (Eq. 2) was determined according the following equations.

Inherent viscosity Eq. 1

$$\eta\ inh = (\frac{t}{to})/C$$

Reduced viscosity (Eq. 2)

$$\eta\ red = \frac{nsp}{C}$$

In the mentioned equations “t” is flow time of the solution, “t_0” is the flow time of the solvent, “nsp” is referred to a specific viscosity and “c” is referred to a concentration of the prepared solutions.

MOLECULAR MASS (MW OR MV) DETERMINATION

The molecular mass was calculated using the equation commonly known as the Mark-Houwink-Sakurada[1] equation (Eq. 3).

Mark-Houwink-Sakurada[1] Eq. 3

$$[n] = KMv^{\alpha}$$

or

$$\log[n] = \log k + \alpha(\log Mv)$$

In the mentioned equations [n] is the instrinsic viscosity; Mv is calculated molar mass and K and α are constants specific for each polymer/solvent and temperature combination. In this reports Mw estimation according Mark-Houwink-Sakurada[1] equation use THF solutions at $K=7.56x10^{-5}$; 12.8^{-5} ; $9.44x10^{-5}$ and α = 0.731; 0.690; 0.719 (dl/g) at 25°C; and Toluene solutions at $K= 78.00x10^{-3}$; $7.80x10^{-3}$; 7.10^{-3} ; $8.12x10^{-3}$ and α = 0.50; 0.73; 0.71(ml/g) at 25°C.

RESULTS AND DISCUSSION

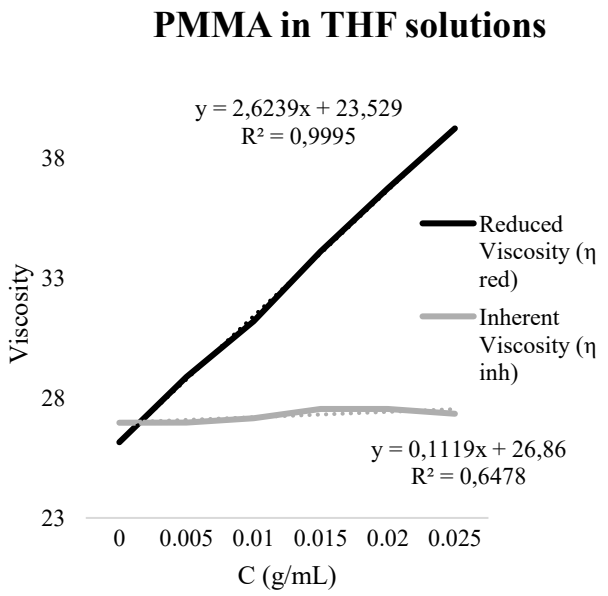
PMMA VISCOSITY IN THF AND TOLUENE

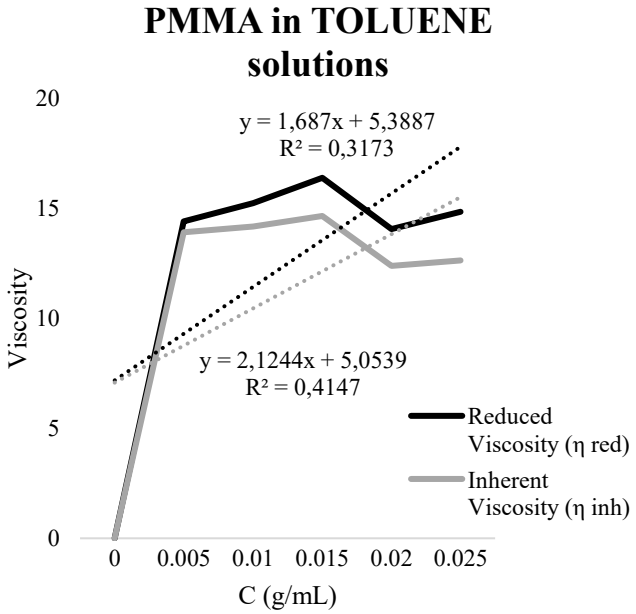
PMMA is currently produced at 3.9 million metric tons per year, being involved in different sectors, due to its high transparency, lightness and bar- rier properties that make this material particularly suitable for optical and electronic applications[3]. Thus, the study and understading of physical-chemical properties of this polymer became a key step for the researchers and industry.

Fig. 3 shows the Reduced viscosity (nred) and Inherent viscosity (ninh) for PMMA at 0; 0.005; 0.01; 0.015; 0.02 and 0.025 g/ml in solutions of THF and Toluene. According the concentration was increasing in the solutions of THF and Toluene, the kinectic viscosity measure based on the time of liquid displacement inside the cannon-fenske capillary indicated by t was also increased base on t_0. Based on this observations $\eta\ inh$ and $\eta\ red$ showed similar tendencies related to the solvent viscosity.

THF based solution $\eta\, red$ shows a linear increase expressed by the equation coeficient R^2=0.99. $\eta\, red$ is an direct function of specific viscosity and relative viscosity, both direct related to *t*, that is demosntrated by the results with the linear increase. $\eta\, inh$ showed an constant behave for all different concentrations of PMMA tested. It is important mention that for PMMA in THF measurements some temperature variations occored in the equipment and this could be an factor to explain the variations.

Figure 3 – PMMA in THF solutions (Different concentracions from 0 to 0.025 g/ml of PMMA in THF and their Reduced viscosity, n_{red} , and Inherent viscosity, n_{inh}). PMMA in Toluene solutions (Different concentracions from 0 to 0.025 g/ml of PMMA in Toluene and their Reduced viscosity, n_{red} , and Inherent viscosity, n_{inh}).





Toluene based solution $\eta\, red$ not expresse a clearly tendency, during the measurements of *t* and t_o, by the equation coeficient R^2=0.31. $\eta\, inh$ showed the same non-linear tendency. It is important also mention that for PMMA in Toluene and THF measurements was composed for 5 work groups, and the human factor during the measurements could bring a lot of variation for the results.

PMMA solutions manifest quite strong polymer-polymer interactions and form a network structure[4]. This network of polymer-solvent-polymer, able to induce both intra- and intermolecular swelling, while poorer solvents exhibit a much less pronounced influence to change parameters as viscosity. In this small case of study we also observe that the PMMA interaction with THF and Toluene are diferent. PMMA solutions should be lower for a constant concentration in good solvents (toluene, MEK, methyl ethyl keton)

as compared to the values recorded in solvents classified as poorer (DMF, dimethylformamide)[4]. Is evidente that the PMMA concentrations in each study mentioned are different, however is an start for the solubility comparisson as we have viscosity parameter to qualify the solutions.

MOLECULAR MASS (MW)

The average PMMA M_W (g/gmol) considering all solvent bases of THF and toluene was 1.2046 g/gmol and $9.485107x10^5$ respectively. We applied 3 different conditions of k and α, as constants, in the equation of Mark-Houwink-Sakurada[1] from our experiments to obtain M_W (g/gmol). One extra condition was also applied for toluene base solution with PMMA resulting in a very high Mw ($3.6817246x10^6$ g/gmol), 10 times higher than the same condition that use k=7.80E-02[6] and α^2=0.5 (mL/g).

Table 1 – Mw estimation according Mark-Houwink-Sakurada[1] equation and their constants. THF solutions at K=$7.56x10^{-5}$; 12.8^{-5} ; $9.44x10^{-5}$ and α = 0.731; 0.690; 0.719 (dl/g) at 25°C. Toluene solutions at K= $78.00x10^{-3}$; $7.80x10^{-3}$; 7.10^{-3} ; $8.12x10^{-3}$ and α = 0.50; 0.73; 0.71(ml/g) at 25°C

Solvent base solution	K	Log K[1]	α^2 (mL/g)	Log $[\eta]^3$	Log Mv[4]	Mw[5] (g/gmol)	Average Mw (g/gmol)[8]
THF[7]	7.56E-06	-5.1215	73.1	1.4243	0.0895	1.2290	1.2046
	1.28E-04	-3.8928	69	1.4243	0.0771	1.1941	
	9.44E-05	-4.0250	71.9	1.4243	0.0758	1.1907	
Toluene	7.80E-02[6]	-1.1079	0.5	1.1751	4.5661	36817.2	948510.7
	7.80E-03	-2.1079	0.5	1.1751	6.5661	3681724.6	
	7.10E-03	-2.1487	0.73	1.1751	4.5532	35746.7	
	8.12E-03	-2.0904	0.71	1.1751	4.5994	39754.5	

K[1] and α^2 (mL/g) = constants in the Mark-Houwink-Sakurada[1] equation- THF solutions at K=$7.56x10^{-5}$; 12.8^{-5} ; $9.44x10^{-5}$ and α = 0.731; 0.690; 0.719 (dl/g) at 25°C. Toluene solutions at K= $78.00x10^{-3}$; $7.80x10^{-3}$; 7.10^{-3} ; $8.12x10^{-3}$ and α = 0.50; 0.73; 0.71(ml/g) at 25°C. $[\eta]^3$=instrinsic viscosity. Mv[4]=Molecular mass in the Mark-Houwink-Sakurada[1] equation. Mw[5]=Molecular mass (g/gmol) resultant from Mark-Houwink-Sakurada[1] equation 7.80E-02[6]= K= $78.00x10^{-3}$ = extra condition at toluene solvent base. THF[7]= Poly(methyl methacrylate). (g/gmol)[8]=Same unit to express g/mol.

According with Bercea, et al. in 2002, to illustrate the influence of the solvent, their finds for PMMA with Mw = $1.290 \cdot 10^7$ in toluene, MEK (methyl ethyl keton) and DMF (dimethylformamide). These solvents range into the series toluene (*a* = 0.75) > MEK (*a* = 0.72) > DMF (*a* = 0.62), where *"a"* values represent the Mark-Houwink exponent, *i.e.*, the poorer solvent is DMF. Compared with this results our Mw for PMMA in THF and toluene

solutions was 1.2046 g/gmol and $9.485107x10^5$ respectively. A higher interaction with PMMA and toluene are finded.

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Mattia Sponchioni, Sibel Altinok, Chapter Seven - Poly(methyl methacrylate): Market trends and recycling, Editor(s): Davide Moscatelli, Matteo Pelucchi, Advances in Chemical Engineering, Academic Press, Volume 60, Issue 1, 2022, Pages 269-287, ISSN 0065-2377, ISBN 9780323957700, https://doi.org/10.1016/bs.ache.2022.09.004.
(4) Bercea, Maria & Simionescu, B.C.. (2002). Rheology of very high molecular weight poly(methyl methacrylate) solutions. Revue Roumaine de Chimie. 47. 155-164.

APENDICES

Table 2 shows the data from all experiments collected in the laboratory.

Table 2 – Collection of data from all viscosities measurements from pure solvents (THF and Toluene); and the polymer (PMMA) in different concentrations in each solvent from all work groups of the laboratory practices.

Solvent base solution	C (g/mL)	t1 (s)	t2 (s)	t3 (s)	Average (s)	Relative Viscosity (n rel)	Specific Viscosity (η sp)	Reduced Viscosity (η red)	ln nrel	Inherent Viscosity (η inh)
THF	0	37.90	37.90	38.00	37.93	1.00	0.00	0.00	0.00	0.00
PMMA1	0.005	43.23	43.46	43.54	43.41	1.14	0.14	28.88	0.13	26.97
PMMA2	0.01	49.80	49.70	49.80	49.77	1.31	0.31	31.20	0.27	27.15
PMMA3	0.015	57.20	57.80	57.00	57.33	1.51	0.51	34.09	0.41	27.54
PMMA4	0.02	65.80	65.70	65.90	65.80	1.73	0.73	36.73	0.55	27.54
PMMA5	0.025	75.10	75.10	75.20	75.13	1.98	0.98	39.23	0.68	27.34
Toluene	0	4.80	4.77	4.87	4.81	1.00	0.00	0.00	0.00	0.00
PMMA1	0.005	5.15	5.14	5.19	5.16	1.07	0.07	14.40	0.07	13.91
PMMA2	0.01	5.40	5.54	5.70	5.55	1.15	0.15	15.24	0.14	14.18
PMMA3	0.015	6.61	5.73	5.65	6.00	1.25	0.25	16.39	0.22	14.65
PMMA4	0.02	6.10	6.20	6.20	6.17	1.28	0.28	14.06	0.25	12.39
PMMA5	0.025	6.70	6.50	6.60	6.60	1.37	0.37	14.85	0.32	12.63

MOLECULAR MASS OF POLYMERS: SIZE EXCLUSION CHROMATOGRAPHY (SEC) AKA GEL PERMEATION CHROMATOGRAPHY (GPC)

ABSTRACT

This laboratory practices uses Tetrahydrofuran (THF), Polystrene (PSt) and Poly(methyl methactylate) (PMMA) to study how to conduct an obtain results from a size exclusion chromatography. The objective of this report was determining polystrene (PSt) and poly(methyl methactylate) (PMMA) molecular size distribution via size exclusion chromatography (SEC) and determine their polydispersivity. Eluent pure solutions of tetrahydrofuran (THF) was prepared and a solution of 3 mg/ml of polystrene (PSt) and another of 10 mg/ml of poly(methyl methactylate) (PMMA) was also prepared and inject at the size exclusion chromatography. SEC Waters Series: Styragel HR3, HR2, HR5 pore size, 103 Ångström (Å), 500 (Å) and 105 (Å) was applied to determine PSt and PMMA molecular mass. Eluent pure solutions of tetrahydrofuran (THF) was injected at a flow rate of 0.8 ml/min at 40 □C in the at the size exclusion chromatography. 100 □l of eluent and PSt and PMMA solutions was injected appling the defined conditions. PSt show lower values of Mn (Da) and Mw (Da) compared with the PMMA used in this laboratory practices. Mn and Mw respectively 48,350 (Da) and 152,509 (Da) for PSt; and 115,085 (Da) and 353,591(Da) for PMMA. According this parameters PI (Mw/Mn) was 3.15 and 3.07 respectively for PSt and PMMA. As an outcome the method of integration in this report was mechanical-manualy, and this could bring possible erros to the technique compared with the values we had from the software for PSt and PMMA of PI (Mw/Mn), 2.52 and 2.70 respectively.

INTRODUCTION

Determination of polymer molecular weight or molecular mass, are an very traditional technique, that's is an important part of the polymer characterization. Exist an enourmeous number of techniques and suggested methodologies that could maybe work for this determination. However the error of each technique is a key factor to the interpretation of the outcome result in this evaluations, and its related to the combinations of eluent solvents, techiniques and methods to measure the parameters.

This laboratory practices uses Tetrahydrofuran (THF), Polystrene (PSt) and Poly(methyl methactylate) (PMMA) to study how to conduct an obtain results from a size exclusion chromatography.

THF is a very knowed aplied solvent to dissolve many polymers and could be used as eluent solution for different techniques as SEC. Some polymer properties as polydispersive in reference to microstructure, degree of chain branching, composition of copolymer, sequence of comonomer units in copolymer among others, could change

depeding of the polymer estructure and classification[2,3]. Indexes as polydispersity are curently used for ploymer studies and understanding of polymer structure.

Polydispersity index[1] is an very knowed property of polymer and is characterized by ratio the ratio of Molecular weight (Mn) (Da) and Molecular Mass (Mw).

When the averages of the monodispersive polymer molecular weight distribution (MwDs) are the same the polydispersity index is equal to 1[2]. This an indicative of the structure and narrow distribution of the polymer.

Considering the method discussed, the objective of this report was determining polystrene (PSt) and poly(methyl methactylate) (PMMA) molecular size distribution via size exclusion chromatography (SEC) and determine their polydispersivity.

EXPERIMENTAL

MATERIALS

Tetrahydrofuran (THF), Polystrene (PSt) and Poly(methyl methactylate) (PMMA) was prepared and inject at the size exclusion chromatography according their concentrations and conditions discussed in the following itens.

SOLUTIONS PREPARATION

Eluent pure solutions of tetrahydrofuran (THF) was prepared and a solution of 3 mg/ml of polystrene (PSt) and another of 10 mg/ml of poly(methyl methactylate) (PMMA) was also prepared and inject at the size exclusion chromatography.

SIZE EXCLUSION CHROMATOGRAPHY (SEC) COLUMN AND ANALYSIS CONDITIONS

Fig. 1 shows a SEC equipment and their aparatus used in this experiment for laboratory practices. An SEC Waters Series: Styragel HR3, HR2, HR5 pore size, 10^3 Ångström (Å), 500 (Å) and 10^5 (Å) was applied to determine PSt and PMMA molecular mass.

Figure 1 – Size exclusion chromatography (SEC) equipment and their apparatus for molecular mass determination.

Size exclusion chromatography (SEC)

SEC and their eluent supply system

THF Eluent solution reservoir

ELUENT AND SOLUTION INJECTION CONDITIONS

Eluent pure solutions of tetrahydrofuran (THF) was injected at a flow rate of 0.8 ml/min at 40 °C in the at the size exclusion chromatography. Fig. 2 shows how 100 µl of eluent and PSt and PMMA solutions was injected appling the defined conditions in this report.

Figure 2 – Detail of injection of eluent and polymer solutions at Size exclusion chromatography (SEC) equipment and their apparatus for molecular mass determination.

MOLECULAR WEIGHT (MN) AND MOLECULAR MASS (MW) DETERMINATION

Molecular mass was calculated using the two methods in this report. One of than was resulted from a computed algoritm by the Sofware OmniSec version 5 (Malvern-Instruments). The second was an mechanical integration according the following equations and their components (Eq. 1, Eq. 2 and 3)[1].

Eq. 1

$$\text{Mw}(\boldsymbol{Da}) = \sum \boldsymbol{Ni\mu i} / \sum \boldsymbol{Ni}$$

Eq. 1 (Mw) is the average molecular mass; Da is the unit in Daltons; (Ni) is the current number of polymer molecules and $\boldsymbol{\mu i}$ is the current mass of each polymer molecule.

Eq. 2

$$\text{Mn}(\boldsymbol{Da}) = \sum \boldsymbol{hi\mu i} / \sum \boldsymbol{hi}$$

Eq. 2 (Mn) is the average molecular weigth; Da is the unit in Daltons; (hi) is distance in milimiters between the base line to the intersection of the refravtive index (mV) in the given data in each point of retention volume (ml) according with their respective molecular mass (Mw, Da). ($\boldsymbol{\mu i}$) is the current mass of each polymer molecule in the same point of intersection.

Eq. 3

$$\mathbf{Mw}\ (\boldsymbol{Da}) = \sum \boldsymbol{hi}(\boldsymbol{\mu i})^{\mathbf{2}} / \sum \boldsymbol{hi\,\mu i}$$

Eq. 3 (Mw) is the average of molecular mass; Da is the unit in Daltons; (hi) is distance in milimiters between the base line to the intersection of the refravtive index (mV) in the given data in each point of retention volume (ml) according with their respective molecular mass (Mw, Da). ($\boldsymbol{\mu i}$) is the current mass of each polymer molecule in the same point of intersection.

POLYDISPERSITY INDEX (MW/MN)

Polydispersity index[1] was calculated according the equation 4.

Eq. 4

$$PI = Mw/Mn$$

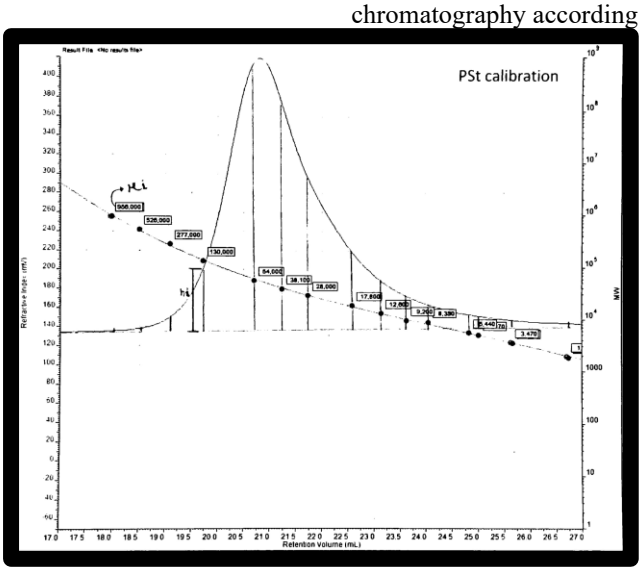
Eq. 4 is the Polydispersivity Index (PI) and their components, Mn (Da) the average molecular weigth and Mw (Da) the average of molecular mass.

RESULTS AND DISCUSSION

SEC CURVE INTEGRATION

Fig. 3 shows the claibration curves of Polystrene (PSt) and poly(methyl methactylate) PMMA according their refractive index (mV), retention volume (ml) distributed by their molecular Mw (Da). This data was sourced by the laboratory after SEC analysis.

Figure 3 – Polystrene (PSt) and poly(methyl methactylate) PMMA calibration curves inject at the size exclusion chromatography according their concentrations and conditions.



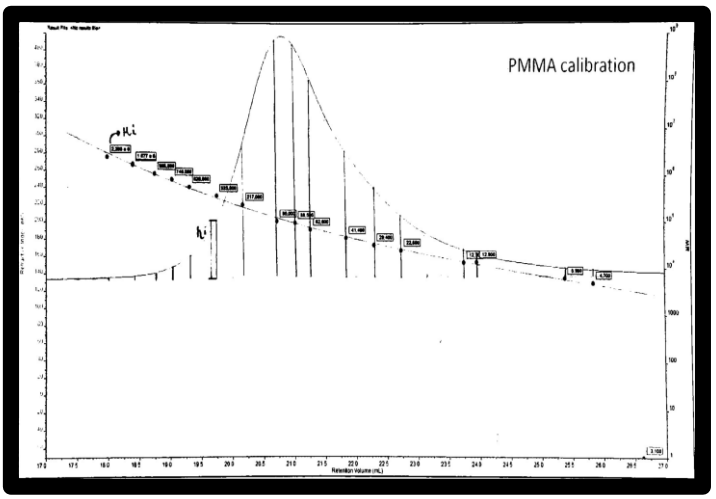


Table 1 below shows the intermediary indexes to apply direct in the equations mentioned in the methodology in this laboratory report. This mecanical integration is an very fast method as an alternative to the results evaluation. PSt curve show a narrow distribution as indicated by the sum for (∑hi) and polymer masses (∑μi) when compared with PMMA. PMMA curve present a sligly flatenning compared with PSt.

Table 1 – Intermediary indexes for Molecular weight (Mn) and Molecular Mass (Mw) determination.

Int_Indexes	∑hi (mm)	∑μi (Da)	∑μiˆ2 (Da)	∑hiμi (mm.Da)	∑hi(μiˆ2) (mm.Da2)
PMMA	372.6	6948980	9.28871E+12	42880490	1.51622E+13
PSt Calibration	370.55	2072470	1.2901E+12	17912456	2.73181E+12

[1]Sum of distance in milimiters between the base line to the intersection of the refravtive index (mV) in the given data in each point of retention volume (ml) according with their respective molecular mass (Mw, Da).[2]Sum of the current mass of each polymer molecule in the same point of intersection.[3]Sum of the squared value of the current mass of each polymer molecule in the same point of intersection.[4] Sum of the product of the distance in milimiters (hi) multiplyed by the current mass of each polymer molecule (μi).[5] Product of the distance in milimiters (hi) multiplyed by the current squared mass of each polymer molecule.

POLYDISPERSIVITY INDEX (PI), MOLECULAR WEIGHT (MN) AND MOLECULAR MASS (MW)

Polydispersity index[1] is an very knowed property of polymer and is characterized by ratio the ratio of Molecular weight (Mn) (Da) and Molecular Mass (Mw). PSt show lower values of Mn (Da) and Mw (Da) compared with the PMMA used in this laboratory practices. Mn and Mw respectively 48,350 (Da) and 152,509 (Da) for PSt; and 115,085 (Da) and 353,591(Da) for PMMA. According this parameters PI (Mw/Mn) was 3.15 and 3.07 respectively for PSt and PMMA.

Higher PI indeed implies the wider Mw. However, contrary to the widely accepted belief, the reverse is not true[2]. As shown in the table 1 and was directed correlated to the data in the apendices, the higher was Mw for PMMA aftec direct the PI indexes, however the lower as Mw of PSt compare with PMMA, PI indexes was not lower according too the same proportionality of incresing linked to Mw as demonstrated in this laboratory practices.

Table 2 - Polydispersivity Index (PI), Molecular weight (Mn) (Da) and Molecular Mass (Mw) (Da) of Polystrene (PSt) and poly(methyl methactylate) PMMA

Indexes	PSt Calibration	PMMA
Mn (Da)	48340	115085
Mw (Da)	152509	353591
Mw/Mn	3.15	3.07

Both PSt and PMMA are dissolved in THF, however if you evaluate the polymers structures, they have an different chain organization. PSt has an long hydrocarbon chain linked to an styrene group. The styrene group in this case could be responsible physicaly creat some regions of high volume when in THF solutions compared with PMMA. This is one of the reasons we teoretical find a higher PI (Mw/Mn). However the method of

integration in this report was mechanical-manualy, and this could bring possible erros to the technique compared with the values we had from the software for PSt and PMMA of PI (Mw/Mn), 2.52 and 2.70 respectively.

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APENDICES

Table 3 and 4 shows the data from all experiments extracted from the given data from the calibration curves from the laboratory.

Table 3 – Collection of data from all Polystrene (PSt)

PSt Calibration					
DP	hi (mm)	μi (Da)	μi^2 (Da)	hiμi (mm.Da)	hi(μi^2) (mm.Da^2)
1	1.000	956000	913936000000	956000	913936000000
2	1.900	526000	276676000000	999400	525684400000
3	6.000	277000	76729000000	1662000	460374000000
4	20.450	130000	16900000000	2658500	345605000000
5	100.300	54000	2916000000	5416200	292474800000
6	90.000	38100	1451610000	3429000	130644900000
7	61.000	28000	784000000	1708000	47824000000
8	31.500	17800	316840000	560700	9980460000
9	19.500	12600	158760000	245700	3095820000
10	13.500	9200	84640000	124200	1142640000
11	9.900	8390	70392100	83061	696881790
12	5.500	5470	29920900	30085	164564950
13	5.000	5440	29593600	27200	147968000
14	3.000	3470	12040900	10410	36122700
15	2.000	1000	1000000	2000	2000000

Table 4 – Collection of data from all Poly(methyl methactylate) (PMMA)

PSt Calibration					
DP	hi (mm)	μi (Da)	μi^2 (Da)	hiμi (mm.Da)	hi(μi^2) (mm.Da^2)
1	0.500	2200000	4840000000000	1100000	2420000000000
2	1.000	1570000	2464900000000	1570000	2464900000000
3	1.900	988000	976144000000	1877200	1854673600000
4	3.500	745000	555025000000	2607500	1942587500000
5	6.900	520000	270400000000	3588000	1865760000000
6	10.800	333000	110889000000	3596400	1197601200000
7	40.000	217000	47089000000	8680000	1883560000000
8	70.200	95000	9025000000	6669000	633555000000
9	71.200	88500	7832250000	6301200	557656200000
10	61.000	62600	3918760000	3818600	239044360000
11	38.900	41400	1713960000	1610460	66673044000
12	27.200	29400	864360000	799680	23510592000
13	19.000	22800	519840000	433200	9876960000
14	8.500	12900	166410000	109650	1414485000
15	7.500	12700	161290000	95250	1209675000
16	2.500	5980	35760400	14950	89401000
17	2.000	4700	22090000	9400	44180000

MOLECULAR MASS OF POLYMERS: MALDI-TOF : MATRIX-ASSISTED-LASER-DESORPTION/IONIZATION TIME OF FLIGHT

ABSTRACT

MALDI-TOF becomes and fast and alternative techique that avoides any curve calibration and enable many different types of stdies according their methodology to work. The objective of this report was determining poly(methyl methactylate) (PMMA) molecular weight (Mn) (Da), molecular Mass (Mw) and their polydispersity via matrix assisted laser desorption/ionization time of flight (MALDI-TOF). C5H8O2 Poly(methyl methactylate) (PMMA) prepared with 2.28 mg/ml and mixtured with the matrix solution and salt solution. For this laboratory practices in the final solution driped at MALDI-TOF sample holder was a combination of matrix (Super DHB) , sample solution (PMMA) and salt solution (NaCl) respectively at 10, 5 and 10 □l. From the mass spectra the number average molecular weight (Mn), weigth average molecular weigth (Mw) and their ratio as polydispersivity (PI= Mw/Mn) was calculated. Polydispersity index is an very knowed property of polymer and is characterized by ratio the ratio of number average molecular weight (Mn) and weigth average molecular weigth (Mw). Mn and Mw was respectively 3030 (Da) and 2308 (Da) for PMMA applying the proposed technique and according this parameters PI (Mw/Mn) calculated for PMMA was igual to 0.76. This loboratory report demonstrates that MALDI-TOF mass spectrometry gives representative molecular mass distribution for narrow molecular mass of PMMA polymer.

INTRODUCTION

Mass spectrometry (MS) was invented in the 19th century and, at the beginning, was only used in the chemical sciences. In the 1980s, matrix assisted laser desorption/ionization time of flight (MALDI-TOF) was introduced and improved the use of MS, allowing its application to identify biological macromolecules[9]. After that, MALDI-TOF MS was developed for generating and analyzing ions from a variety of molecules, particularly large, nonvolatile, and thermally labile compounds such as proteins, polymers, and oligonucleotides, which provides the basis for the use of MS in biomedical research. In the decade since being awarded the Nobel Prize in Chemistry in 2002, MALDI-TOF MS has been largely developed for proteomics/metabolomics studies through the qualitative and quantitative analysis of proteins/metabolites[10].

MALDI-TOF becomes and fast and alternative techique that avoides any curve calibration and enable many different types of stdies according their methodology to work.

Key properties of polymers as number average molecular weight (Mn) and weigth average molecular weigth (Mw) determination could be determined applying this techinique. Some polymer properties as polydispersive in reference to microstructure, degree of chain branching, composition of copolymer, sequence of comonomer units in

copolymer among others, could change depeding of the polymer estructure and classification[2,3] and fast methods as MALDI-TOF allow us to study indexes as polydispersity.

Polydispersity index[1] is an very knowed property of polymer and is characterized by ratio the ratio of molecular weight (Mn) (Da) and molecular mass (Mw). When the averages of the monodispersive polymer molecular weight distribution are the same the polydispersity index is equal to 1[2], this an indicative of the structure and narrow distribution of the polymer and their chains.

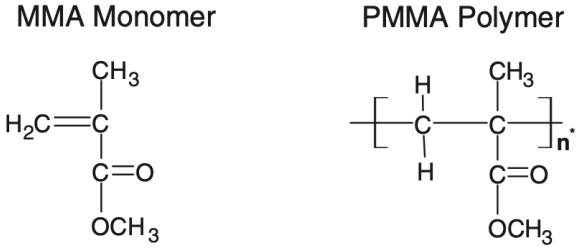
Considering the method discussed and the main polymer properties studied, the objective of this report was determining poly(methyl methactylate) (PMMA) molecular weight (Mn) (Da), molecular Mass (Mw) and their polydispersity via matrix assisted laser desorption/ionization time of flight (MALDI-TOF).

EXPERIMENTAL

PMMA SOLUTION

Fig. 1 shows chemical structure of $C_5H_8O_2$[5] Poly(methyl methactylate) (PMMA) prepared with 2.28 mg/ml and mixtured with the matrix solution and salt solution for molecular mass distribution via matrix assisted laser desorption/ionization time of flight.

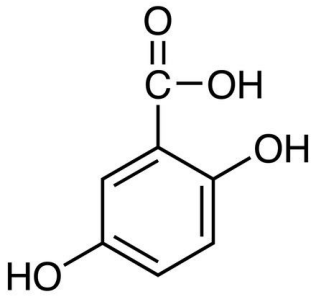
Figure 1 – MMA-PMMA. MMA, Monomer; PMMA, polymer of Poly(methyl methactylate)[5].



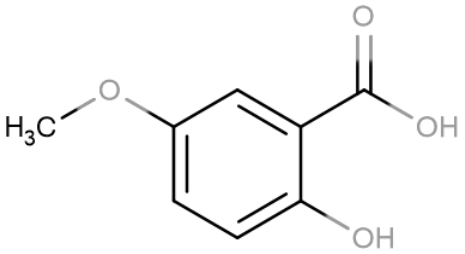
MATRIX SOLUTION

Fig. 2 shows chemical structure of matrix solutions are composed for “super DHB”, 2,5-dihydroxybenzoic acid and 2-hydroxy-5-methoxybenzoic acid at final concentration of 30 mg/ml. “Super-DHB” matrix consists of a 9:1 (w/w) mixture of 2,5-DHB (2,5-dihydroxybenzoic) and 2-hydroxy-5-methoxybenzoic acid, respectively[4].

Figure 2 – Matrix solution for MALDI-TOF PMMA molecular mass determination. (A+B) Super DHB; A) 2,5-dihydroxybenzoic[6] and B) 2-hydroxy-5-methoxybenzoic acid[7].



A[6]

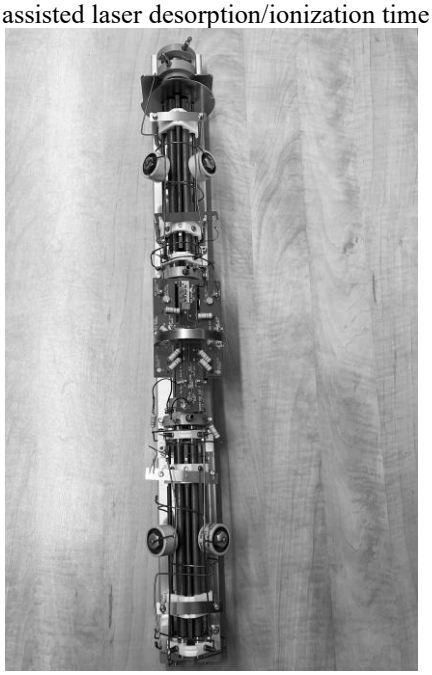


B[7]

MALI-TOF COLUMN AND ANALYSIS CONDITIONS

Fig. 3 shows a MALDI-TOF column used in the equipment. For this laboratory practices in the final solution driped at MALDI-TOF sample holder was a combination of matrix (Super DHB) , sample solution (PMMA) and salt solution (NaCl) respectively at 10, 5 and 10 μl.

Figure 3 – Matrix assisted laser desorption/ionization time of flight column.



NUMBER AVERAGE MOLECULAR WEIGHT (MN) AND WEIGTH AVERAGE MOLECULAR WEIGTH (MW) DETERMINATION

From the mass spectra the number average molecular weight (Mn) and weigth average molecular weigth (Mw) was calculated based on the following equations. The method following a mechanical integration according the equations and their components (Eq. 1 and Eq. 2)[1,8].

Eq. 1

$$\mathrm{Mn}(\boldsymbol{Da}) = \sum(\boldsymbol{NiMi})/\sum \boldsymbol{Mi}$$

Eq. 1[8] (Mn) is the average molecular weigth; Da is the unit in Daltons; (Ni) is signal intensity at point i. ($\boldsymbol{Mi}$) is the current mass of each polymer molecule in the same point i.

Eq. 2

$$\mathbf{Mw}\ (\boldsymbol{Da}) = \sum \boldsymbol{Ni}(\boldsymbol{Mi})^{\mathbf{2}}/\sum(\boldsymbol{Ni\,Mi})$$

Eq. 2[8] (Mw) is the average of molecular mass; Da is the unit in Daltons; (Ni) is signal intensity at point i. ($\boldsymbol{Mi}$) is the current mass of each polymer molecule in the same point i.

POLYDISPERSITY INDEX (MW/MN)

Polydispersity index[1,8] was calculated according to the equation 3.

Eq. 3

$$\boldsymbol{PI} = \boldsymbol{Mw}/\boldsymbol{Mn}$$

Eq. 3[8] is the Polydispersivity Index (PI) and their components, Mn (Da) the average molecular weigth and Mw (Da) the average of molecular mass.

RESULTS AND DISCUSSION

PMMA MALDI-TOF MASS SPECTRA

Fig. 4 shows the molecular mass spectra for PMMA samples using Matrix assisted laser desorption/ionization time of flight. A standard sample of PMMA with 3100 Da was prepared in a mixture with the matrix solution and salt solution. MALDI-TOF is able to provide absolute molecular-mass information of individual species. This makes MALDI-TOF useful for compositional analyses of individual species, allowing end-group information to be obtained and providing an insight into polymerisation mechanisms. In MALDI-TOF, molecules are separated by molecular mass, whereas SEC separates molecules according to their hydrodynamic size and is sensitive to polymer architecture (e.g. branching)[11].

Figure 4 – Molecular mass distribution spectra from PMMA prepared samples in a matrix of “Super DHB” and NaCl measured at MALDI-TOF.

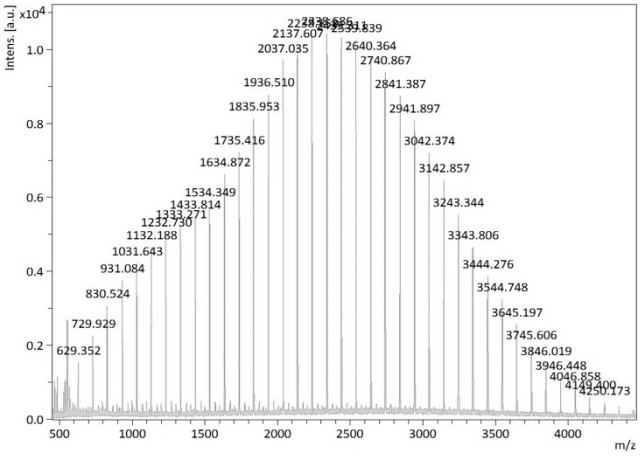


Table 1 below shows the intermediary indexes to apply direct in the equations mentioned in the methodology in this laboratory report. This integration is an very fast method as an alternative to the results evaluation. PMMA curve spectra show a narrow distribution as indicated by poisson like distribution according to each Mi at Ni intensity in the figure 4.

Table 1 – Intermediary indexes for number average molecular weight (Mn) and weigth average molecular weigth (Mw) determination for PMMA aplying MALDI-TOF

Int_Indexes[1]	∑Ni (a.u.)	∑Mi (m/z)	∑Mi^2 (m/z)	∑NiMi	∑Ni(Mi^2)
PMMA	134559	90247.886	262759116.8	273449190.1	6.311E+11

[1](Ni) is signal intensity at point i. (***Mi***) is the current mass of each polymer molecule in the same point i. ∑Ni = total sum of cumulative signal intensity at point i. ∑Mi = total sum of cumulative mass of each polymer molecule in the same point i. ∑Mi^2 = total sum of square of the current mass of each polymer molecule in the same point i. ∑NiMi = product of (Ni) signal intensity at point i per (***Mi***) the current mass of each polymer molecule in the same point i. ∑Ni(Mi^2) = total sum of cumulative product of (Ni) signal intensity at point i per (***Mi***) square of the current mass of each polymer molecule in the same point i.

POLYDISPERSIVITY INDEX (PI), NUMBER AVERAGE MOLECULAR WEIGHT (MN) AND WEIGTH AVERAGE MOLECULAR WEIGTH (MW)

Polydispersity index[1,2,8] is an very knowed property of polymer and is characterized by ratio the ratio of number average molecular weight (Mn) and weigth average molecular weigth (Mw). Table 2 shows Mn and Mw respectively 3030 (Da) and 2308 (Da) for PMMA applying the proposed technique. According this parameters PI (Mw/Mn) calculated for PMMA and igual 0.76.

Table 2 - Polydispersivity Index (PI), Molecular weight (Mn) (Da) and Molecular Mass (Mw) (Da) for poly(methyl methactylate) PMMA applying MALDI-TOF

Indexes	PMMA
Mn (Da)	3030
Mw (Da)	2308
Mw/Mn	0.76

This loboratory report demonstrates that MALDI-TOF mass spectrometry gives representative molecular mass distribution for narrow molecular mass of PMMA polymer. Finally table 3 shows even the mathematic equations and methods used for polydispersivity index (PI), molecular weight (Mn) and molecular mass (Mw) are very well know, the equation could change as according the table 3 applying different reference methods. These changes in methodology will impact in the final reported values of PI.

Table 3 – Polydispersivity Index (PI), Molecular weight (Mn) (Da) and Molecular Mass (Mw) (Da) for poly(methyl methactylate) PMMA applying MALDI-TOF, according different mathematic equations suggested by different references[1,8]

Eq.[1]	Reference	Mn (Da)	Mw (Da)	Mw/Mn
∑NiMi/ ∑Ni	(1) Andrew, et al., Dissemination of IT for the Promotion of Materials Science (DoITPoMS), Centre for Materials Education and the Department of Materials Science and Metallurgy, UK, University of Cambridge https://www.doitpoms.ac.uk/tlplib/polymerbasics/mw.php, (Accessed October 1, 2024)	2032	2308	1.14
∑NiMi/ ∑Mi	(8) Räder, Hans Joachim and Wolfgang Dr Schrepp. "MALDI-TOF mass spectrometry in the analysis of synthetic polymers." Acta Polymerica 49 (1998): 272-293	3030	2308	0.76

[1](Ni) is signal intensity at point i. ($\boldsymbol{Mi}$) is the current mass of each polymer molecule in the same point i. ∑Ni = total sum of cumulative signal intensity at point i. ∑Mi = total sum of cumulative mass of each polymer molecule in the same point i.

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APENDICES

Table 3 shows the data from all experiments extracted from the given data from PMMA MALDI-TOF spectrum.

Table 3 – Collection of data of Poly(methyl methactylate) (PMMA) molecular mass integration from MALDI-TOF spectrum

PMMA molecular mass integration from MALDI-TOF spectrum					
IP	Ni (a.u.)	Mi (m/z)	Mi^2 (m/z)	NiMi	Ni(Mi^2)
1	1407	629.352	396083.94	885498.264	557290103.4
2	2112	729.929	532796.345	1541610.048	1125265881
3	3024	830.524	689770.115	2511504.576	2085864826
4	3737	931.084	866917.415	3479460.908	3239670380
5	4248	1031.643	1064287.28	4382419.464	4521092363
6	4666	1132.188	1281849.67	5282789.208	5981110548
7	5037	1232.73	1519623.25	6209261.01	7654342325
8	5249	1333.271	1777611.56	6998339.479	9330683076
9	5572	1433.814	2055822.59	7989211.608	11455043453
10	5798	1534.349	2354226.85	8896155.502	13649807298
11	6056	1634.872	2672806.46	9900784.832	16186515900
12	6291	1735.416	3011668.69	10917502.06	18946407748
13	6537	1835.953	3370723.42	12001624.76	22034418985
14	6592	1936.51	3750070.98	12765473.92	24720467901
15	6788	2037.035	4149511.59	13827393.58	28166884681
16	6704	2137.607	4569363.69	14330517.33	30633014154
17	6472	2238.152	5009324.38	14485319.74	32420347356
18	6202	2338.686	5469452.21	14504530.57	33921542585
19	5737	2439.311	5950238.15	13994327.21	34136516294
20	5370	2539.839	6450782.15	13638935.43	34640700124
21	4827	2640.364	6971522.05	12745037.03	33651536947
22	4358	2740.867	7512351.91	11944698.39	32738829631
23	3844	2841.387	8073480.08	10922291.63	31034457442
24	3307	2941.897	8654757.96	9728853.379	28621284569

25	2911	3042.374	9256039.56	8856350.714	26944331147
26	2456	3142.857	9877550.12	7718856.792	24259263101
27	2010	3243.344	10519280.3	6519121.44	21143753408
28	1614	3343.806	11181038.6	5396902.884	18046196245
29	1268	3444.276	11863037.2	4367341.968	15042331124
30	1010	3544.748	12565238.4	3580195.48	12690890767
31	767	3645.197	13287461.2	2795866.099	10191482716
32	571	3745.606	14029564.3	2138741.026	8010881219
33	428	3846.019	14791862.1	1646096.132	6330916999
34	336	3946.448	15574451.8	1326006.528	5233015810
35	221	4046.858	16377059.7	894355.618	3619330188
36	599	4149.4	17217520.4	2485490.6	10313294696
37	433	4250.173	18063970.5	1840324.909	7821699239

THERMAL ANALYSIS OF POLYMERS: TGA/DTA

ABSTRACT

Thermal degration of polymers are one of the basics properties always elucidated for many reseachers in their studies. This property is result of a combination of factors as chemical composition and polymer structure. the objective of this report was determining thermal events and their ranges for poly(methyl methactylate) (PMMA) and polystyrene (PSt). TGA 2950 (TA instruments), Thermogravimetric Analyzer, with capacity of 0.1 to 100°C/min in 0.01°C/min increments was aplied to determine thermal degradation of PSt and PMMA. 10 °C/min and 20 °C/min heating rates was applied for this study. PMMA samples in this study start temperature of degradation (Tonset-TOS) at 187.5 □C for the first TE (Thermal event) and 250 and 312.5 for the respectively TE`s for the same curve A. The TOS values for curve B are higher than curve A due to the heating rate 2 times higher. Curve A and B shows the decomposition range (DCR) at 187.5 to 412.5 and 200 to 418.75 □C respectively. WL (Weigth losses) could be observed in the last TE, respectively 60 and 65 % for A and B, considering the 2 heating rates applied. PSt samples in this study start temperature of degradation (Tonset-TOS) at 387 □C and 375 for curves C and D respectively. The TOS values for curve D are lower than curve C due to the heating rate 2 times lower. Curve C and D shows the decomposition range (DCR) at 387 to 425 and 375 to 412.5 □C respectively. Chemical composition and structure of this both polymers5,6,7 PMMA and PSt explain the difference of thermal degradation. PMMA are easly degraded compared PSt. PSt thermal events start at higher temperatures compared with PMMA. The presence of phenol group2 as also the polymer linearity and their cristalinity will affect this thermal parameter.

INTRODUCTION

Thermal degration of polymers are one of the basics properties always elucidated for many reseachers in their studies. This property is result of a combination of factors as chemical composition and polymer structure. Several approaches to this problem can be found in literature from the point of view of the mechanism[3].

$C_5H_8O_2$[5] , poly(methyl methactylate) (PMMA) and $(C_8H_8)_n$ [6,7] , polystyrene (PSt) was choosed for this evaluation.

TGA/DTA curves are mainly divided into three major parts; stage-I, stage-II and stage-III[2]. Each stage are related of one specif event an interaction with the heat source. Stage I is attributed to the moisture vaporization adsorbed on to the surface of the molecules[2]. In this part, the weight loss is very low and even appear as an distinguished event sometimes. Stage II may be attributed to the main chain thermal decomposition accoding each polymer. And finally the Stage III, in the TGA/DTA curve shows the residue of the samples at the end of the experiment[2].

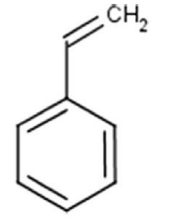
Considering the method discussed and the main polymer properties studied, the objective of this report was determining thermal events and their ranges for poly(methyl methactylate) (PMMA) and polystyrene (PSt).

EXPERIMENTAL

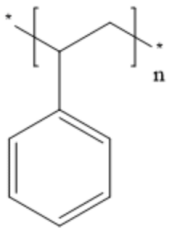
PMMA AND PST

Fig. 1 shows chemical structure of $C_5H_8O_2$[5], poly(methyl methactylate) (PMMA) and $(C_8H_8)_n$ [6,7], polystyrene (PSt) was choosed for this evaluation. 5 to 10 mg of each dried polymer was used in this study.

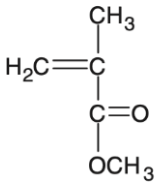
Figure 1 – St-PSt and MMA-PMMA. MMA, Monomer; PMMA, polymer of Poly(methyl methactylate)[5]. St, Monomer[6]; PSt polymer of Poly(Stryne)[7].



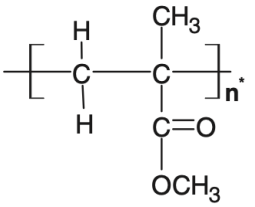
St Monomer[6]



PSt Polymer[7]



MMA Monomer[5]



PMMA Polymer[5]

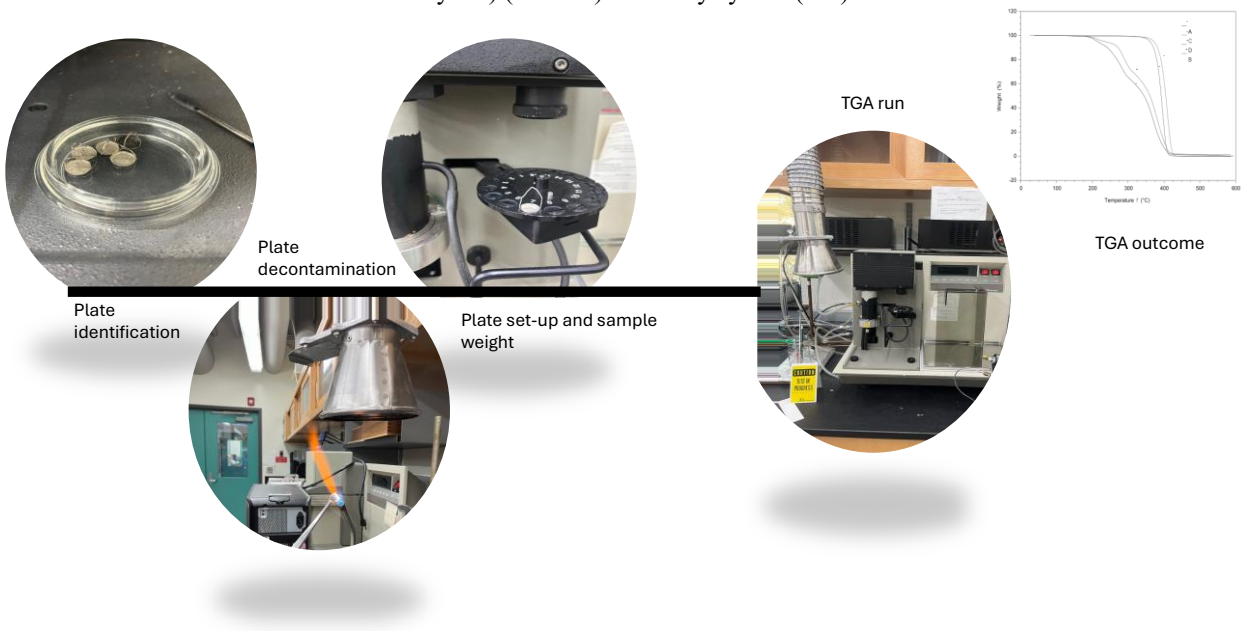
TGA INSTRUMENT AND CONDITIONS

TGA 2950[4] (TA instruments), Thermogravimetric Analyzer, with capacity of 0.1 to 100°C/min in 0.01°C/min increments was aplied to determine thermal degradation of PSt and PMMA. 10 °C/min and 20 °C/min heating rates was applied for this study.

SAMPLE PREPARATION

Fig. 2 shows the 4 steps of sample preparation for the study of thermal events of poly(methyl methactylate) (PMMA) and Polystyrene (PSt). The following steps could be described as: 1 – Plate identification; 2 – Plate decontamination; 3 – Plate set-up and sample weight; 4 TGA run and curve outcome to generate the results of thermal degradation.

Figure 2 – Sample preparation steps. 4 steps for TGA curves as an outcome. 1 – Plate identification; 2 – Plate decontamination; 3 – Plate set-up and sample weight; 4 TGA run and curve outcome as results for Poly(methyl methactylate) (PMMA) and Polystyrene (PSt).



THERMAL EVENTS

Thermal events in this report will be divided in: Temperature starting point of degradation (Tonset) in graus celcius (°C); Decomposition range, range in graus celcius (°C) that occurr the thermal degradation event and the last named as weight loss indicated for the vertical cordinate (Y) in percentage (%) covering the entire region of the same

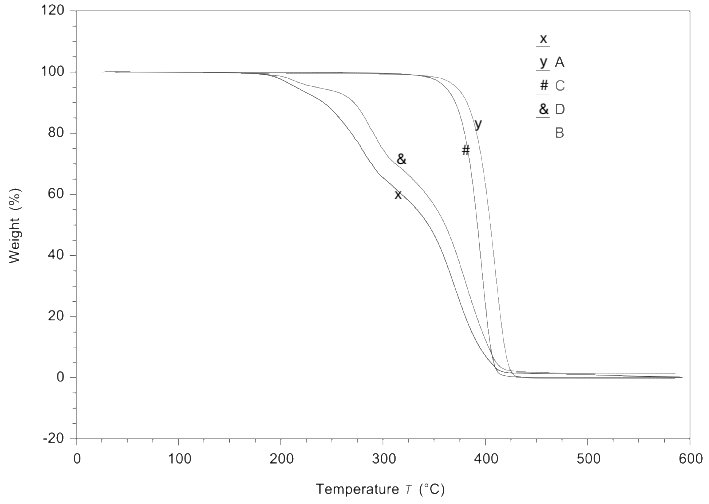
thermal event. All this 3 events was identified in the curves manualy and an interpretation table was produced for the result discussion.

RESULTS AND DISCUSSION

PMMA AND PST TGA CURVES

4 TGA curves was carried out from the TG 2950, to identify the thermal events of PMMA and PSt as showed in the fig. 3. TGA named by curve A characterize a PMMA thermal degration at 10°C/min. In B TGA curve characterize the PMMA at 20°C/min. The noted distance both curves imply in the difference of the heating rate chosen. In each curve for PMMA 3 thermal events was identified and will be further discussed. Curves C and D are characterized as PSt TGA curves. For PSt one event of thermal degradation was identified. In C curve characterize the PSt at 20°C/min and D curve characterize the PSt at 10°C/min.

Figure 3 – Thermal degradation curves (TGA) for Poly(methyl methactylate) (PMMA) and PolystyrenePSt and poly(styrene). Curves A to D. A – PMMA at 10°C/min and B – PMMA at 20°C/min; C – PSt at 10°C/min and B – PSt at 20°C/min.



PMMA AND PST THERMAL EVENTS

Table 1 shows the thermal events (TE) for all polymers in curves A to D. PMMA was discussed was characterized in this study for 3 TE. Pure PMMA decomposed in two stages according Ulu, A. et al[1]. The first stage assigned roughly 5% weight loss ratio at between 200 and 350 8 °C[1]. This mass loss indicated that degradation of the side groups in the polymeric structure. The second loss peak (90%) starting at above 350 °C[1] was ascribed to thermal degradation of the PMMA[1]. PMMA samples in this study start temperature of

degradation (Tonset-TOS) at 187.5 °C for the first TE and 250 and 312.5 for the respectively TE`s for the same curve A. The TOS values for curve B are higher than curve A due to the heating rate 2 times higher.

Curve A and B shows the decomposition range (DCR) at 187.5 to 412.5 and 200 to 418.75 °C respectively. Table 1 shows the detailed values for each TE characterized. Considering the DCR ranges for A and B the following weight loss (WL) linked with each TE was characterized and the higher WL could be observed in the last TE, respectively 60 and 65 % for A and B, considering the 2 heating rates applied.

Table 1 - Thermal degradation events (TGA) for Poly(methyl methactylate) (PMMA) and Polystyrene (PSt). Curves A to D. A – PMMA at 10°C/min and B – PMMA at 20°C/min; C – PSt at 10°C/min and B – PSt at 20°C/min

ID	Curve (C)[1]	Thermal events (TE)[2]	Tonset (TOS) (∘C)[3]	Decomposition range (DCR) (∘C)[4]	Weight loss (WL) (%)[5]
PMMA	A*	1	187.5	187.5-250	13.5
		2	250	250-312.5	25
		3	312.5	312.5-412.5	60
	B*	1	200	200-275	10
		2	275	275-325	25
		3	325	325-418.75	65
PSt	C	1	387.5	387.5-425	98
	D	2	375	375-412.5	98

* 3 events of thermal degradation was idedntified for PMMA at both heating rates of 10°C/min and 20°C/min.
[1]C-curve; [2]TE-Thermal events; [3]TOS-temperature of on set; [4]DCR-decomposition range and [5]WL- weight loss.

Ansari et al.[2] showed the thermal decomposition of PS and Co/PS composites in the temperature range of 300–440 °C, where the maximum weight loss occurs in their evaluations. The same hypothesis discussed in this study was ellucidated in their work as the maximum weight loss in this thermal decomposition process may be attributed to the main chain pyrolysis and the evolution of aromatics from the degradation of the styrene[2]. PSt samples in this study start temperature of degradation (Tonset-TOS) at 387 °C and 375 for curves C and D respectively. The TOS values for curve D are lower than curve C due to the heating rate 2 times lower.

Curve C and D shows the decomposition range (DCR) at 387 to 425 and 375 to 412.5 °C respectively. Table 1 shows the detailed values for each TE characterized.

Considering the DCR ranges for C and D the following weight loss (WL) about 98 % for both TE according their temperatures.

Chemical composition and structure of this both polymers[5,6,7] PMMA and PSt explain the difference of thermal degradation. PMMA are easly degraded compared PSt. PSt thermal events start at higher temperatures compared with PMMA. The presence of phenol group[2] as also the polymer linearity and their cristalinity will affect this thermal parameter.

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APENDICES

Table 2 shows the data from all experiments extracted from the given curves of PMMA and PSt polymers.

Table 2 – Collection of data of Poly(methyl methactylate) (PMMA) and Polystyrene (PSt)

ID	Curve (C)[1]	Thermal events (TE)[2]	Tonset (TOS) (∘C)[3]	Decomposition range (DCR) (∘C)[4]	Weight loss (WL) (%)[5]
PMMA	A*	1	187.5	187.5-250	13.5
		2	250	250-312.5	25
		3	312.5	312.5-412.5	60
	B*	1	200	200-275	10
		2	275	275-325	25
		3	325	325-418.75	65
PSt	C	1	387.5	387.5-425	98
	D	2	375	375-412.5	98

* 3 events of thermal degradation was idedntified for PMMA at both heating rates of 10°C/min and 20°C/min.
[1]C-curve; [2]TE-Thermal events; [3]TOS-temperature of on set; [4]DCR-decomposition range and [5]WL- weight loss.

DIFFERENTIAL SCANNING CALORIMETRY DSC

ABSTRACT

Differential scanning calorimetry (DSC) and the thermal properties linked to this analysis and their thermal degration events will be explored as research technique in this laboratory report. Considering the method discussed and the main polymer properties studied, the objective of this report was determining thermal events and their ranges for polyethylene Glycol (PEG), using DSC. DSC, differential scanning calorimetry, at 10 °C/min and 20 °C/min heating rates was applied for this laboratory study. 2 DSC thermograms, indentified as A (TH01) and B (TH02) characterized the thermal events of PEG. In both thermograms 3 main thermal events was named, 1st heating, cooling and 2nd heating. TH01 shows 62.5 °C melting temperature (Tm), using both methods in this laboratory practices. A slight difference between the temperatures ranges of onset and endset was founded for the 1st and 2nd heating cycles, 52 – 73.74 °C and 56.25 – 73.74 °C respectively. In the case of this report we didn't explore the cooling rates, however is evident the difference between TH01 and TH02 due to the presence of the 2 peaks indicated by the crystalinization event at 39 and 36 °C in TH01 and only one peak in TH02 at 36 °C. TH02 shows 62.5 and 63 °C of melting temperature (Tm) for 1st and 2nd heating cycles, using both methods in this laboratory practices. Same temperatures range of onset and endset was founded for the 1st and 2nd heating cycles, 51 to 75 °C and 52 to 73.74 °C respectively. It is relevant mention the TH02 applies a heating rate 2 time higher than TH01. Also, only one event of crystallization was detected for the cooling cycle in the TH02. Finally the data in this laboratory report confirmed by the existent background that at lower heating rates new crystalization events could appear in the cooling cycle as noted here.

INTRODUCTION

Differential scanning calorimetry (DSC) and the thermal properties linked to this analysis and their thermal degration events will be explored as research technique in this laboratory report. The DSC events results is a combination of factors as chemical composition, polymer structure and their physico-chemical state, liquid or solid.

Phase change materials (PCMs) store heat and cold during the phase transition from solid to liquid and reversed[2]. Over the past years, poly(ethylene glycol) (PEG) gained attention in the PCM[2] industrial applications due to their resilient properties and safety.

Polyethylene Glycol (PEG), chemical formula $H(OCH_2CH_2)_nOH$[1], PEG is widely used in the pharmaceutical industry as a drug carrier, as a plasticizer for some biopolymers, and to prevent phase separation in inorganic PCM. It is a water-soluble polymer that is nonflammable, nontoxic, and biodegradable and thereby also harmless to the environment[2].

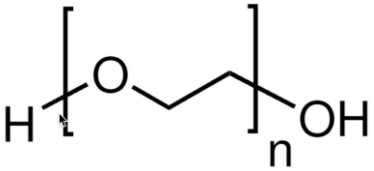
Considering the method discussed and the main polymer properties studied, the objective of this report was determining thermal events and their ranges for polyethylene Glycol (PEG), using DSC.

EXPERIMENTAL

PEG, POLYETHYLENE GLYCOL

Fig. 1 shows the chemical structure of the Polyethylene Glycol (PEG). $H(OCH_2CH_2)_nOH$ is the chemical formula of this polymer, used in this report to evaluate the differential scanning calorimetry (DSC) and the thermal properties linked to this analysis.

Figure 1 – Chemical structure of the Polyethylene Glycol (PEG)[1].



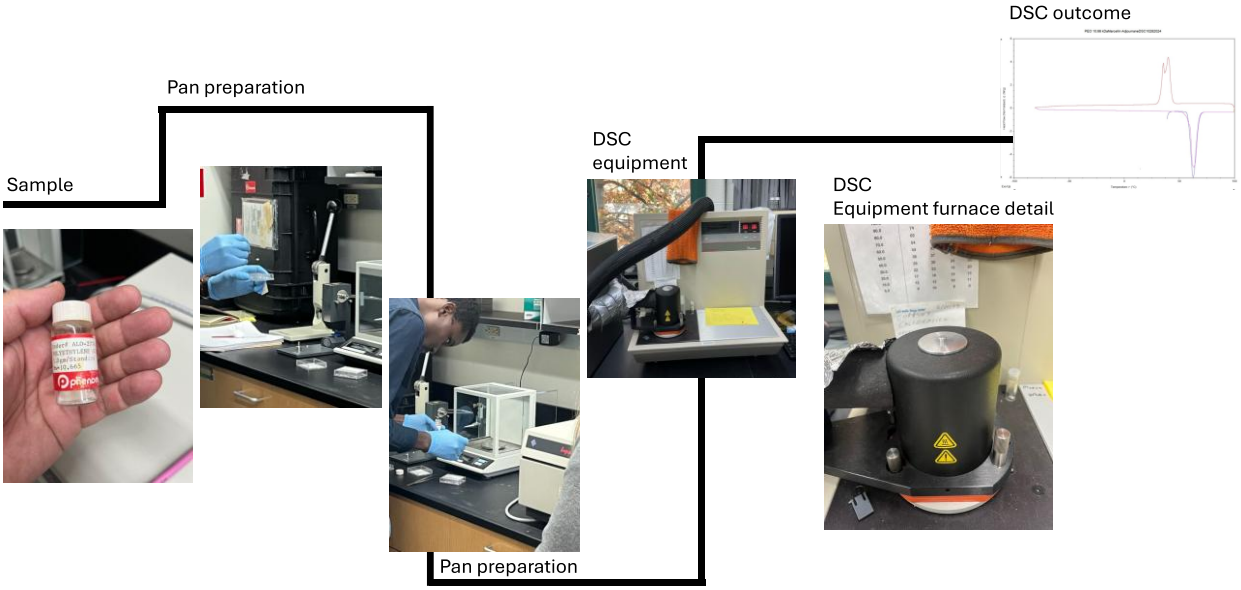
DSC INSTRUMENT AND CONDITIONS

DSC, differential scanning calorimetry, at 10 °C/min and 20 °C/min heating rates was applied for this laboratory study. The equipment conditions are defined by the operator and not shared in this report.

SAMPLE PREPARATION

6.9 mg of dried PEG sample was weighted in the DSC pan for this analysis in the equipment. Fig. 2 show this procedure.

Figure 2 – DSC sample preparation in 4 steps. 1- Polymer selection, 2 – Pan preparation and sample weigth, 3 – DSC equipment runing and furnace details and finaly 4 – DSC outcome results.



THERMAL EVENTS

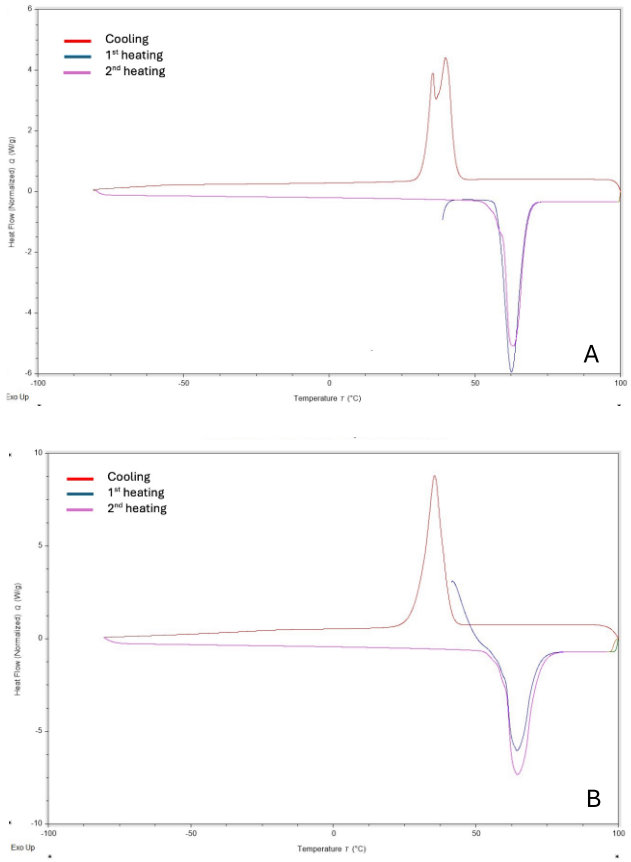
To define the temperature of the melting transition (Tm) and the temperature of the crystallizatizarion two methods discussed in the laboratory practices preparation as: 1) intersecting tangents and 2) peak minimum will be applied in this study.

RESULTS AND DISCUSSION

PEG DSC CURVES

2 DSC thermograms, indentified as A (TH01) and B (TH02) characterized the thermal events of PEG as showed in the fig. 3. DSC named by curve A characterize a PEG at thermal degration heating of 10°C/min. In B DSC curve characterize the PEG at 20°C/min. In both thermograms 3 main thermal events was named, 1st heating, cooling and 2nd heating.

Figure 3 – DSC, differential scanning calorimetry curves of PEG samples: at A) 10 °C/min and B) 20 °C/min heating rates. 3 main thermal events was named, 1st heating, cooling and 2nd heating.



TH01 shows similar conditions for 1st and 2nd heatings cycles, however 2 events of crystalization are founded at the lower heating rate compared with the second TH02, B, described in the figure 3A.

PEG THERMAL EVENTS

Table 1 shows the thermal events (TE) for PEG considering 2 conditions of heating rates for TH01 and TH02, TH01at 10 °C/min and TH02 at 20 °C/min.

TH01 shows 62.5 °C melting temperature (Tm), using both methods in this laboratory practices. A slight difference between the temperatures ranges of onset and endset was founded for the 1st and 2nd heating cycles, 52 – 73.74 °C and 56.25 – 73.74 °C respectively. TH01 also shows 2 peaks in the cooling cycle characterized as crystallization events, crystallization and melting of PEG may exhibit one or two peaks during cooling and heating steps[2]. According Paberit, et al. (2020) the presence of two heat flow maxima during cooling reflects the presence of two different crystallization mechanisms, one at higher temperatures and the other at lower temperatures. In general, this behavior can be induced by the presence of two crystals with different nucleation and growth kinetics or with different enthalpies of crystallization. Consequently, when the PEG samples are cooled rapidly, it favors crystalline structures that grow at low temperatures under a high rate of cooling. On the other hand, a reduced cooling rate results in crystalline structures that grow at high temperatures becoming more favored[2]. In the case of this report we didn't explore the cooling rates, however is evident the difference between TH01 and TH02 due to the presence of the 2 peaks indicated by the crystalinization event at 39 and 36 °C in TH01 and only one peak in TH02 at 36 °C.

Table 1 - Thermal degradation events (DSC) for PEG samples. Curves TH01 and TH02. TH01at 10°C/min and TH02 at 20°C/min

ID	Heating rate (°C/min)	Thermal events	Method	Tm (°C)	Re-crystalization (°C)	Tonset (°C)	Tendset (°C)
TH01	10	Cooling	P	*	36	*	*
			P	*	39	*	*
		1st heating	T	62.5	*	52	73.74
			P	62.5	*	*	*
		2nd heating	T	62.5	*	56.25	73.74
			P	63	*	*	*
TH02	20	Cooling	P	*	36	*	*
		1st heating	T	62.5	*	51	75
			P	63	*	*	*

		2nd heating	T	63	*	52	75
			P	63	*	*	*

3 main thermal events was named, 1st heating, cooling and 2nd heating. * Non-determined property. Methods: P: Peak determination and T: Tangent determination. Tm: Melting temperature. Tonset: Onset of melting temperature and Tendset: End of melting temperature.

TH02 shows 62.5 and 63 °C of melting temperature (Tm) for 1st and 2nd heating cycles, using both methods in this laboratory practices. Same temperatures range of onset and endset was founded for the 1st and 2nd heating cycles, 51 to 75 °C and 52 to 73.74 °C respectively. It is relevant mention the TH02 applies a heating rate 2 time higher than TH01. Also, only one event of crystallization was detected for the cooling cycle in the TH02. Paberit, et al. (2020) evaluate crystallization and melting of PEG were at the same rate of temperature change, 5 °C/min and also found 2 peaks of crystalization in the cooling cycle. One of the hypothesis in the data in this laboratory report confirmed by the existent background is that at lower heating rates new crystalization events could appear in the cooling cycle as noted here.

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APENDICES

Table 2 shows the data from all experiments extracted from the given curves of PEG.

Table 2 – Collection of data of Thermal degradation events (DSC) for PEG samples. Curves TH01 and TH02. TH01at 10°C/min and TH02 at 20°C/min

ID	Heating rate (°C/min)	Thermal events	Method	Tm (°C)	Re-crystalization (°C)	Tonset (°C)	Tendset (°C)
TH01	10	Cooling	P	*	36	*	*
			P	*	39	*	*
		1st heating	T	62.5	*	52	73.74
			P	62.5	*	*	*
		2nd heating	T	62.5	*	56.25	73.74

			P	63	*	*	*
TH02	20	Cooling	P	*	36	*	*
		1st heating	T	62.5	*	51	75
			P	63	*	*	*
		2nd heating	T	63	*	52	75
			P	63	*	*	*

3 main thermal events was named, 1st heating, cooling and 2nd heating. * Non-determined property. Methods: P: Peak determination and T: Tangent determination. Tm: Melting temperature. Tonset: Onset of melting temperature and Tendset: End of melting temperature.R-decomposition range and [5]WL- weight loss.

POLYMER SPECTROSCOPY: INFRA-RED ANALYSIS - FTIR

ABSTRACT

PMMA polymer could be classified according their Tg (Transition temperature) and their chemical groups structure organization influenced by the quiral carbon as: atactic, syndiotactic and isotactic.This polymer presents three main tacticities (isotactic, syndiotactic, and atactic). In this laboratory practices report PMMA chemical strucutres and tacticities will be explored throughout an FTIR, type fourier transform infrared spectrometer with mid-IR (8300–350 cm−1) and far-IR (700–30 cm−1), Perkin Elmer Frontier, MIR mode (4000 – 550 cm−1) applying 15 scans per each spectra analysis. PMMA vibrational bands are characterized in this study (A, B and C) and compared with the background information available in the literature (D). C-C, CH3, CH2, OCH3, C-O-C, C-C-O, C-H, C=O and their vibrational bonds identified in the PMMA`s evaluated. C=O stretching vibrational band are one of very disseminated in the literature. The wavelengths for atactic, syndiotactic and isotactic PMMA was respectively 1723.23; 1723.88 and 1724.2 cm-1. C-O-C asymmetric stretch wavelengths for atactic, syndiotactic and isotactic PMMA was respectively 1142.1, 1143.37 and 1144.05 cm-1. Vibrational bonds identified in this study have showed the PMMA structure and their predicted spatial organization.

INTRODUCTION

Poly (methyl methacrylate) (PMMA) is a transparent thermoplastic synthesized by emulsion polymerization, solution polymerization, and bulk polymerization from the MMA monomer[7]. $C_5H_8O_2$[1] , poly(methyl methactylate) (PMMA) and $(C_8H_8)_n$ [4,5] is a widely used polymer with many applications due the polymer safety and structure characteristics. Even there are still classified as a plastic material and their recyclabililty remains as challenging. PMMA are used primarily in plastic applications, derivative of acrylic acid, present excellent mechanical properties and uses in many areas as biomaterial[6].

PMMA polymer could be classified according their Tg (Transition temperature) and their chemical groups structure organization influenced by the quiral carbon as: atactic, syndiotactic and isotactic.This polymer presents three main tacticities (isotactic, syndiotactic, and atactic), where pendant groups or hydrogens are laid in certain positions. The chiral central's orientation will determine the transition temperature and crystallinity, thermal resistance, solubility, degree of biocompatibility, hydrolyzation, and other properties. For example, the Tg is the lowest (55 °C) for the isotactic structure when ester groups are disposed on one single side of the backbone structure, from a random or regular order, respectively. The chemical structure is more stable for the atactic and syndiotactic

structures, so automatically increasing the Tg to 120 and 130 °C, respectively. The different percentages of tacticities result in an almost specific Tg for each PMMA[7].

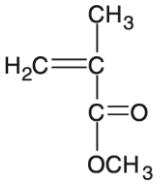
In this laboratory practices report PMMA chemical strucutres and tacticities will be explored throughout an FTIR, type fourier transform infrared spectrometer with mid-IR (8300–350 cm^{-1}) and far-IR (700–30 cm^{-1}), Perkin Elmer Frontier.

EXPERIMENTAL

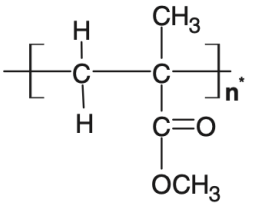
PMMA

Fig. 1 shows the chemical structure of the MMA, Monomer; PMMA, polymer of Poly(methyl methactylate)[1]. Dry samples of PMMA was used in this laboratory report.

Figure 1 – MMA-PMMA. MMA, Monomer; PMMA, polymer of Poly(methyl methactylate)[1].



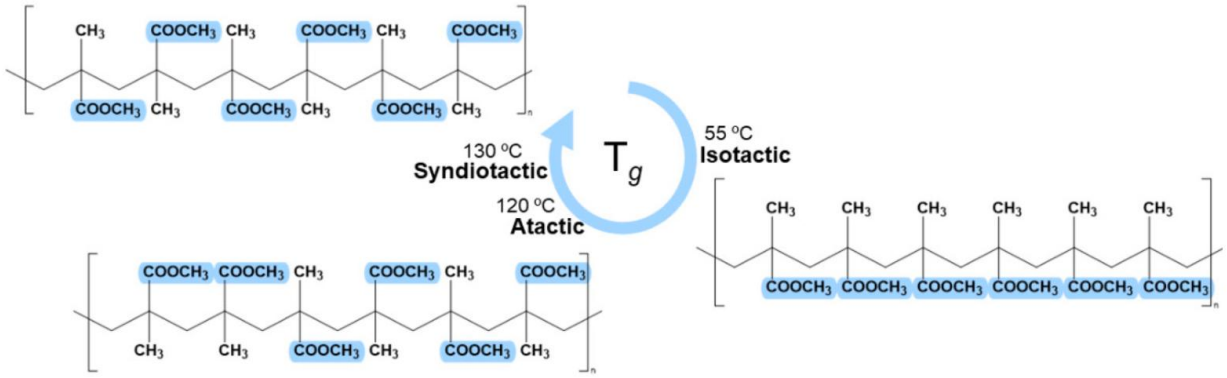
MMA Monomer[1]



PMMA Polymer[1]

3 PMMA tacticities was evaluated in this report according the structures showed in the figure 2.

Figure 2 – Adapted from Fort eat al. (2021). PMMA tacticities: isotactic, syndiotactic, and atactic and respective glass transition temperature[7].



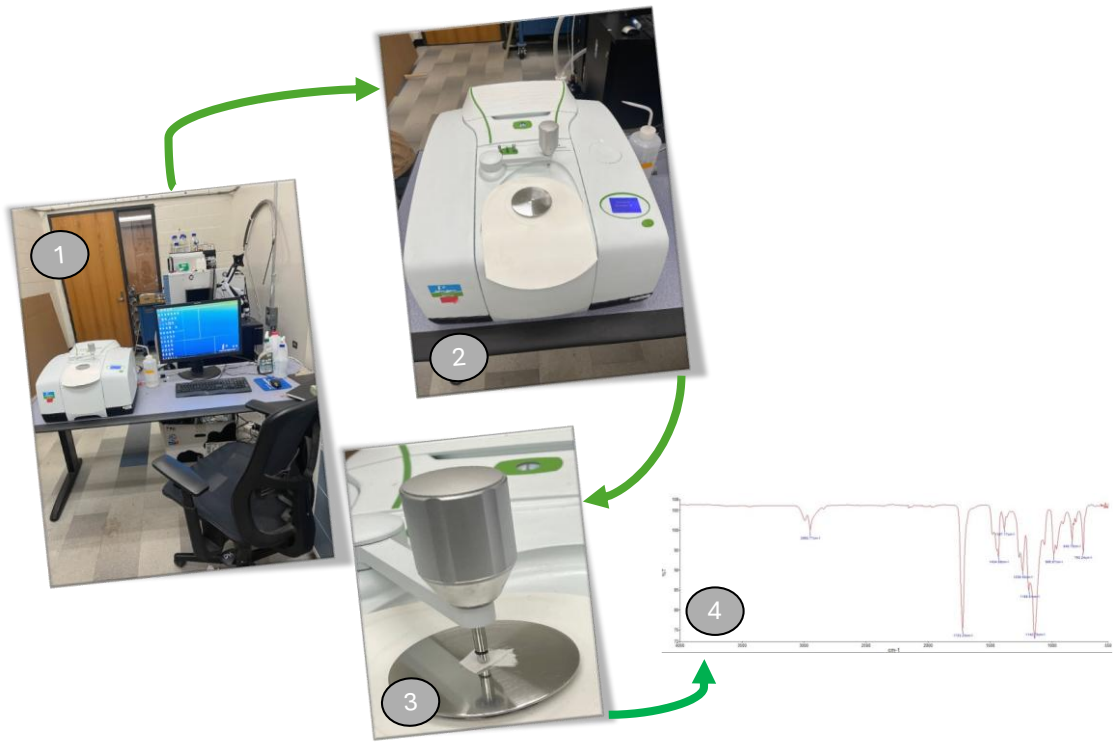
FTIR INSTRUMENT AND CONDITIONS

FTIR, type fourier transform infrared spectrometer with mid-IR (8300–350 cm^{-1}) and far-IR (700–30 cm^{-1}), Perkin Elmer Frontier[2,3], was used in the MIR mode (4000 – 550 cm^{-1}) applying 15 scans per each spectra analysis.

SAMPLE PREPARATION

Prepared dry samples of comercial PMMA was prepared and analised in the equipment described. Fig. 3 show the 4 step procedure for this laboratory practices.

Figure 3 – FTIR sample preparation in 4 steps. 1- FTIR equipment, 2 – Equipment set up, 3 – Sample placement 4 – FTIR spectras result.

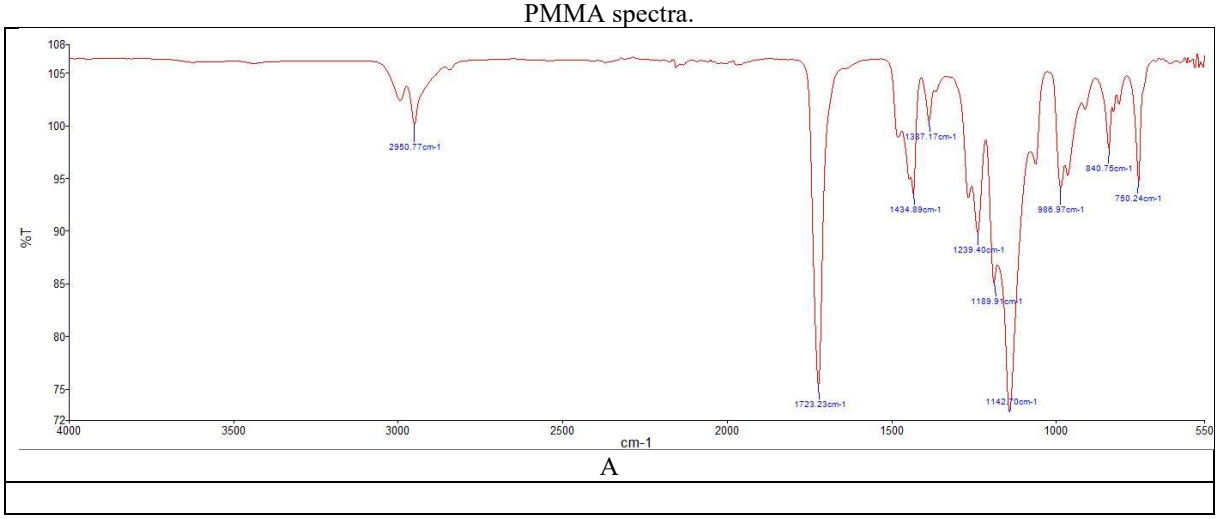


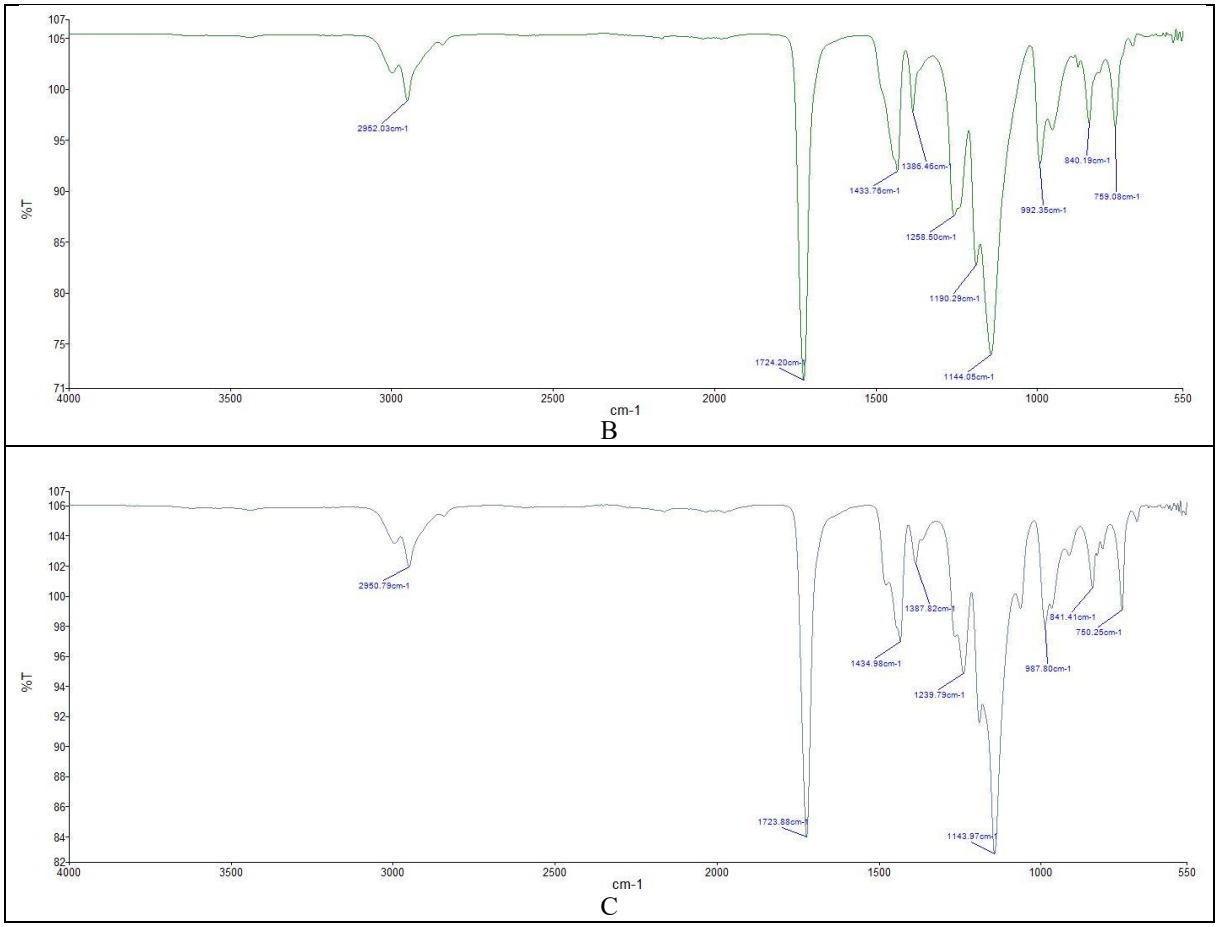
RESULTS AND DISCUSSION

FTIR SPECTRAS

Fig. 4 shows 3 FTIR spectras in the MIR mode (4000 – 550 cm^{-1}) applying 15 scans per each spectra analysis, A -Atactic PMMA spectra; B – Syndioyactic PMMA spectra and C – Isotactic PMMA.

Figure 4 – FTIR, type fourier transform infrared spectrometer in the MIR mode (4000 – 550 cm^{-1}) applying 15 scans per each spectra analysis. A -Atactic PMMA spectra; B – Syndioyactic PMMA spectra and C – Isotactic PMMA spectra.





PMMA VIBRATIONAL ASSIGNMENTS

Table 1 shows the main vibrational bands for the PMMA types of tacticity and the comparisson with literature background when founded. Atactic PMMA (A) spectra; syndioyactic PMMA (B) spectra, isotactic PMMA (C) spectra and literature backgroung (D).

Table 1 – Vibrational band assignments for PMMA tacticities, A -Atactic PMMA spectra; B – Syndioyactic PMMA spectra, C – Isotactic PMMA spectra and D – literature backgroung

Vibrations Assignments for types of PMMA (cm-1)						
Chemical bond (CB)	Atactic(A)	D	Syndiotactic (B)	D	Isotactic (C)	D
C-C	750.24	750 (3)	750.25	750 (3)	*	*
CH3+skeletal	*	*	*	*	759.08	759 (1)
Not clear CH2 rocking	840.75	*	841.41	*	840.19	842 (2)
OCH3 rocking	986.97	*	987.8	988 (1)	992.35	996 (2 and 1)
C-O-C asymmetric stretch	1142.1	1144 (3)	1143.37	1144 (3)	1144.05	1150 (2 and 3)
No clear, possibility C-O-C+Skeletal	1189.91	*	*	1190 (1)	1190.29	1190 (2)

C-C-O strech	1239.4	1240 (3)	1239.79	1252 (1)	1258.5	1255 (1, 2 and 3)
C-H deformation, CH3	1387.17	1388 (3)	1387.82	1388 (2 and 3)	1385.45	1388 (2 and 3)
OCH3	1434.89	*	1434.88	1438 (1)	1433.76	1445 (2)
C=O stretching vibration	1723.23	1718 (3)	1723.88	*	1724.2	1734 (2)
C-H	2850.77	2853 (3)	2850.79	2853 (3)	2852.03	2948 (2)

CB – chemical bond, A - Atactic PMMA, B – Syndiotactic PMMA, C – Isotactic PMMA, D – Literature background, * - non defined or identified value of vibration in cm^{-1}, (1) Brinkhuis and Schouten (1991), (2) O'Reilly and Mosher (1981) and (3) Rai et al. (2017).

PMMA vibrational bands are characterized in this study in the table one (A, B and C) and compared with the background information available in the literature (D). Table 1 shows C-C, CH3, CH2, OCH3, C-O-C, C-C-O, C-H, C=O and their vibrational bonds identified in the PMMA`s evaluated. C=O stretching vibrational band are one of very disseminated in the literature. The wavelengths for atactic, syndiotactic and isotactic PMMA was respectively 1723.23; 1723.88 and 1724.2 cm^{-1}. C-O-C asymmetric stretch wavelengths for atactic, syndiotactic and isotactic PMMA was respectively 1142.1, 1143.37 and 1144.05 cm^{-1}.

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R. H. G. Brinkhuis and A. J. Schouten, Thin-film behavior of poly(methyl methacrylates). 2. An FT-IR study of Langmuir-Blodgett films of isotactic PMMA, *Macromolecules* 1991 *24* (7), 1496-1504, DOI: 10.1021/ma00007a010

APENDICES

Table 2 – Collection of data of vibrational band assignments for PMMA tacticities, A -Atactic PMMA spectra; B – Syndioyactic PMMA spectra, C – Isotactic PMMA spectra and D – literature backgroung

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CB – chemical bond, A - Atactic PMMA, B – Syndiotactic PMMA, C – Isotactic PMMA, D – Literature background, * - non defined or identified value of vibration in cm^{-1}, (1) Brinkhuis and Schouten (1991), (2) O'Reilly and Mosher (1981) and (3) Rai et al. (2017).

POLYMER SPECTROSCOPY: NUCLEAR MAGNETIC RESONANCE - NMR

ABSTRACT

PMMA presents three main tacticities (isotactic, syndiotactic, and atactic). In this laboratory practices report PMMA chemical strucutres and tacticities will be explored throughout an NMR. ^{1}H NMR equipment used was an Bruker 800 MHz Spectrometer, utilizes an 18.8 Tesla superconducting magnet and has a sample temperature range of -40 to 80 C. Full NMR spectra collected in this study contains the signals of PMMA polymers in different chemical structures, called tacticities. The relative intensity of the chemical groups belongs to the protons in $-OCH_3$, $C-CH_3$ and $-CH_2-$ radicals. PMMA expanded spectras in the upfield region could be characterized between 0-1.3 ppm and the middle region 1.3-2.5 ppm in this study. Spectra A, B and C are characterized as atactic, syndiotactic and isotactic. $CDCl_3$ residuals was identified in a sigle peak at 7.5 to 7 ppm for all spectras. Ester groups (O-CH3) was identified between 4 – 3.5 ppm for all 3 spectras. -CH2 (Metylene groups) showed two strong peaks at 2.2 – 2 and 1.6 – 1.4 ppm for isotactic PMMA (Spectra C). Finally C-CH3 groups was identified for atactic and syndiotactic with 2 – 1.8 ppm of relative intensity.

INTRODUCTION

Since the early 1960s, NMR spectroscopy has become an indispensable tool for the characterization of organic mole- cules. Although early spectrometers were relatively insensitive and performed simple experiments at lowfield strengths, they gave reliable measurements of chemical shifts and coupling constants. NMR became a practical alternative to X-ray crystallography for the eluci- dation of natural products[3].

Poly (methyl methacrylate) (PMMA) is a transparent thermoplastic synthesized by emulsion polymerization, solution polymerization, and bulk polymerization from the MMA monomer[7]. $C_5H_8O_2$[1] , poly(methyl methactylate) (PMMA) and $(C_8H_8)_n$ [4,5] is a widely used polymer with many applications due the polymer safety and structure characteristics. Even there are still classified as a plastic material and their recyclabililty remains as challenging. PMMA are used primarily in plastic applications, derivative of acrylic acid, present excellent mechanical properties and uses in many areas as biomaterial[6].

PMMA polymer could be classified according their Tg (Transition temperature) and their chemical groups structure organization influenced by the quiral carbon as: atactic, syndiotactic and isotactic.This polymer presents three main tacticities (isotactic, syndiotactic, and atactic), where pendant groups or hydrogens are laid in certain positions. The chiral central's orientation will determine the transition temperature and crystallinity,

thermal resistance, solubility, degree of biocompatibility, hydrolyzation, and other properties. For example, the Tg is the lowest (55 °C) for the isotactic structure when ester groups are disposed on one single side of the backbone structure, from a random or regular order, respectively. The chemical structure is more stable for the atactic and syndiotactic structures, so automatically increasing the Tg to 120 and 130 °C, respectively. The different percentages of tacticities result in an almost specific Tg for each PMMA[7].

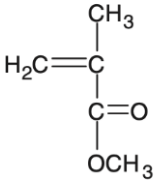
In this laboratory practices report PMMA chemical strucutres and tacticities will be explored throughout an ^{1}H NMR, nuclear magnetic resonance.

EXPERIMENTAL

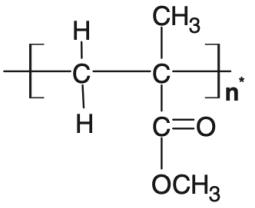
PMMA

Fig. 1 shows the chemical structure of the MMA, Monomer; PMMA, polymer of Poly(methyl methactylate)[1]. PMMA was used in this laboratory report.

Figure 1 – MMA-PMMA. MMA, Monomer; PMMA, polymer of Poly(methyl methactylate)[1].



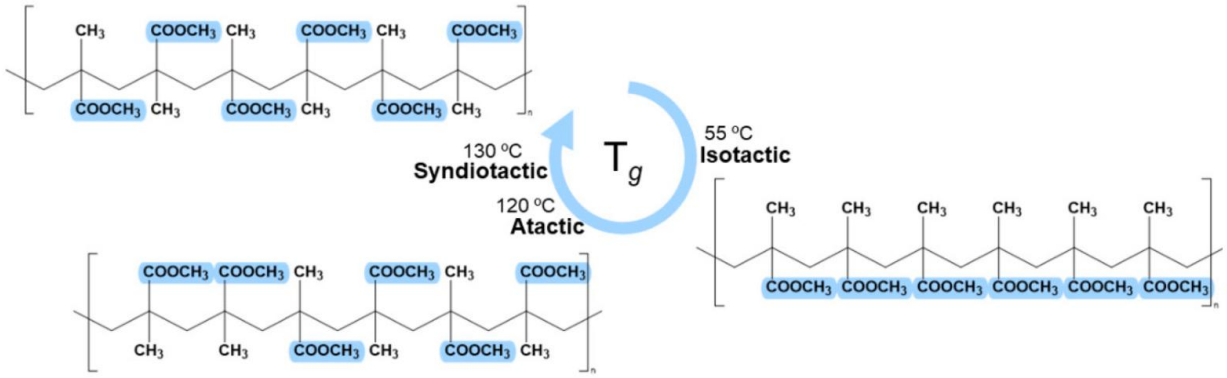
MMA Monomer[1]



PMMA Polymer[1]

3 PMMA tacticities was evaluated in this report according the structures showed in the figure 2.

Figure 2 – Adapted from Fort eat al. (2021). PMMA tacticities: isotactic, syndiotactic, and atactic and respective glass transition temperature[7].



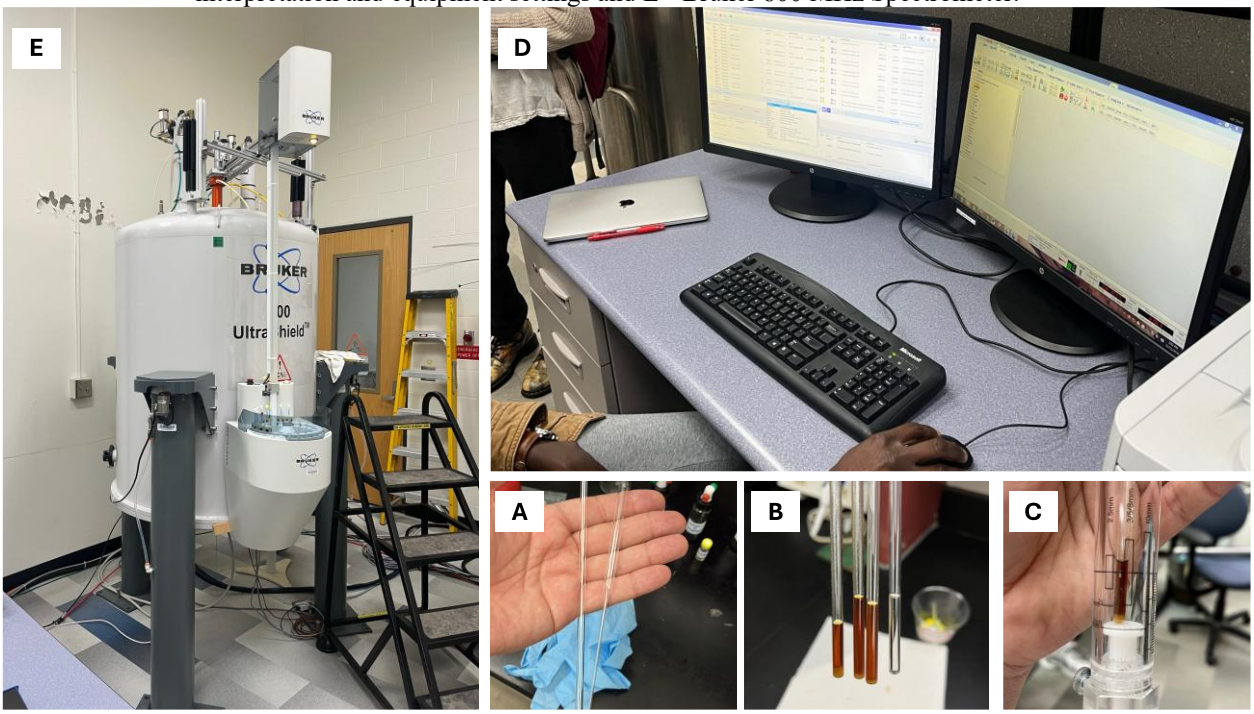
NMR INSTRUMENT AND CONDITIONS

^{1}H NMR equipment used was an Bruker 800 MHz Spectrometer, utilizes an 18.8 Tesla superconducting magnet and has a sample temperature range of -40 to 80 C. The system has a sample transport autosampler that allows up to 24 samples to be run unattended. This NMR spectrometer is ultrasensitive and equipped with four channels with gradients and is capable of analyzing liquid samples[2].

SAMPLE PREPARATION

PMMA samples was prepared and analized in the equipment described. Fig. 3 show the 5 step procedure for this laboratory practices, example of sample preparation, sample placement and equipment.

Figure 3 – NMR sample preparation and placement in 5 steps (A to E). A – NMR tube and pipette, B – Liquid samples example inside the NMR tubes, C – NMR tube holder, D – Software accoplad for spectra generation, interpretation and equipment settings and E - Bruker 800 MHz Spectrometer.

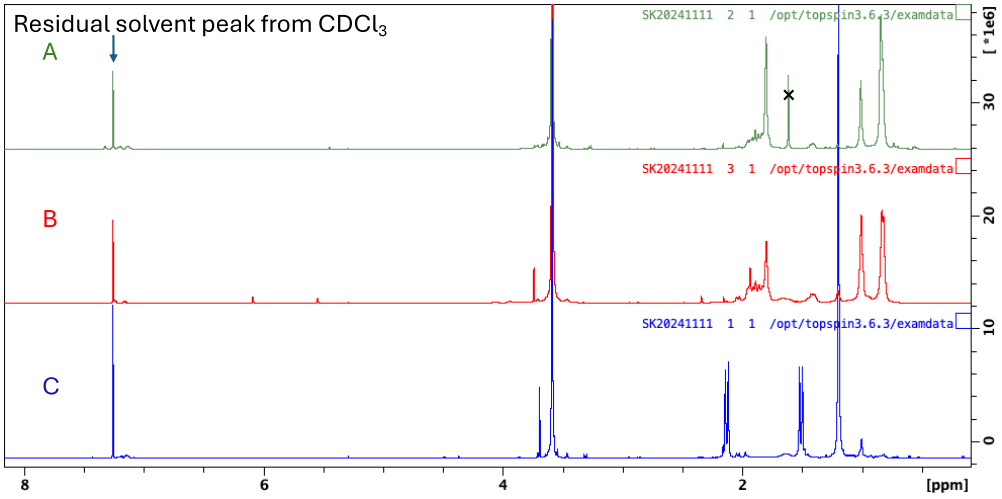


RESULTS AND DISCUSSION

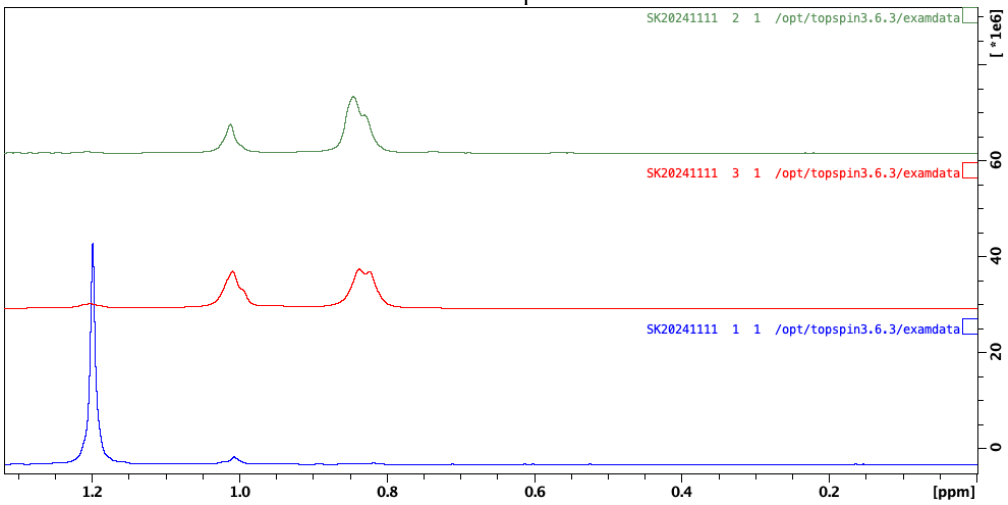
NMR SPECTRA'S

Fig. 4 shows 3 sets of NMR spectras of PMMA. First set of spectra contains the NMR spectra of the three polymers and the signals belongs to the protons in $-OCH_3$, $C-CH_3$ and $-CH_2-$ could be observed. The second and third sets of spectras have the expanded spectra in the upfield region (0-1.3 ppm) and middle region (1.3-2.5 ppm). For those (Set 2 and 3) the PMMA tacticities will be described as atactic, isotactic and syndiotactic according which functional group and their signals.

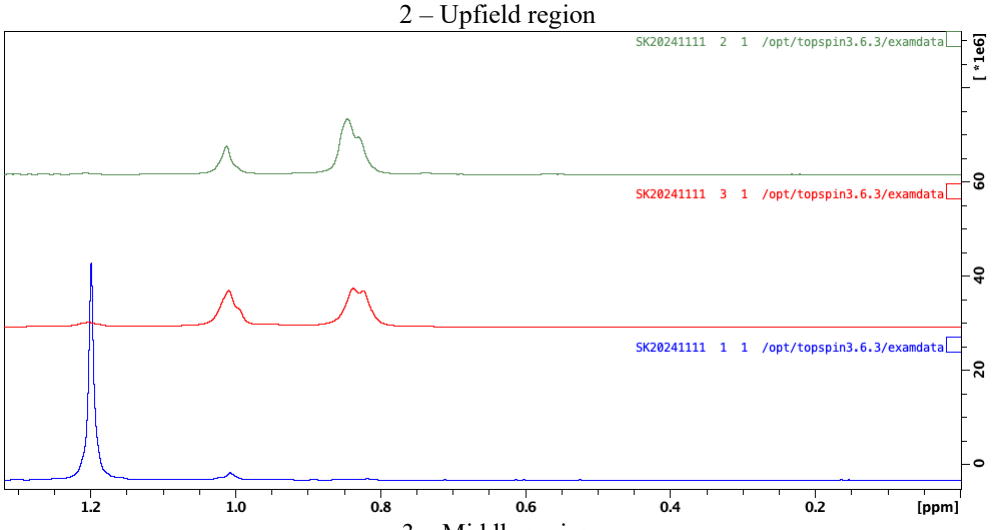
Figure 4 – 3 sets of ^{1}H NMR spectras for PMMA (1 to 3). 1 – Full NMR spectra contains polymers and the signals belongs to the protons in -OCH_3, C-CH_3 and -CH_2-. 2 and 3 – PMMA expanded spectras in the upfield region (0-1.3 ppm) and middle region (1.3-2.5 ppm) for PMMA tacticities studies.



1 – Full spectra



2 – Upfield region



3 – Middle region

PMMA CHEMICAL GROUPS AND TACTICITIES

Table 1 shows the ^{1}H NMR spectras for PMMA (fig. 4) describle according different PMMA tacticities, their chemical groups and relative intensity (ppm).

Table 1 - ^{1}H NMR spectras for PMMA (1 to 3) describle according different PMMA tacticities, their chemical groups and relative intensity (ppm)

1H NMR spectras relative intensity [ppm]						
Types of PMMA	CDCl3 Residual	O-CH3	C-CH3	CH2	C-CH3	Spectra
Atactic	7.5 - 7	4 - 3.5	2 - 1.8	ND	ND	A
Syndiotactic	7.5 - 7	4 - 3.5	2 - 1.8	ND	ND	B
Isotactic	7.5 - 7	4 - 3.5	ND	2.2 - 2 and 1.6 - 1.4	1.3 -1.25	C

*ND = non detected; [ppm] = part per million; PMMA = Poly (methyl methacrylate); CDCl3 = Deuterated chloroform or chloroform-d.

Full NMR spectra collected in this study contains the signals of PMMA polymers in different chemical structures, called tacticities. The relative intensity of the chemical groups belongs to the protons in $-OCH_3$, $C-CH_3$ and $-CH_2-$ radicals. PMMA expanded spectras in the upfield region could be characterized between 0-1.3 ppm and the middle region 1.3-2.5 ppm in this laboratory report. Table 1 summarizes all the relative intensity for each identified spectra according their tacticities as spectra A, B and C characterized as atactic, syndiotactic and isotactic. $CDCl_3$ residuals was identified in a sigle peak at 7.5 to 7 ppm for all spectras. Ester groups (O-CH3) was identified between 4 – 3.5 ppm for all 3 spectras. -CH2 (Metylene groups) showed two strong peaks at 2.2 – 2 and 1.6 – 1.4 ppm for isotactic PMMA (Spectra C). Finally C-CH3 groups was identified for atactic and syndiotactic with 2 – 1.8 ppm of relative intensity.

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Isotactic	7.5 - 7	4 - 3.5	ND	2.2 - 2 and 1.6 - 1.4	1.3 -1.25	C

*ND = non detected; [ppm] = part per million; PMMA = Poly (methyl methacrylate); CDCl3 = Deuterated chloroform or chloroform-d.

SYNTHESIS OF POLYMERS: BULK RADICAL POLYMERIZATION OF POLYSTYRENE (PST)

ABSTRACT

The outcome of this laboratory practices will be the study an observance of I) polymer yield dependence on the initiator to monomer ratio; II) molecular mass dependence on the initiator to monomer ratio and if the initiator concentration truly affect the polymer molecular mass. The radical polymerization of styrene will be carried out in bulk (no solvent) at different molar ratio of the initiator 2,2'-Azobisisobutyronitrile (AIBN) to the monomer: 1:400; 1:300; 1:200; 1:100; 1:50 (performed as duplicates). Eluent pure solutions of tetrahydrofuran (THF) was injected at a flow rate of 0.8 ml/min at 40 °C in the at the size exclusion chromatography. A SEC Waters Series: Styragel HR3, HR2, HR5 pore size, 10^3 Ångström (Å), 500 (Å) and 10^5 (Å) was applied to determine PSt and molecular mass according the tested conditions. Many chemical reactions efficiency and yield change since the monomer/initiator ratios changed accordingly the experimental design. Table 2 bellow shows the summarized results of styrene yield after, molecular mass and dispersivity after bulk polymerization. The higher amount of AIBN, initiator, 400/400 to 50/50, the higher reaction yield for styrene polymerization was founded in this laboratory report. 66 % of yield was the lower yield finded for the styrene polymerization instead 90 % of yield was the higher result for the maximum amount of AIBN applied for the tested condition. Also is noted that the molecular weight (Mn) and molecular mass (Mw) showed an tendency affected by the AIBN mainly for the maximum and minimum aditions of AIBN, values of initiator, in the condition 50/50 and 400/400.

INTRODUCTION

Polystyrene (PSt) is an odorless, tasteless, rigid thermoplastic. Polystyrene is the fourth largest thermoplastic by production volume. It is used in applications in the following major markets (listed in order of consumption): packaging, consumer/institutional goods, electrical/electronic goods, building/construction, furniture, industrial/machinery, and transportation[2].

High-impact polystyrene (HIPS) has been produced through the bulk process for over 50 years. However, many details of its complex physical chemistry are still unknown and/or are a matter of controversy. The bulk HIPS process can be either batch or con- tinuous, and the following stages can be identified: dissolution, prepolymerization, finishing, and devolatilization[3]. According the procedure of polymerization applied for Soto et al. in the dissolution stage, grated rubber is dissolved into the monomer at a relatively low tem- perature (50 –70°C), to minimize thermal polymeriza- tion.The prepolymerization stage proceeds between 90 and 120°C under well-stirred conditions and gen- erally in the presence of a chemical initiator. In a batch reaction, the system is homogeneous up to around 3% conversion, when a PS-rich phase begins to separate from

the (continuous) PB-rich phase. In our study the dissolution and prepolymerization occurs instatannealy each after the injection of liquid stryne mediated by our initiator 2,2'-Azobisisobutyronitrile (AIBN) at 65 °C during 1.5 hours. For Soto et al. the dispersed PS-rich phase grows in volume, and a phase inversion period takes place between 10 and 15% conversion of the polymer. After the phase inversion, the number of rubber particles is fixed, and the PS–monomer solution remains as the continuous phase until the end of the reaction. The initiator half-life is selected such that the initiator is almost totally consumed during the prepolymerization stage. In the case of our study, toluene was choosen for the quick dissolution of the polymerization mixture, and as mentioned AIBN initiator at this stage was comsumed according the ratio of the study.

Finally our last stage in the finishing, for Soto et al. the polymerization proceeds with an increasing temperature, from around 30 to 75% conversion. During finishing, the free radicals are basically produced by thermal monomer decomposition, and the stirring is moderated to avoid destruction of the developed morphology. Finally, the reaction mixture is heated up to 230°C and devolatilized *in vacuo* to eliminate the solvent and residual monomer. In your case of study pure grade of methanol was dropwise add into the vials allowing a physical with PSt precipitation formation into the reaction environmental.

The complexity of the HIPS process results from the combination of several effects: (1) the polymer- ization proceeds in two immiscible liquid phases; (2) the mass transfer of reagents and products be- tween phases is a function of many variables (which change along the reaction), such as temperature, viscosity, stirring rate, molar mass, grafting effi-ciency, and interfacial surface; and (3) the graft co- polymer promotes a stable liquid–liquid dispersion, and it is extremely difficult (if not impossible) to determine the composition and molecular structure in each of the phases or subphases[3]. Also the morphological studies during the polymerization reaction was primordial for many different polymers, however wasn't carried out in your study.

The outcome of this laboratory practices will be the study an observance of I) polymer yield dependence on the initiator to monomer ratio; II) molecular mass dependence on the initiator to monomer ratio and if the initiator concentration truly affect the polymer molecular mass.

EXPERIMENTAL

The radical polymerization of styrene will be carried out in bulk (no solvent) at different molar ratio of the initiator 2,2'-Azobisisobutyronitrile (AIBN) to the monomer: 1:400; 1:300; 1:200; 1:100; 1:50 (performed as duplicates).

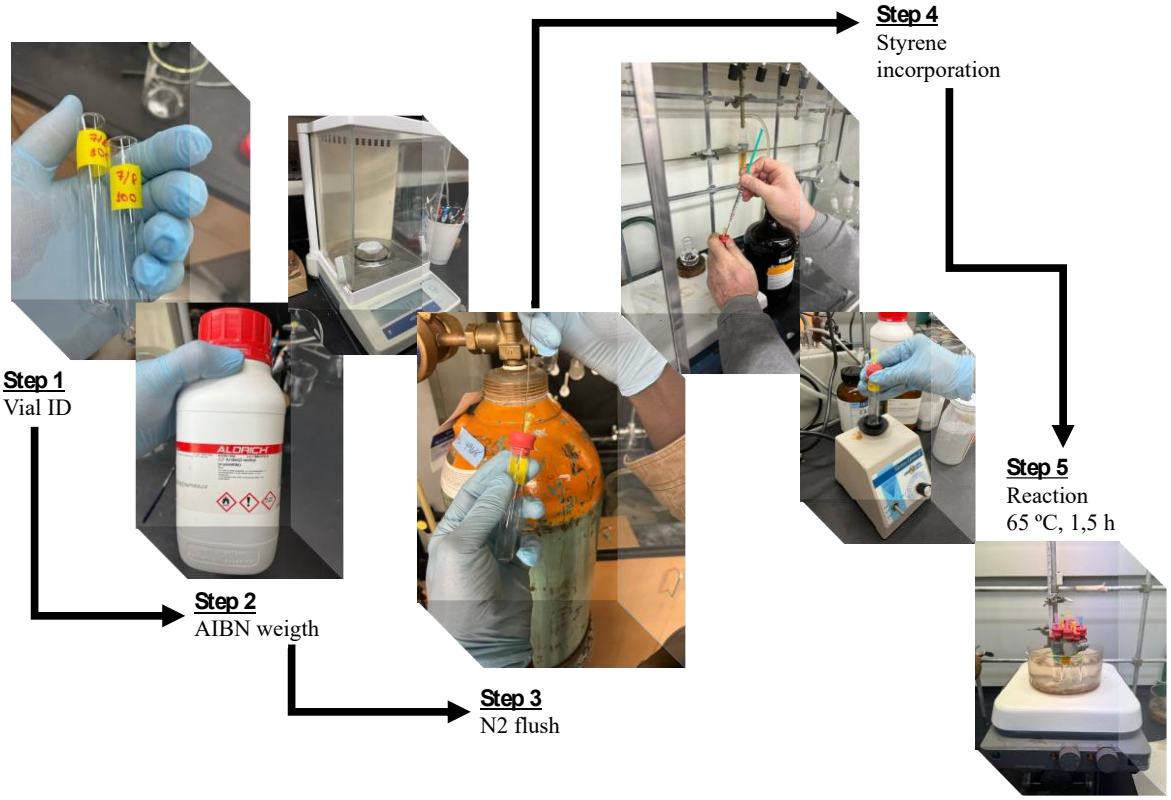
REAGENTS AND MATERIALS

The following reagents was used for this styrene radical polymerization: (1) Styrene, distilled, (2) 2,2'-Azobisisobutyronitrile (AIBN), (3) Toluene, reagent grade and (4) Methanol, reagent grade.

PST POLYMERIZATION

Figure 1 illustrate the radical polymerization of styrene in 5 steps. (1) Vial identification according the reaction condition; (2) 2,2'-Azobisisobutyronitrile (AIBN) weight; (3) Air flush into the vial environmental (N2 in this laboratory practices); (4) Styrene, distilled incorporation and mechanical homogenization and finally step (5) Polymerization reaction.

Figure 1 – Radical polymerization of styrene in 5 steps. (1) Vial identification according the reaction condition; (2) 2,2'-Azobisisobutyronitrile (AIBN) weight; (3) Air flush into the vial environmental (N2 in this laboratory practices); (4) Styrene, distilled incorporation and mechanical homogenization and finally step (5) Polymerization reaction.



The experiment use 10 test tubes. Each of them with a fixed amount of styrene – 1 g. Each condition according the reagent composition ratio is presented in the table 1.

Table 1 – Polimerization conditions applied in this Styrene radical polymerization reaction. 5 conditions of Stryne/AIBN was used

Tube #	1/2	1/4	1/6	1/8	1/9
St/initiator ratio	400	300	200	100	50
Styrene (ml)	1.1	1.1	1.1	1.1	1.1
AIBN (g)	0.0039	0.0053	0.0079	0.0158	0.0315

The following steps was taken for the polymerization according the conditions discussed.

1. Test tubes from the oven. Let them cool down to room temperature.
2. Weigh the necessary amount of initiator.
3. Add the initiator to each test tube. Cap the tubes with stoppers, flush with Ar.
4. Inject with the syringe the precalculated amount of styrene. Mix on the vortex.

5. Place the tubes in the oil bath at 65°C, and heat for 1.5h (polymerization could take longer).
6. At the proper time, remove each tube from the bath and cool quickly under the water tap (to quench).
7. Open the tube and dilute the mixture with 5 mL of toluene. Toluene is a good solvent for the monomer and polymer. Stir well.
8. When the polymerization mixture is dissolved, poor the contents dropwise into a beaker containing 5 fold excess of cold methanol under stirring. White precipitate of poly(styrene) should appear.
9. Filter and wash the formed precipitate with three 5 mL portions of methanol.
10. Dispose the liquid organic fractions in the designated waste container.
11. Place the isolated polymer in the vacuum oven to dry overnight at 50°C.
12. When dry, weigh the product, calculate yields.

SIZE-EXCLUSION CHROMATOGRAPHY (SEC)

Eluent pure solutions of tetrahydrofuran (THF) was injected at a flow rate of 0.8 ml/min at 40 °C in the at the size exclusion chromatography. A SEC Waters Series: Styragel HR3, HR2, HR5 pore size, 10^3 Ångström (Å), 500 (Å) and 10^5 (Å) was applied to determine PSt and molecular mass according the following itens.

MOLECULAR WEIGHT (MN) AND MOLECULAR MASS (MW) DETERMINATION

Molecular mass was calculated using a computed algoritm by the Sofware OmniSec version 5 (Malvern-Instruments). according the following equations and their components (Eq. 1, Eq. 2 and 3)[1].

Eq. 1

$$\mathrm{Mw}(\boldsymbol{Da}) = \sum \boldsymbol{Ni\mu i} / \sum \boldsymbol{Ni}$$

Eq. 1 (Mw) is the average molecular mass; Da is the unit in Daltons; (Ni) is the current number of polymer molecules and $\boldsymbol{\mu i}$ is the current mass of each polymer molecule.

Eq. 2

$$\mathrm{Mn}(\boldsymbol{Da}) = \sum \boldsymbol{hi\mu i} / \sum \boldsymbol{hi}$$

Eq. 2 (Mn) is the average molecular weigth; Da is the unit in Daltons; (hi) is distance in milimiters between the base line to the intersection of the refravtive index (mV) in the given data in each point of retention volume (ml) according with their respective molecular mass (Mw, Da). ($\boldsymbol{\mu i}$) is the current mass of each polymer molecule in the same point of intersection.

Eq. 3

$$\mathbf{Mw}\ (\boldsymbol{Da}) = \sum \boldsymbol{hi}(\boldsymbol{\mu i})^{\mathbf{2}} / \sum \boldsymbol{hi\,\mu i}$$

Eq. 3 (Mw) is the average of molecular mass; Da is the unit in Daltons; (hi) is distance in milimiters between the base line to the intersection of the refravtive index (mV) in the given data in each point of retention volume (ml) according with their respective molecular mass (Mw, Da). ($\boldsymbol{\mu i}$) is the current mass of each polymer molecule in the same point of intersection.

POLYDISPERSITY INDEX (MW/MN)

Polydispersity index[1] was calculated according the equation 4.

Eq. 4

$$\boldsymbol{PI = Mw/Mn}$$

Eq. 4 is the Polydispersivity Index (PI) and their components, Mn (Da) the average molecular weigth and Mw (Da) the average of molecular mass.

RESULTS AND DISCUSSION

POLY(STYRENE) POLYMERIZATION

Huang & Donald (1995) carried out cis-Polybutadiene polymerization along with the grafting monomer and AIBN initiator, were dissolved in benzene and placed in glass capillary tubes[4]. Our laboratory practices applied a similar polymerization methodology for styrene bulk radical polymerization using toluene instead benzene. Fig 2 shows the solid styrene polymer obtained after bulk polymerization in laboratory. The solid start formation during the drop wise methanol addition. The volume network increase since the addition of methanol starts. An with network of styrene starting, an cloud-like structure aspect are formed in the end of the polymerization step.

Figure 2 – Solid Poly(Styrene) obtained from a bulk radical polymerization in laboratory after washing and filtration step with pure methanol grade solvent.

POLIMERIZATION YIELD AND POLYDISPERSITY INDEX (MW/MN)

Many chemical reactions efficiency and yield change since the monomer/initiator ratios changed accordingly the experimental design. Table 2 bellow shows the summarized results of styrene yield after, molecular mass and dispersivity after bulk polymerization.

The higher amount of AIBN, initiator, 400/400 to 50/50, the higher reaction yield for styrene polymerization was founded in this laboratory report. 66 % of yield was the lower yield finded for the styrene polymerization instead 90 % of yield was the higher result for the maximum amount of AIBN applied for the tested condition. Also is noted that the molecular weight (Mn) and molecular mass (Mw) showed an tendency affected by the AIBN mainly for the maximum and minimum aditions of AIBN, values of initiator, in the condition 50/50 and 400/400. The initiator action in their higher concentration will prevent bad polymer formation and carried out the stryne polymerization for more

homodisperse specimens. However, many variations was founded in our results indicating that this relation is not clear enough and another factores in the bulk polymerization were affecting the reaction once the polidispersivity was indicating a significative variation in this practices.

Table 2 – Styrene Yield after polymerization, molecular and dispersivity, according the ratios defined in this laboratory report

[M]/[I] ratio	Yield (%)	Mn and Mw (Da)	Polidispersity
400/400	66	(A) 47500(Mn),103000(Mw) / (B) 57700(Mn),175300(Mw)	(A) 2.17 / (B) 3.04
300/300	64	(A) 54600(Mn),146800(Mw) / (B) 67300(Mn),162200(Mw)	(A) 2.69 / (B) 2.41
200/200	85	(A) 45300(Mn),120200(Mw) / (B) 45700(Mn),123700(Mw)	(A) 2.66 / (B) 2.71
100/100	79	(A) 33900(Mn),103600(Mw) / (B) 33200(Mn),98200(Mw)	(A) 3.07 / (B) 2.96
50/50	90	(A) 20700(Mn),60300(Mw) / (B) 21000(Mn),71500(Mw)	(A) 2.92 / (B) 3.41

*Yield data was expressed in average values for the two samples repetitions; Molecular mass and dispersivity was presented for each sample (A and B) without mathematical average; M/I: ratio AIBN/styrene.

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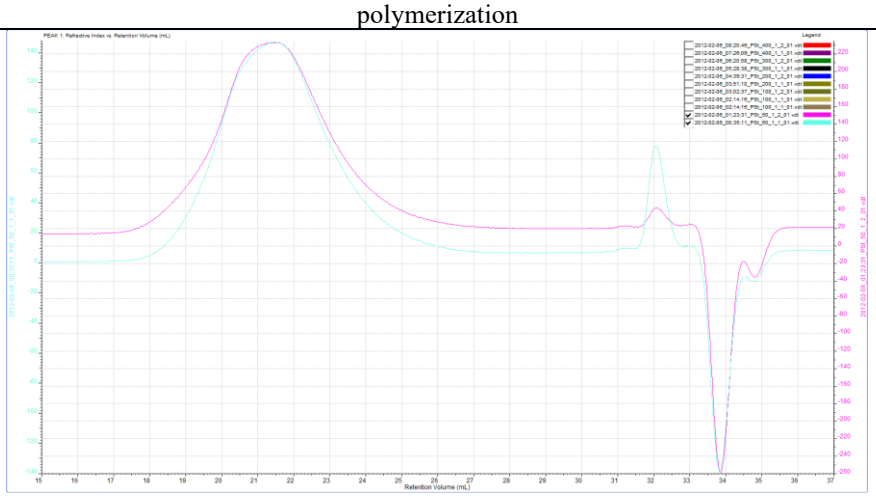
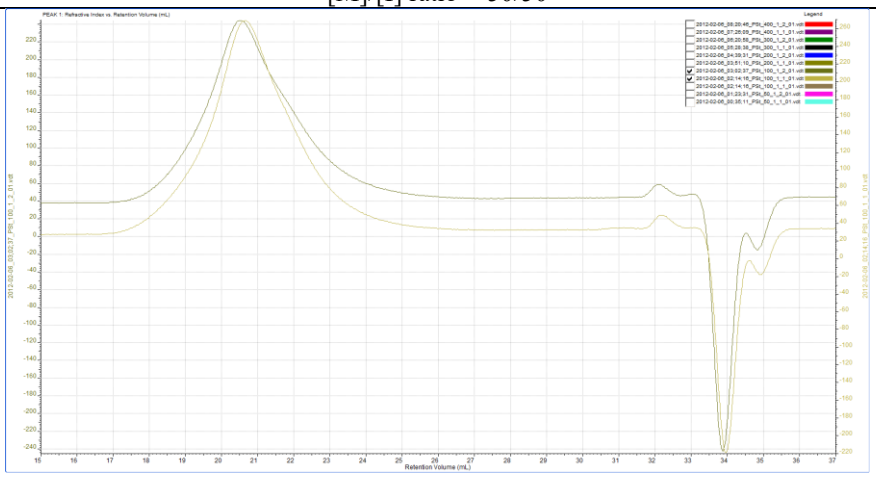
APENDICES

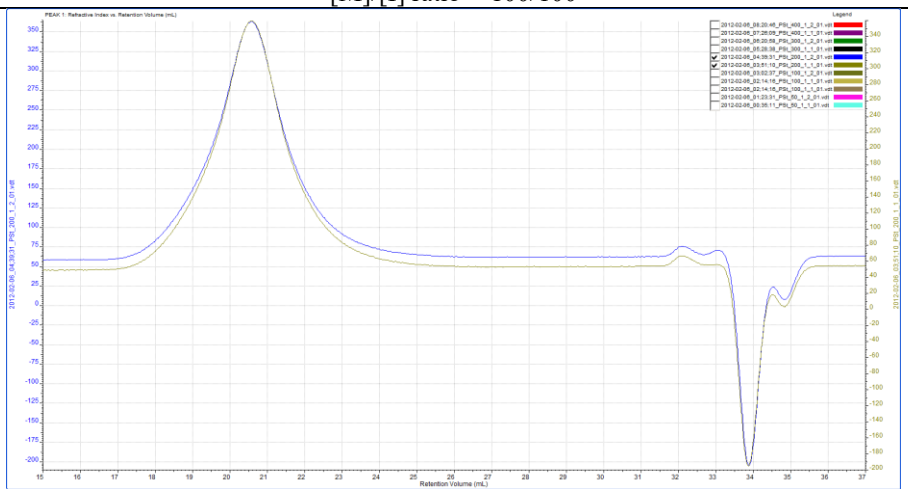
Table 3 – Set of graphycal results from SEC/GPC analysis of styrene samples produced in laboratory via bulk polymerization



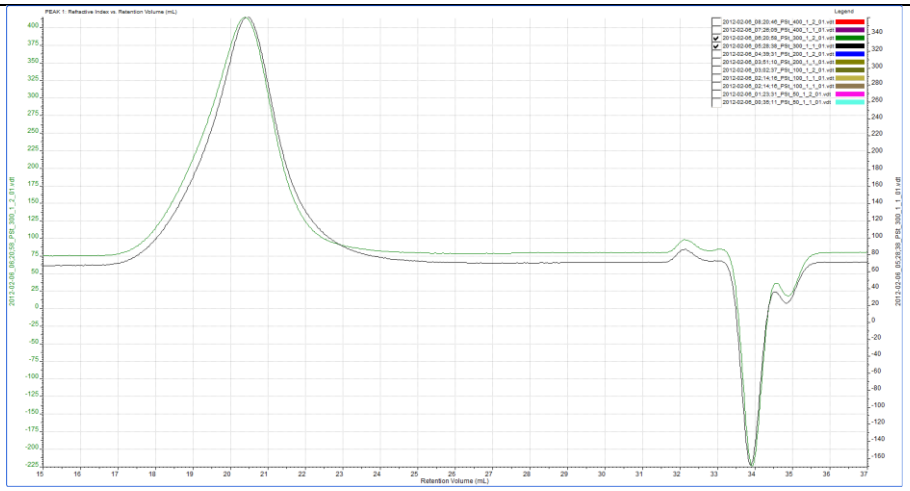
[M]/[I] ratio - 50/50



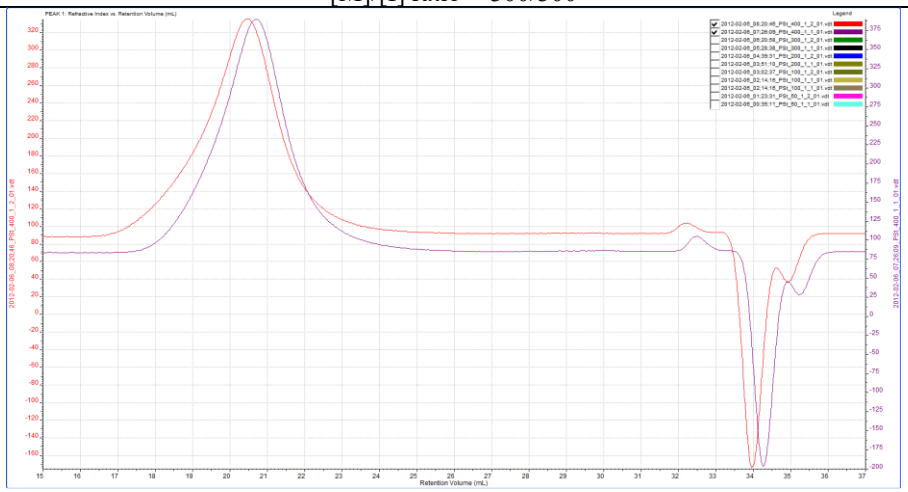
[M]/[I] ratio - 100/100



[M]/[I] ratio - 200/200



[M]/[I] ratio - 300/300



[M]/[I] ratio - 400/400

Table 4 – Polystyrene masses according to each polymerization condition after oven dried step from bulk polymerization procedure

Condition	Mass (mg)	Mass (g)	Filter Paper Mass (g)	Polystyrene mass (g)
50-1	1232.21	1.232	0.33904	0.893
50-2	1249.36	1.249	0.34085	0.909
100-1	1083.13	1.083	0.33436	0.749
100-2	1154.4	1.154	0.32575	0.829
200-1	1127.19	1.127	0.33148	0.796
200-2	1227.5	1.228	0.32818	0.899
300-1	872.22	0.872	0.33904	0.533
300-2	1094.96	1.095	0.34085	0.754
400-1	1036.39	1.036	0.32464	0.712
400-2	935.95	0.936	0.3274	0.609

SYNTHESIS OF POLYMERS: LIQUID-SOLVENT POLYMERIZATION OF POLYSTYRENE (PST)

ABSTRACT

Polymerization are well know reactions used by many different polymers syntesis and studies. Some of these reactions could be divided into steps of formation by a free-radical, chain addition mechanism. This process consists of three steps: initiation, propagation, and termination. This study will observe: I) polymer yield dependence on the initiator to monomer ratio; II) molecular mass dependence on the initiator to monomer ratio and if the initiator concentration truly affect the liquid-solvent polymerization. Radical polymerization of styrene will be carried out in liquid phase mediated by toluene at different molar ratio of the initiator 2,2'-Azobisisobutyronitrile (AIBN) to the monomer: 1:400; 1:300; 1:200; 1:100; 1:50. Eluent pure solutions of tetrahydrofuran (THF) was injected at a flow rate of 0.8 ml/min at 40 °C in the at the size exclusion chromatography. A SEC Waters Series: Styragel HR3, HR2, HR5 pore size, 10^3 Ångström (Å), 500 (Å) and 10^5 (Å) was applied to determine PSt and molecular mass according the tested conditions. Granulated-like structure are formed for the liquid-phase in the end of the polymerization step obtained in this study. Higher reaction yields was presented for the conditions 50 and 200, 72 % (1) / 71 % (2) for 50/50 and 77 % (1) / 87 % (2) for 200/200 M/I (ratio AIBN/styrene) respectively. The lower yields in this study was expalined by the chain transfer to solvent and monomer that have significant impact for solution polymerization. Molecular weight (Mn) and molecular mass (Mw) was clearly affected by the AIBN mainly for the maximum and minimum aditions in the condition 50/50 and 400/400 in the bulk polymerization. AIBN in their higher concentration will prevent bad polymer formation and carried out the stryne polymerization instead to growing chains only. For liquid-solvent polymerization the polidyspersivity was lower than results finded in the bulk polymerization as discussed above (1.62 to 3.84).

INTRODUCTION

Polystyrene (PSt) is an odorless, tasteless, rigid thermoplastic[2]. There are four different varieties clear, or so called general purpose polystyrene (GPPS), impact modified polystyrene (IPS), more commonly called HIPS (high impact polystyrene, see Polymer Glasses, Fracture of: Factors Controlling Toughness), expanded polystyrene (EPS), and the recently introduced syndiotactic polystyrene (sPS, see Polystyrene: Syndiotactic). Polystyrene owes its high sales to good all round properties, easy processing and to an environmentally safe production[5].

Polymerization are well know reactions used by many different polymers syntesis and studies. Some of these reactions could be divided into steps of formation as for example Methylmethacrylate is often polymerized by a free-radical, chain addition mechanism. This process consists of three steps: initiation, propagation, and termination[7].

The prepared solution polymerization in our study start from the dissolution and pre-polymerization occurs instatannealy each after the injection of liquid stryne mediated

by our initiator 2,2'-Azobisisobutyronitrile (AIBN) in liquid toluene environmental at 65 °C during 1.5 hours. In the case of our study, toluene was choosen for the quick dissolution of the polymerization mixture liquid-phase, and as mentioned AIBN initiator at this stage was comsumed according the ratio of the study.

In emulsion polymerization, particle nuclei are produced in the monomer-swollen micelles (micellar nucleation) or in the aqueous phase (homogeneous nucleation). Nucleation in the emulsified monomer droplets is insignificant because of the extremely small oil-water interfacial area available for competing with micelles for free radicals generated in the aqueous phase[6]. Surfactants could be used coupled agents in between the phases of these reactions however was not applied in our laboratory studies for bulk and liquid reactions.

For the termination stage of our reaction (Bulk and liquid polymerizations) pure grade of methanol was dropwise add into the vials allowing a physical with PSt precipitation formation into the reaction environmental.

The outcome of this laboratory practices will be the study an observance of I) polymer yield dependence on the initiator to monomer ratio; II) molecular mass dependence on the initiator to monomer ratio and if the initiator concentration truly affect the polymer molecular mass.

EXPERIMENTAL

The radical polymerization of styrene will be carried out in liquid phase mediated by toluene at different molar ratio of the initiator 2,2'-Azobisisobutyronitrile (AIBN) to the monomer: 1:400; 1:300; 1:200; 1:100; 1:50 (performed as duplicates).

REAGENTS AND MATERIALS

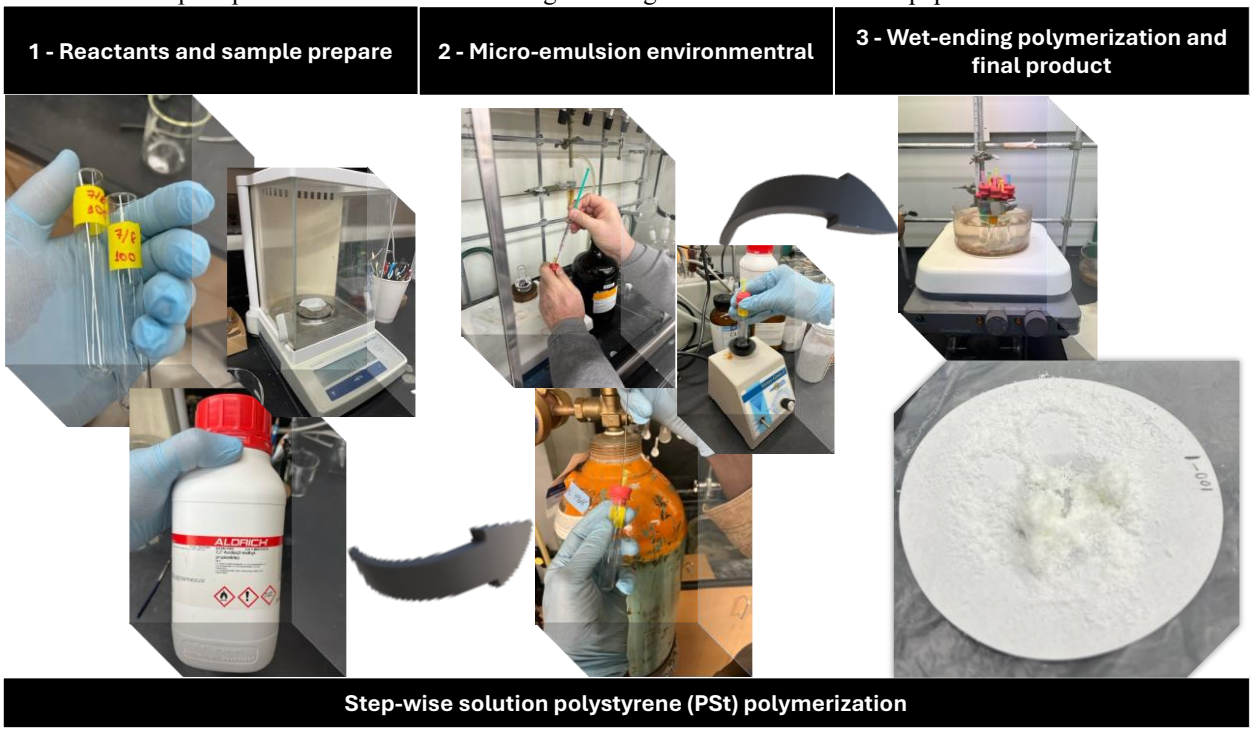
The following reagents was used for this styrene radical polymerization: (1) Styrene, distilled, (2) 2,2'-Azobisisobutyronitrile (AIBN), (3) Toluene, reagent grade and (4) Methanol, reagent grade.

PST POLYMERIZATION STEP-WISE REACTION

Figure 1 illustrate the polymerization of styrene in 3 steps. (1) Reactants and sample prepare; (2) Micro-emulsion environmental and (3) Wetending polymerization and final

product. Phase 1 is composed by vial identification according the reaction condition; 2,2'-Azobisisobutyronitrile (AIBN) weight and addition. Phase 2 is composed by nitrogen flush into the vial; Liquid toluene addition into the vial and mechanical homogenization via vortex. Finally phase 3 is composed by the polymerization reaction into the vials followed by the drop-wise precipitation and chemical washing resulting in the final solid at the paper filter.

Figure 1 – Step-wise solution polystyrene (PSt) polymerization. (1) Reactants and sample prepare; (2) Micro-emulsion environmental and (3) Wetending polymerization and final product. Phase 1 is composed by vial identification according the reaction condition; 2,2'-Azobisisobutyronitrile (AIBN) weight and addition. Phase 2 is composed by nitrogen flush into the vial; Liquid toluene addition into the vial and mechanical homogenization via vortex. Finally phase 3 is composed by the polymerization reaction into the vials followed by the drop-wise precipitation and chemical washing resulting in the final solid at the paper filter.



The experiment use 10 test tubes. Each of them with a fixed amount of styrene – 1 g. Each condition according the reagent composition ratio is presented in the table 1.

Table 1 – Polimerization conditions applied in this styrene radical polymerization reaction. 5 conditions of Stryne(St)/AIBN was used

Tube #	1/2	1/4	1/6	1/8	1/9
St/initiator ratio	400	300	200	100	50
Styrene (ml)	1.1	1.1	1.1	1.1	1.1
AIBN (g)	0.0039	0.0053	0.0079	0.0158	0.0315

The following steps was taken for the polymerization according the conditions discussed.

1. Test tubes from the oven. Let them cool down to room temperature.
2. Weigh the necessary amount of initiator.
3. Add the initiator to each test tube. Cap the tubes with stoppers, flush with Ar.
4. Inject with the syringe the precalculated amount of styrene. Mix on the vortex.
5. Open the tube and dilute the mixture with 3 mL of toluene. Toluene is a good solvent for the monomer and polymer. Stir well.
6. Place the tubes in the oil bath at 65°C, and heat for 1.5h (polymerization could take longer).
7. At the proper time, remove each tube from the bath and cool quickly under the water tap (to quench).
8. When the polymerization mixture is dissolved, poor the contents dropwise into a beaker containing 5 fold excess of cold methanol under stirring. White precipitate of poly(styrene) should appear.
9. Filter and wash the formed precipitate with three 5 mL portions of methanol.
10. Dispose the liquid organic fractions in the designated waste container.
11. Place the isolated polymer in the vacuum oven to dry overnight at 50°C.
12. When dry, weigh the product, calculate yields.

SIZE-EXCLUSION CHROMATOGRAPHY (SEC)

Eluent pure solutions of tetrahydrofuran (THF) was injected at a flow rate of 0.8 ml/min at 40 °C in the at the size exclusion chromatography. A SEC Waters Series: Styragel HR3, HR2, HR5 pore size, 10^3 Ångström (Å), 500 (Å) and 10^5 (Å) was applied to determine PSt and molecular mass according the following itens.

MOLECULAR WEIGHT (MN) AND MOLECULAR MASS (MW) DETERMINATION

Molecular mass was calculated using a computed algoritm by the Sofware OmniSec version 5 (Malvern-Instruments). according the following equations and their components (Eq. 1, Eq. 2 and 3)[1].

Eq. 1

$$\mathrm{Mw}(\boldsymbol{Da}) = \sum \boldsymbol{Ni\mu i} / \sum \boldsymbol{Ni}$$

Eq. 1 (Mw) is the average molecular mass; Da is the unit in Daltons; (Ni) is the current number of polymer molecules and $\boldsymbol{\mu i}$ is the current mass of each polymer molecule.

Eq. 2

$$\text{Mn}(\boldsymbol{Da}) = \sum \boldsymbol{hi\mu i} / \sum \boldsymbol{hi}$$

Eq. 2 (Mn) is the average molecular weigth; Da is the unit in Daltons; (hi) is distance in milimiters between the base line to the intersection of the refravtive index (mV) in the given data in each point of retention volume (ml) according with their respective molecular mass (Mw, Da). ($\boldsymbol{\mu i}$) is the current mass of each polymer molecule in the same point of intersection.

Eq. 3

$$\textbf{Mw}\ (\boldsymbol{Da}) = \sum \boldsymbol{hi}(\boldsymbol{\mu i})^{\mathbf{2}} / \sum \boldsymbol{hi}\,\boldsymbol{\mu i}$$

Eq. 3 (Mw) is the average of molecular mass; Da is the unit in Daltons; (hi) is distance in milimiters between the base line to the intersection of the refravtive index (mV) in the given data in each point of retention volume (ml) according with their respective molecular mass (Mw, Da). ($\boldsymbol{\mu i}$) is the current mass of each polymer molecule in the same point of intersection.

POLYDISPERSITY INDEX (MW/MN)

Polydispersity index[1] was calculated according the equation 4.

Eq. 4

$$\boldsymbol{PI = Mw/Mn}$$

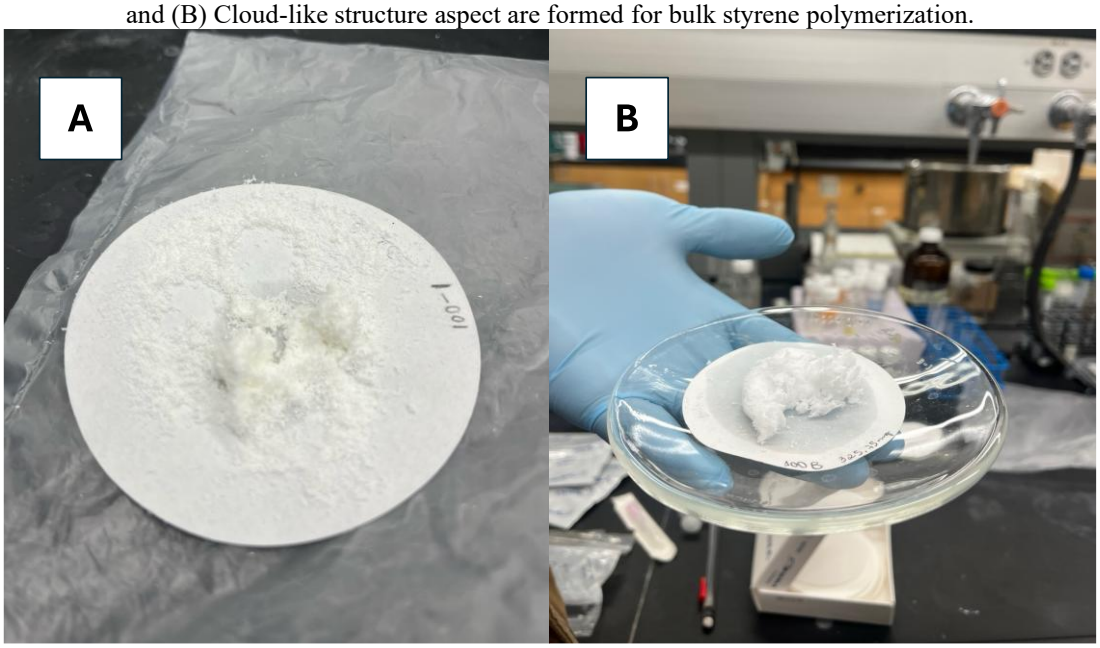
Eq. 4 is the Polydispersivity Index (PI) and their components, Mn (Da) the average molecular weigth and Mw (Da) the average of molecular mass.

RESULTS AND DISCUSSION

POLY(STYRENE) POLYMERIZATION

Fig 2 shows the solid styrene polymer obtained after liquid-phase polymerization in laboratory. The solid start formation during the drop wise methanol addition. The volumetric network increase since the addition of methanol starts. An with network of styrene starting, a cloud-like structure aspect are formed for bulk styrene polymerization obtained in the first report and a granulated-like structure are formed for the liquid-phase in the end of the polymerization step obtained in this report.

Figure 2 – Poly(Styrene) obtained from a solvent radical polymerization after washing and filtration step with pure methanol grade solvent. (A) Granulated-like structure aspect are formed for liquid-phase polymerization and (B) Cloud-like structure aspect are formed for bulk styrene polymerization.



POLIMERIZATION YIELD AND POLYDISPERSITY INDEX (MW/MN)

Many chemical reactions efficiency and yield change since the monomer/initiator ratios changed accordingly the experimental design. Table 2 bellow shows the summarized results of styrene yield, molecular weigth, molecular mass and polidispersivity after solvent polymerization.

The Yields obtained from each reaction was significative different from the yield obtained from the bulk polymerization as seing in the table 3. The higher yields was presented for the conditions 50 and 200, 72 (1) / 71 (2) for 50/50 and 77 (1) / 87 (2) for 200/200 M/I (ratio AIBN/styrene) respectively. The remained conditions showed higher variations compared with the first laboratory practices when the conditions 50 and 400 of M/I (ratio AIBN/styrene) presented the higher and lower yields respectively.

As mentioned above the main steps characterized in a polymerization reaction are initiation, propagation, and termination[7]. All the phases are significative important for the reactions however to explain the poor yield obtained in the liquid-solvent polymerization compared with the bulk polymerization specific steps into initiation as chain initiation and into propagation to termination as chain transfer and free radical formation will be shortly discussed.

Free radicals are usually produced by the thermal decomposition of an initiator, such as benzoyl peroxide (BPO) or 2,2'-azobisisobutyronitrile (AIBN). Both fragments easily into two primary radicals and a gas molecule. The primary radicals then react with surrounding monomers to initiate growing polymer chains[7]. The gas formation was an indicative of these reaction in the bulk polymerization in the first laboratory practices. Not every propagation step leads to lengthening of the radical chain. Transfer of the active site from one macroradical to another molecule is yet another possibility. This radical transfer process terminates the growing radical and initiates a new polymer chain. The process involves abstracting a hydrogen atom from a donor molecule, converting it into a transfer radical. The donor molecule can be (1) the monomer, (2) the polymer, (3) the initiator, or (4) any solvent. Any impurities in the reacting medium can also cause chain transfer. Growth of the new chain occurs when the transferred radical reacts with more monomer. Chain transfer reactions are usually ignored in modeling bulk polymerization. However, chain transfer to solvent and monomer may have significant impact for solution polymerization[7]. The step-wise addition of toluene in the liquid-solvent polymerization could be an factor com compete with the monomer/AIBN impacting then in the yields compared with bulk polymerization.

Finally, when termination occurs when two radicals react via a bimolecular process. For PMMA produced during the polymerization raises the viscosity of the reacting medium and can affect the mobility of the macroradicals[7]. Same mechanics could be considered for PSt in this case for both bulk and liquid solvent polymerization reactions. When termination occurs by disproportionation, a terminal double bond remains. Branching may occur if this double bond is attacked and incorporated into another growing radical. This side reaction increases both molecular weight (Mn) and molecular mass (Mw), by decreasing the number of polymer chains while increasing the weight of the polymer formed[7]. This effect was clearly observed for the bulk and liquid-solvent polymerization reactions for both laboratory practices. Was noted that the molecular weight (Mn) and molecular mass (Mw) showed an tendency affected by the AIBN mainly for the maximum

and minimum aditions of AIBN, values of initiator, in the condition 50/50 and 400/400 in the bulk polymerization. The initiator addtion in their higher concentration will prevent bad polymer formation and carried out the stryne polymerization instead to growing chains only. For liquid-solvent polymerization the polidyspersivity was lower than results finded in the bulk polymerization as discussed above.

Table 2 – Styrene yield, molecular weigth, molecular mass and dispersivity, according their ratios after solution polymerization

[M]/[I] ratio	Yield (%)	Molecular Mass (Da)	Polydispersity
		M_n,$M_{w\,(1)}$ / M_n,$M_{w\,(2)}$	
400/400	39 (1) / 40 (2)	19400,31300 (1) / 20100,33000 (2)	1.62 (1) / 1.64 (2)
300/300	8 (1) / 48 (2)	4300,16200 (1) / 22200,37500 (2)	3.81 (1) / 1.69 (2)
200/200	77 (1) / 87 (2)	2300,4300 (1) / 2300,4500 (2)	1.89 (1) / 1.94 (2)
100/100	41 (1) / 51 (2)	9100,16700 (1) / 16300,27200 (2)	1.84 (1) / 1.67 (2)
50/50	72 (1) / 71 (2)	3400,6600 (1) / 3800,7200 (2)	1.94 (1) / 1.90 (2)

*Yield (%) data; Molecular weigth (Mn) (Da); Molecular mass (Mw) (Da) and Dispersivity was presented for each sample (1 and 2) without mathematical average; M/I: ratio AIBN/styrene.

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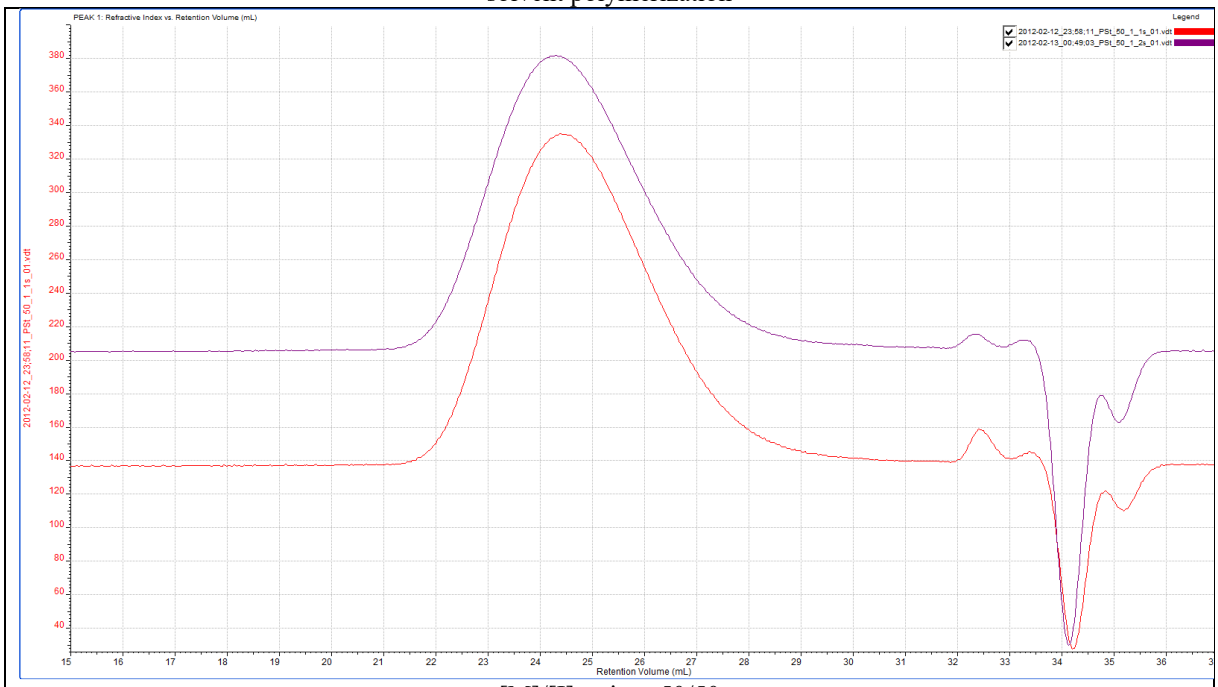
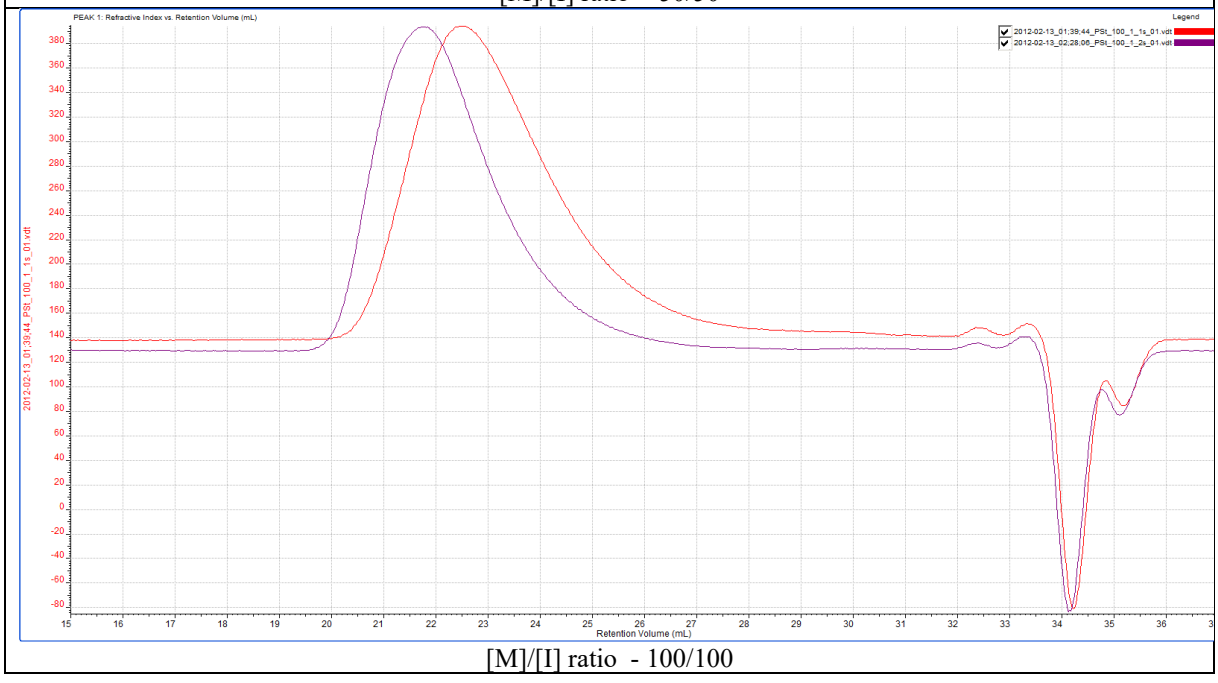
APENDICES

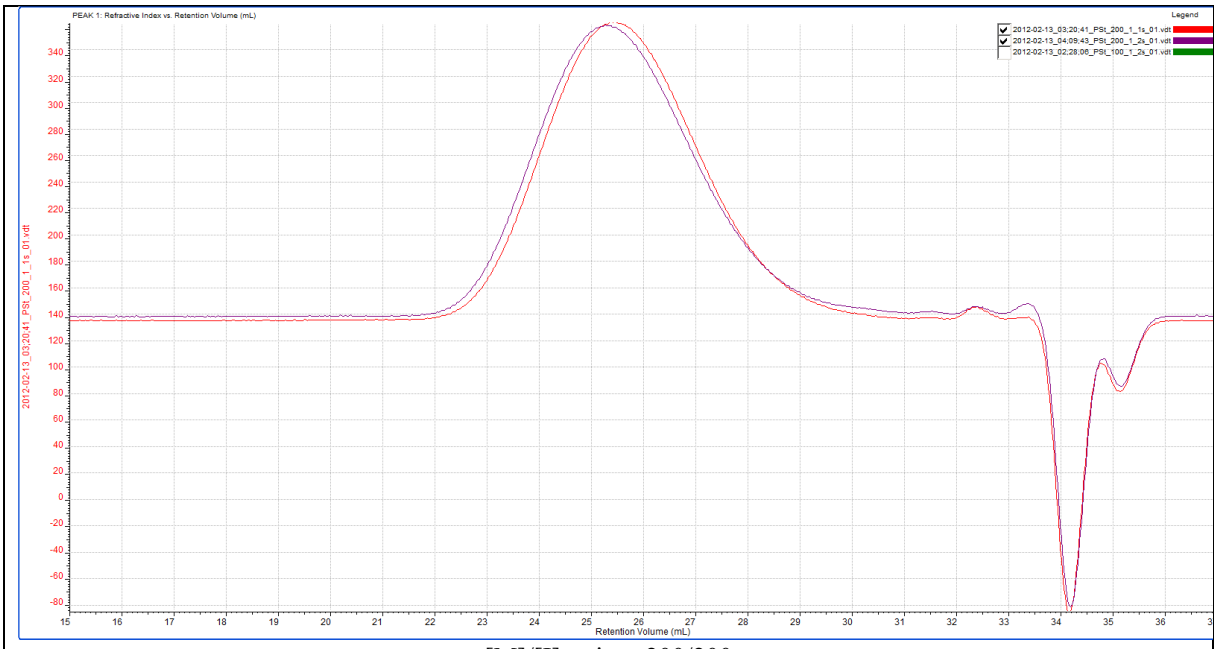
Table 3 – Set of graphycal results from SEC/GPC analysis of styrene samples produced in laboratory via liquid-solvent polymerization



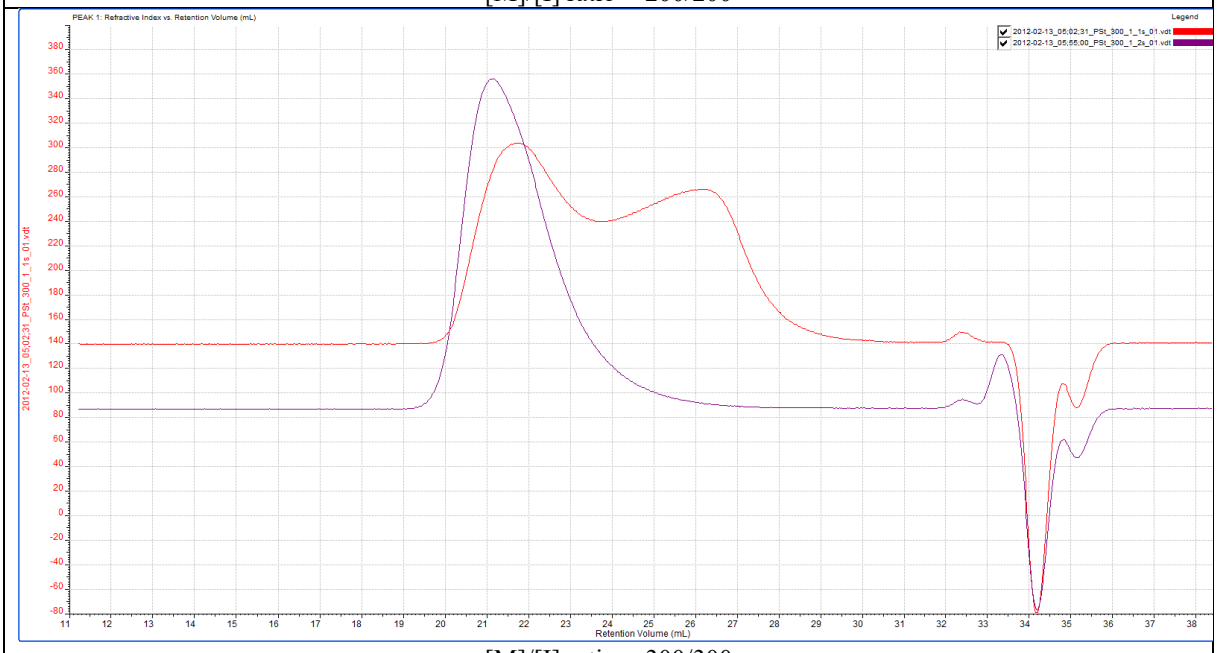
[M]/[I] ratio - 50/50



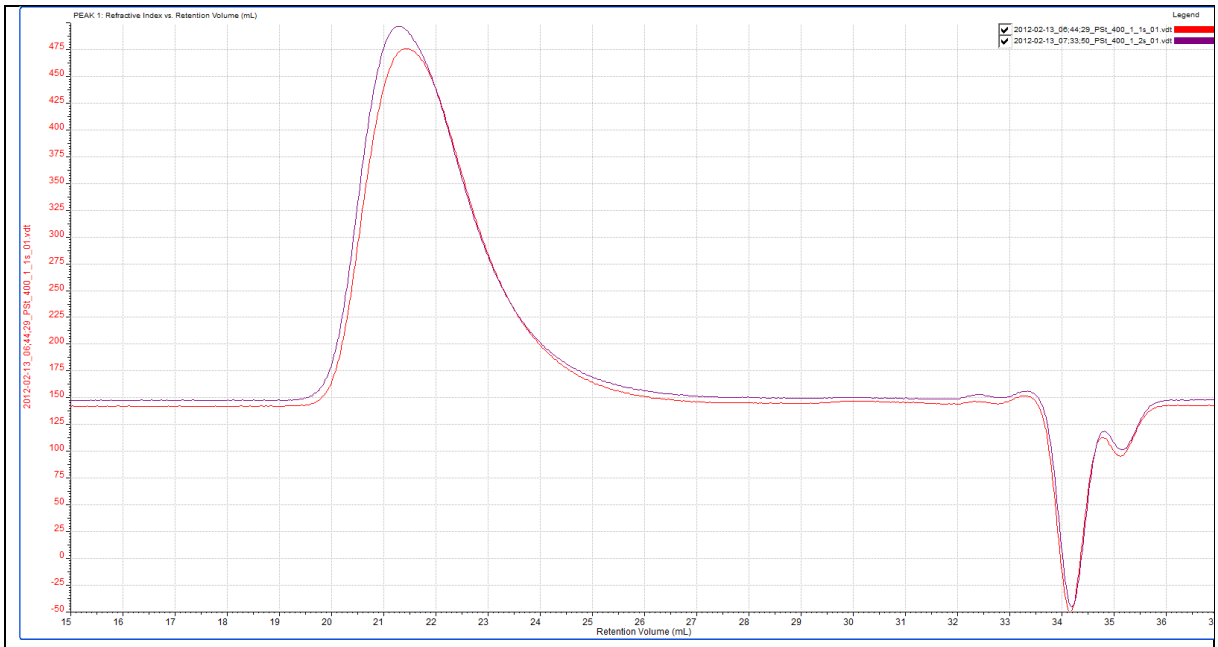
[M]/[I] ratio - 100/100



[M]/[I] ratio - 200/200



[M]/[I] ratio - 300/300



[M]/[I] ratio - 400/400

Table 4 – Polystyrene (PSt) masses according to each liquid-solvent polymerization condition after oven dried step

Condition	Mass filter paper+PSt (mg)	Mass filter paper+PSt (g)	Filter Paper Mass (g)	PSt (g)	Yield, %
50-1	1055.82	1.06	0.34	0.72	72%
50-2	1034.75	1.03	0.32	0.71	71%
100-1	730.86	0.73	0.32	0.41	41%
100-2	830.92	0.83	0.32	0.51	51%
200-1	1096.53	1.10	0.32	0.77	77%
200-2	1197.42	1.20	0.33	0.87	87%
300-1	410.76	0.41	0.33	0.08	8%
300-2	793.31	0.79	0.31	0.48	48%
400-1	708.95	0.71	0.32	0.39	39%

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