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UNIVERSAL CALIBRATION FOR GPC OF NITROCELLULOSE

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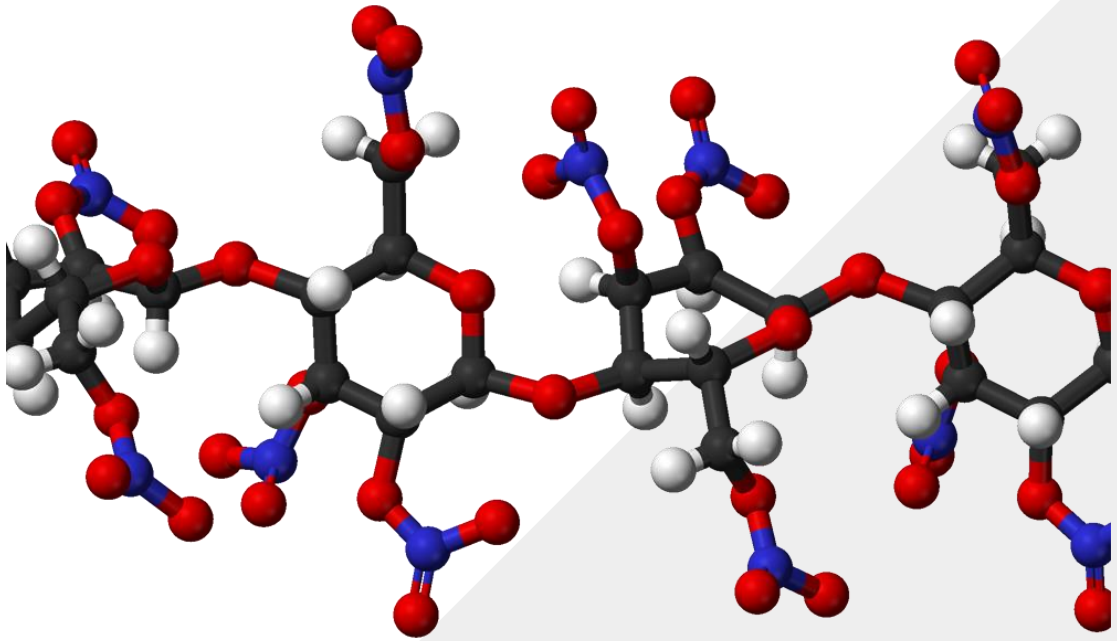
MOST IMPORTANT MOLECULAR PROPERTIES OF NITROCELLULOSE

a) Degree of nitration of Nitrocellulose

b) Degree of polymerization of Nitrocellulose.



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DEGREE OF POLYMERIZATION AND NITROCELLULOSE BEHAVIOUR

a) Procesability of NC doughts

b) Mechanical properties of propellants.

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CHARACTERIZATION OF THE DEGREE OF POLYMERIZATION OF NITROCELLULOSE

Viscosity	
Pros	Cons
- Cheap method	- Not a unique method for characterizing NC viscosity (falling ball, Höppler, Capillary viscosity)
- Reproducible	-Viscosity is dependent on degree of polimerization and degree of nitration
- More representative NC sample. On the range of grams	- Indirect method for measuring the degree of polymerization

CHARACTERIZATION OF THE DEGREE OF POLYMERIZATION OF NITROCELLULOSE

- *"Scientific/Technical Workshop on Nitrocellulose Testing"*, NC Symposium Montreal, 2016
GPC good alternative to viscosity for the characterization of polymeric properties

- Well defined procedure for analysis by GPC of nitrocellulose samples in STANAG-4178 Ed.2

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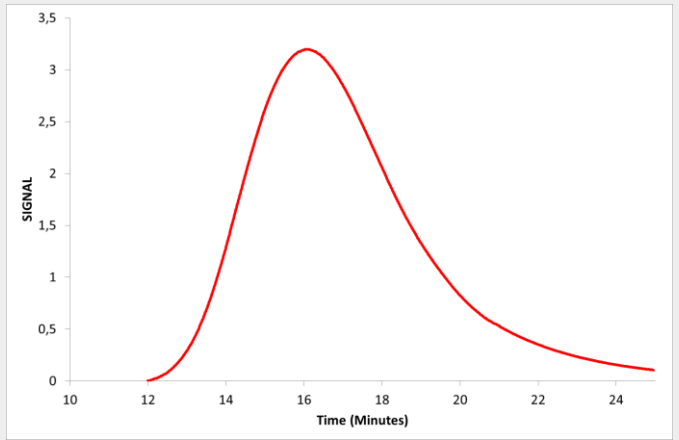
SETTING-UP OF GPC AT MAXAM. CHARACTERIZATION BY GPC AND BERGERAC TYPE VISCOSITY OF 40 SAMPLES OF GRADE B NITROCELLULOSE.

40 Samples of Grade B NC

Bergerac Type Viscosity

GPC



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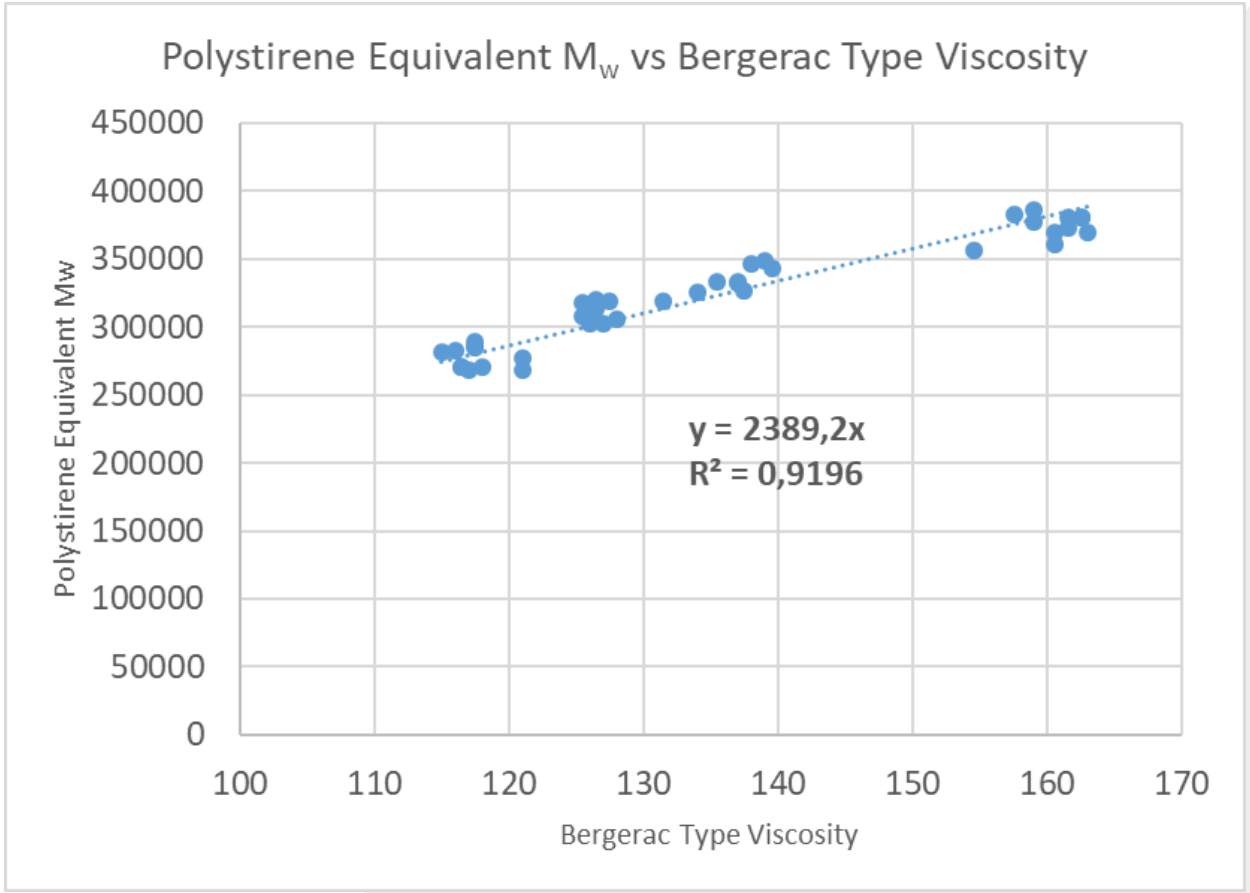
- Correlation between Type Viscosity and Weight Average Molecular Weight.



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- **Degree of polymerization of NC is to high considering the one of the cellulose used in the manufacturing of Grade B Nitrocellulose Samples.** The cellulose used in the manufacturing of the Grade B nitrocellulose has a degree of polymerization between **1000-1200** calculated from its intrisic viscosity (ISO-5351).

Samples	Polystirene Equivalent Mw	DP from Polystirene Equivalent Mw for 13,5% Nitrogen Nitrocellulose
Cellulose		**1000-1200**
1	308403	**1078**
2	285900	**999**
3	369920	**1292**
4	270767	**946**
5	329677	**1152**

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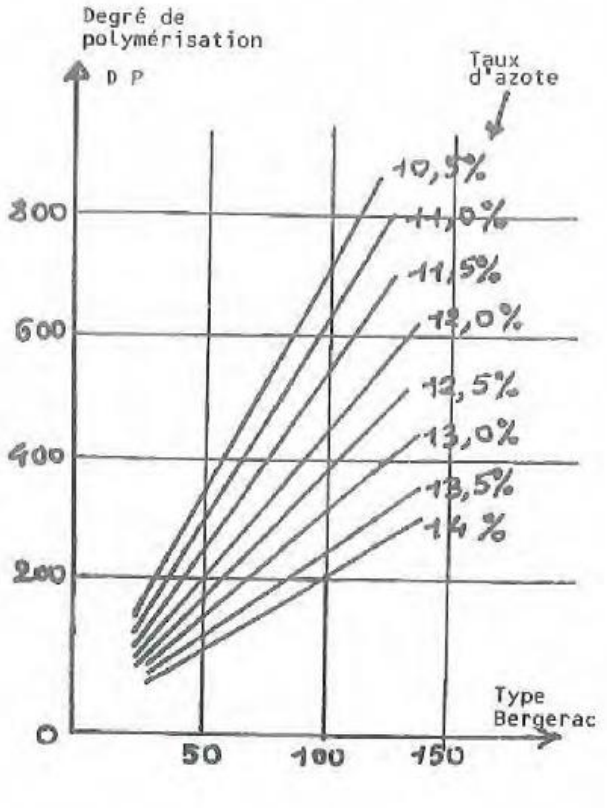
- **Degree of polymerization by GPC of Grade B Nitrocellulose vs Degree of polymerization obtained from Bergerac Type Viscosity.**



Samples	DP from Polystirene Equivalent Mw for 13,5% Nitrogen Nitrocellulose	Bergerac Type Viscosity	DP from Bergerac Type Viscosity
1		137,5	339
2		125,5	309
3		160,5	395
4		116,5	287
5		142	350

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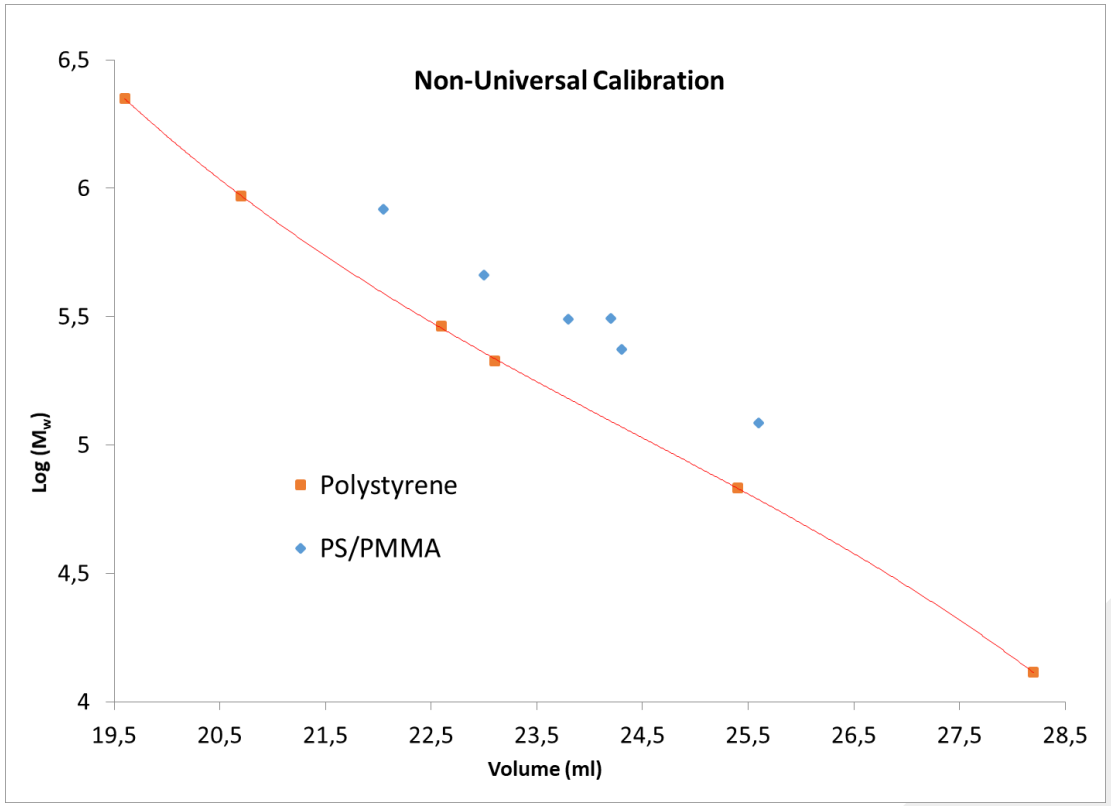
Two approaches for getting real Molecular Weights:

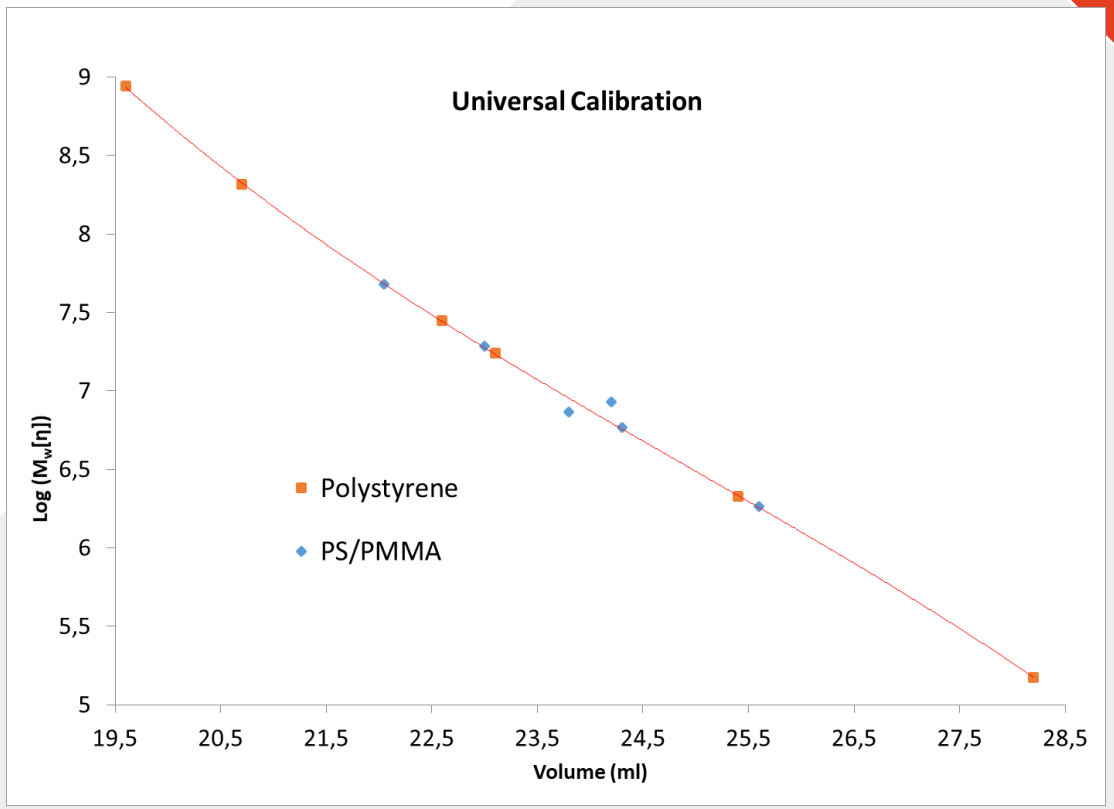
1) Use of a multidetector method with a Multiangle Ligth detector (MALS) that provides direct measurement of NC molecular weight. Approach presented during the Montreal NC Symposium.

Progress toward reliable NC molecular mass distribution by GPC *by* Dr E Stubbs

Main Disadvantage: Quite expensive equipment

2) **Use of the universal calibration approach**. In 1967 H. Benoit shows curve of the logarithm of the Hydrodinamic volume of the polymer standars versus the volume behaves like a universal calibration curve and can be used to know the Mw of other polymers





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Universal calibration needs Hydrodinamic volume calculation

Hydrodinamic Volume= $[\eta] * M_w$ $[\eta]$ Intrinsic Viscosity

Hydrodinamic volume calculation needs Intrinsic Viscosity calculation on the GPC solvent (THF) from Mark-Houwink Equation

$[\eta]= K*(M_w)^a$ *K* and *a* are the Mark-Houwink parameters

We need Mark-Houwink Parameters in THF for Nitrocellulose and Polystirene.

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Mark-Houwink Parameters in THF for Polistyrene.

$$[\eta] = K^*(M_w)^a$$

	K	a
Polistyrene (THF)	0,00011	0,725

Kurata, M., & Tsunashima, Y. (2003). Viscosity – molecular weight relationships and unperturbed dimensions of linear chain polymers, Table 1, in Brandrup, J., Immergut, E. H., & Grulke, E. A., (Eds.), Polymer Handbook, 4th edition (Section VII, Solution properties), New York :Wiley.

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Mark-Houwink Parameters in THF for Nitrocellulose.

$[\eta] = K^*(M_w)^a$

	Reference	Range N% Samples	K	a
Nitrocellulose (THF)	Timpa (1971)	13,5-13,9	0,000321	0,83
Nitrocellulose (THF)	Chang (1972)	13,8	0,000219	0,89
Nitrocellulose (THF)	French (1981)	11,95-13,13	0,00013	0,8

J. D. Timpa, L. Segal, J. Polym. Sci., Part A-I, 9, 2099 (1971)

M. Chang, Tappi, 55, 1253 (1972)

D. M. French, G. W. Nauflett, J. Liq. Chromatogr. 4, 197 (1981)

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- **Degree of polymerization of Grade B Nitrocellulose manufactured with cellulose of 1000-1200 monomers.**

Samples	DP from Polystirene Equivalent Mw for 13,5% Nitrogen Nitrocellulose	DP from Mw (Timpa 1971) for 13,5% Nitrogen Nitrocellulose	DP from Mw (Chang 1972) for 13,5% Nitrogen Nitrocellulose	DP from Mw (French 1981) for 13,5% Nitrogen Nitrocellulose
Mark-Houwink K		0,000321	0,000219	0,00013
Mark-Houwink a		0,83	0,89	0,8
1	1078	295	249	594
2	999	277	233	556
3	1292	329	275	664
4	946	247	209	495
5	1152	293	246	591

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- **GPC Degree of polymerization of Grade B Nitrocellulose vs Bergerac Type Viscosity Degree of polymerization.**

Samples	DP from Bergerac Type Viscosity	DP from Mw (Timpa 1971) for 13,5% Nitrogen Nitrocellulose	DP from Mw (Chang 1972) for 13,5% Nitrogen Nitrocellulose	DP from Mw (French 1981) for 13,5% Nitrogen Nitrocellulose
Mark-Houwink K		0,000321	0,000219	0,00013
Mark-Houwink a		0,83	0,89	0,8
% N Parameters Setting		13,5-13,9	13,8	11,95-13,13
1	339	295	249	594
2	309	277	233	556
3	395	329	275	664
4	287	247	209	495
5	350	293	246	591

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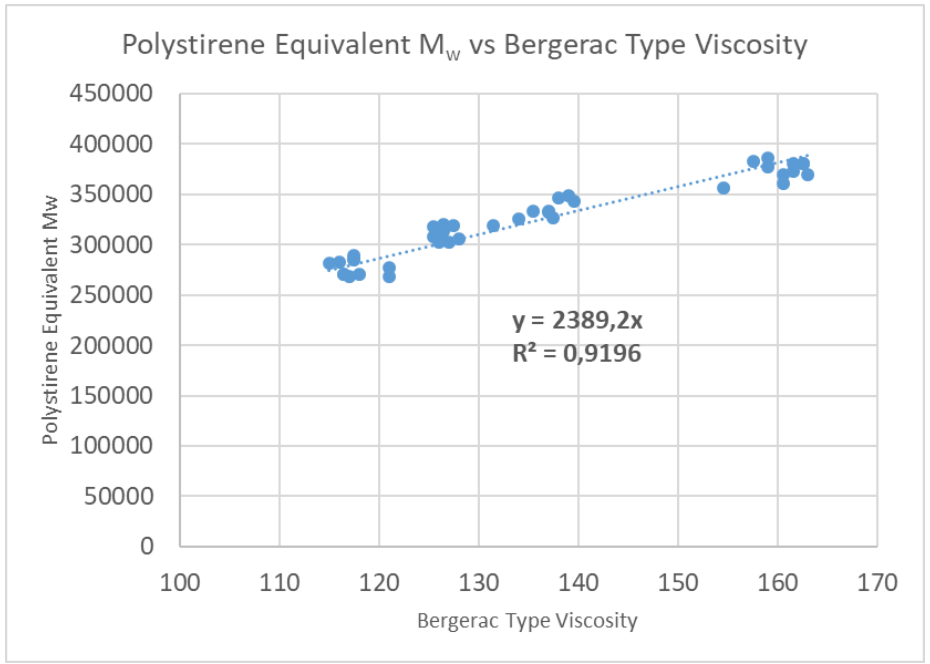
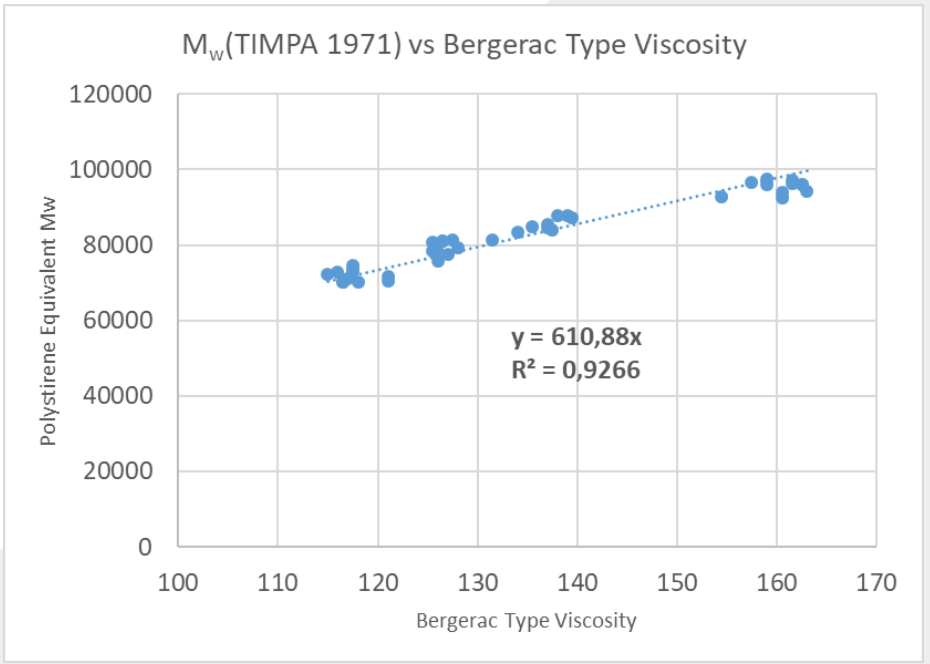
- Correlation between Type Viscosity and Weight Average Molecular Weight.





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CONCLUSIONS

- Calculation of M_w from Polystyrene Calibration curve overestimates its value.

- The M_w obtained by application of the Universal Calibration are lower than the Polistyrene equivalent M_w. The degree of polymerization predicted for Nitrocellulose from the application of the Universal Calibration are lower than the one of the raw Cellulose.

- The Mark-Houwink Parameters from Timpa (1971) obtained from samples of nitrogen 13,5-13,9 give the best results for our Grade B Nitrocellulose samples.

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Thanks Very Much for your attention !