Preparation of Polydimethylsiloxane Modified Polypropylene by Olefin Cross Metathesis Reactions

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Outline

- Background
- Objective
- Experimental
- Characterization
- Conclusion

Olefin Metathesis

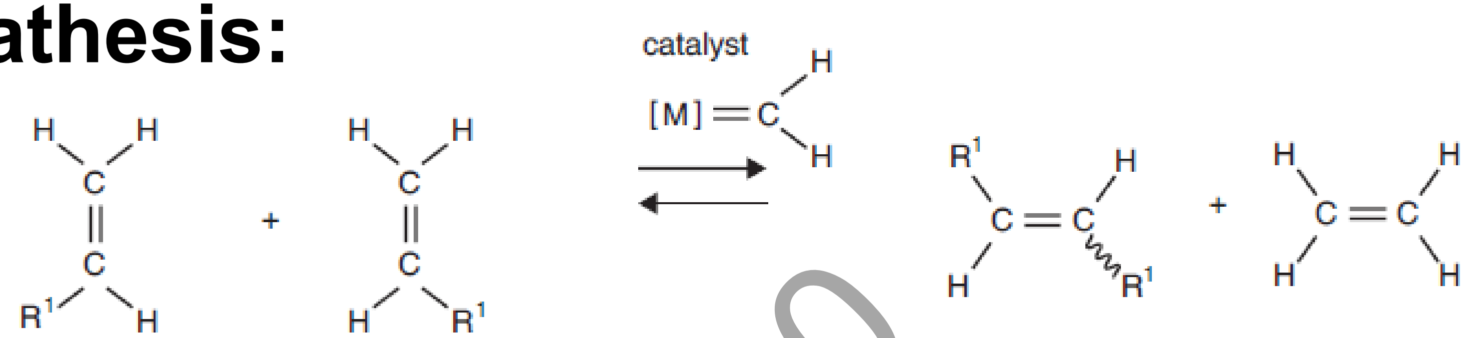
- Metal – catalyzed reaction
- Rearrange carbon – carbon bonds via cleavage and reassembly
- Types of olefin metathesis:

Cross Metathesis: CM

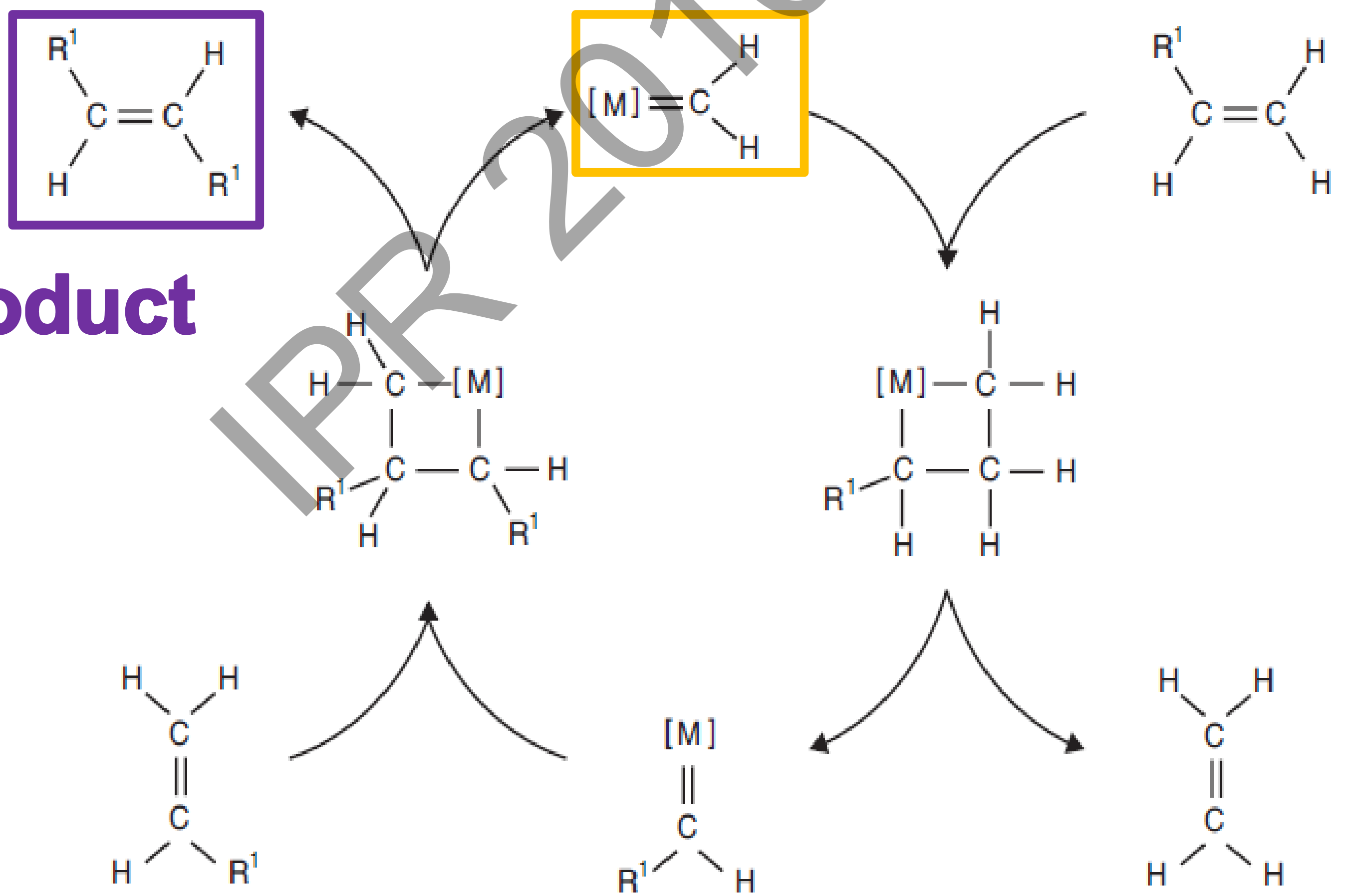
Ring Opening Cross Metathesis: ROCM

Chauvin Mechanism

Cross Metathesis:



Mechanism:



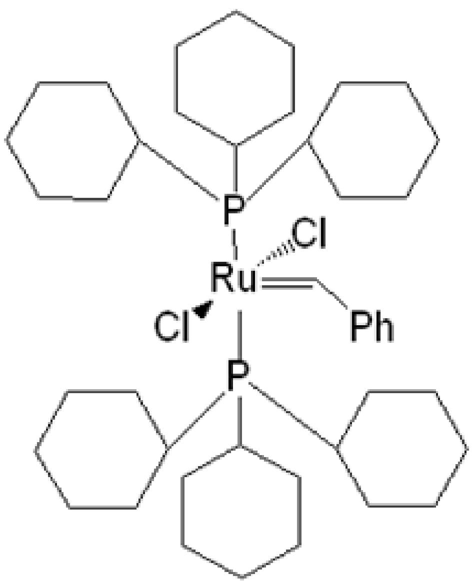
CM Product

- Y. Chauvin. *Angew. Chem. Int. Ed.* **2006**, 45, 3741

Grubbs Catalyst

First Generation

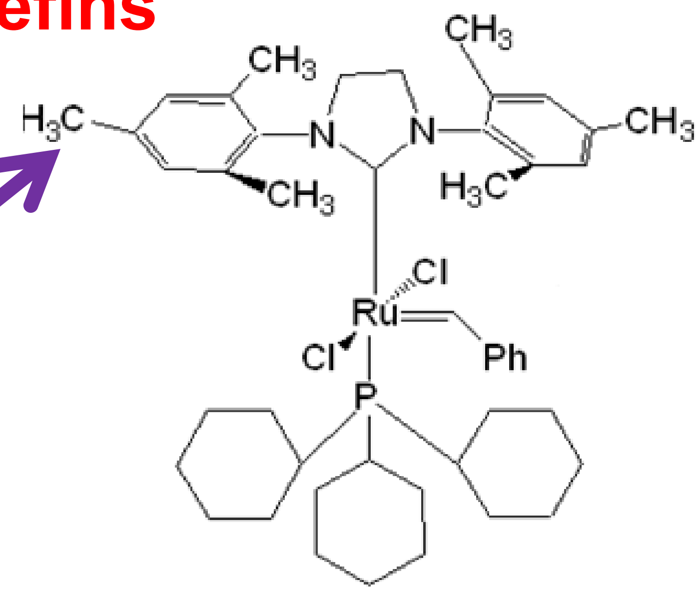
- Stable in air, well-defined structure
- High functional groups tolerance and selectivity
- Active in alcohol, water or carboxylic acids.



Second Generation

- High stability, functional groups tolerance and selectivity
- **100 times higher reactivity**
- **Catalyze formation of tri and tetra-substitutied olefins**

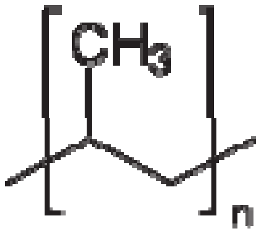
N-Heterocyclic Carbene (NHC)



- Robert H. Grubbs. *Tetrahedron* **2004**, 60, 7117

Materials

Vinyl-terminated Polypropylene (PP)



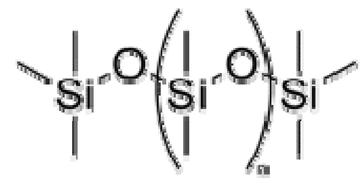
- Good thermal and mechanical properties
- Excellent chemical resistance
- Low price

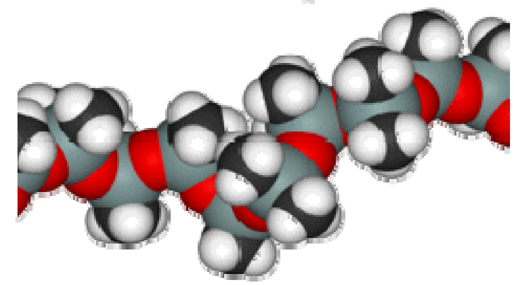
PROPERTY	PP
Density (g/ml)	0.902
Number Average MW (g/mol)	5000
Weight Average MW (g/mol)	12,000
Ring and Ball Softening Point (°C)	163
Vinylidene Concentration (mol/g polymer)	$8.4*10^{-5}$

Materials

Monovinyl-terminated Polydimethylsiloxane (PDMS)

- High thermal and chemical stability
- Lubricant properties
- Low glass transition temperature





PROPERTY	PDMS
Boiling Point (°C)	>205
Melting Point (°C)	<-60
Molecular Weight (g/mol)	60,000-70,000
Viscosity (cSt)	9000-11,000

Hydrosilylation of PP through Reactive Extrusion

- In 1998, Tzoganakis and Malz proved feasibility of hydrosilylation of terminal double bonds in PP in **melt phase, screw extruder**

Solution Phase:

- Mild conditions
- Good homogenization
- Energy and labor consuming

Melt Phase:

- Simultaneous extrusion and functionalization
- Save time, equipment, energy and labor

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Objective

- ❑ Mono-vinyl terminated PDMS chemically modified vinyl-terminated PP through CM in **melt phase: PP-PDMS Copolymers**

1) Expect change in properties: chemical reactivity and adhesion

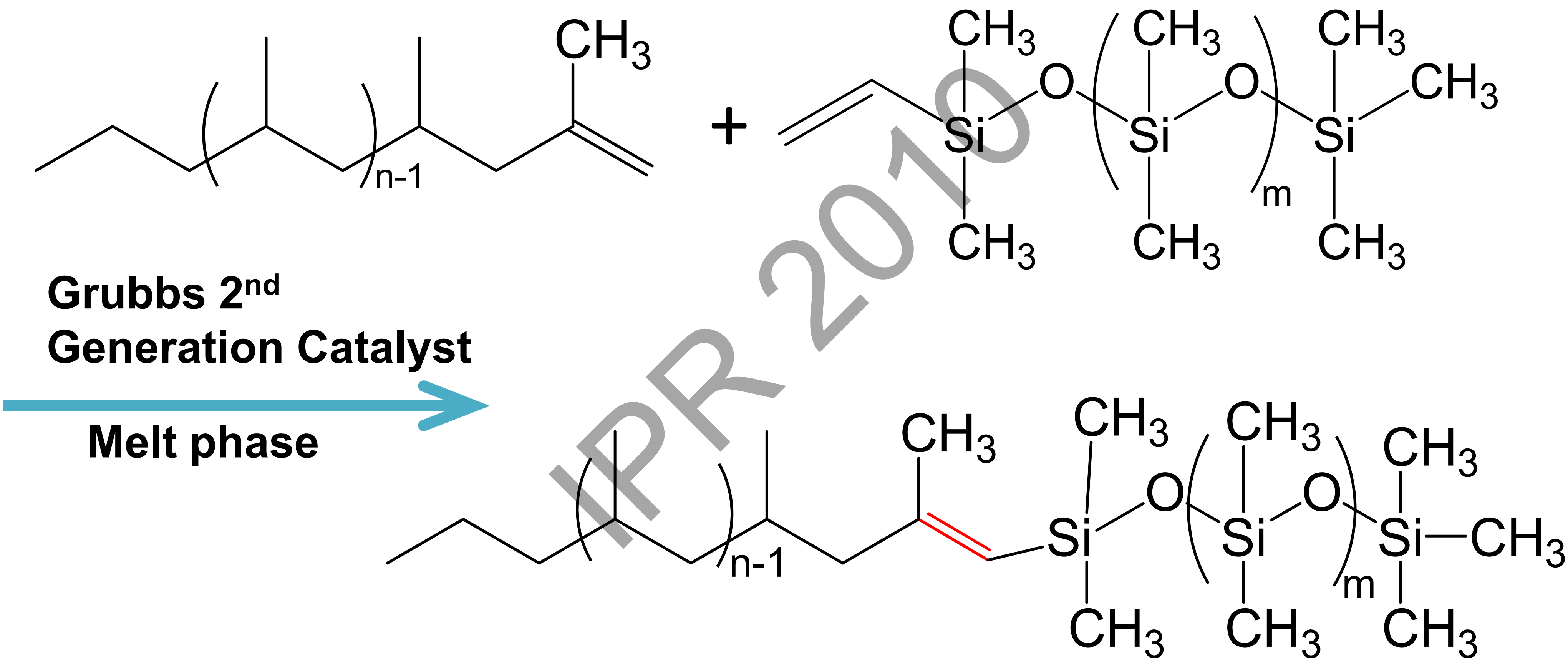
2) Expand its applications in highly profitable areas: engineering and aerospace industries

- Hauke Malz and Costas Tzoganakis. *Polymer Engineering and Science* **1998**, 38(2), 7117

Objective

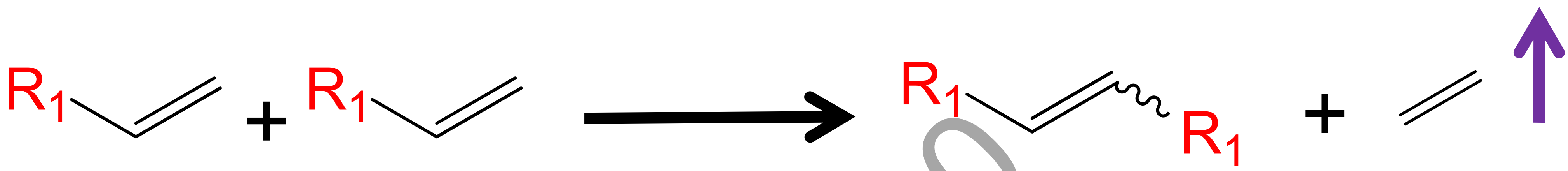
- Characterize chemical, physical and viscoelastic properties of synthesized copolymers
- Detect and quantify relationship among experimental factors through factorial design analysis

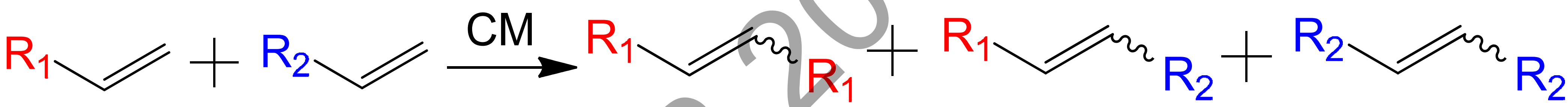
Reaction Scheme



Reaction Scheme Cont'd

Homodimerization in CM:





R_1 : R_2	CM Product Selectivity
1 : 1	50%
2 : 1	66%
4 : 1	80%
10 : 1	91%

- Arnab K. C.; Tee L.C.; Daniel P.S.; Robert H.G. *J.Am. Chem. Soc.* **2003**, 125, 11360

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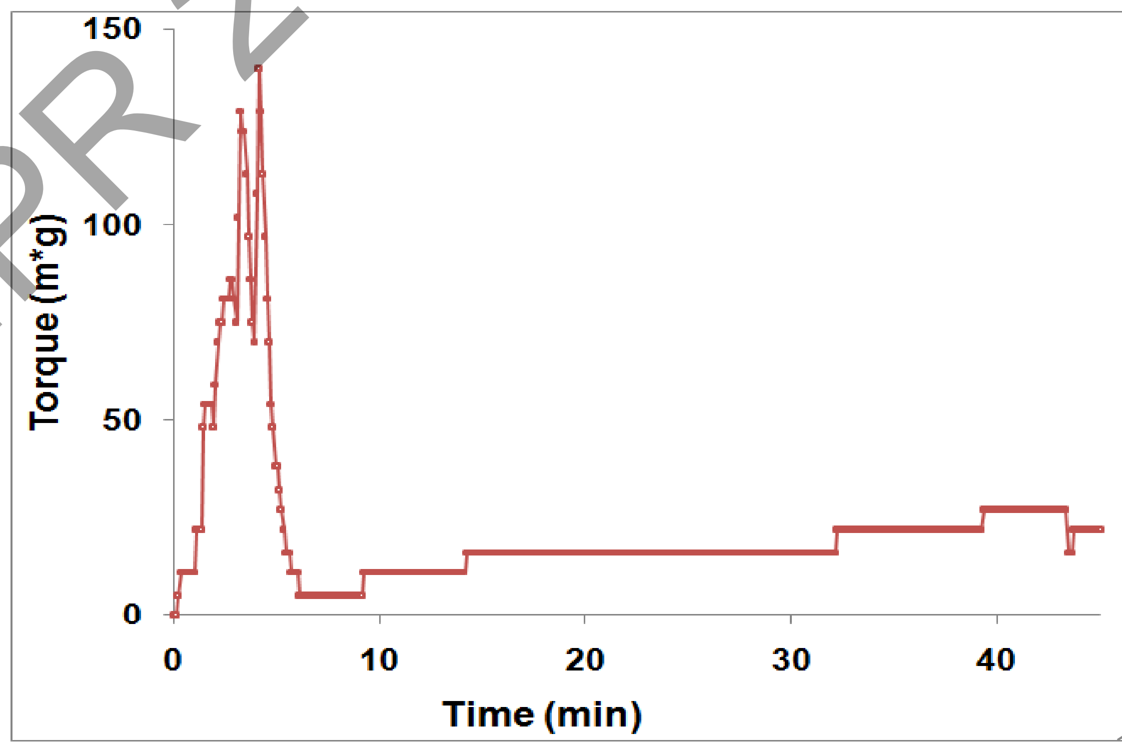
Experimental Process

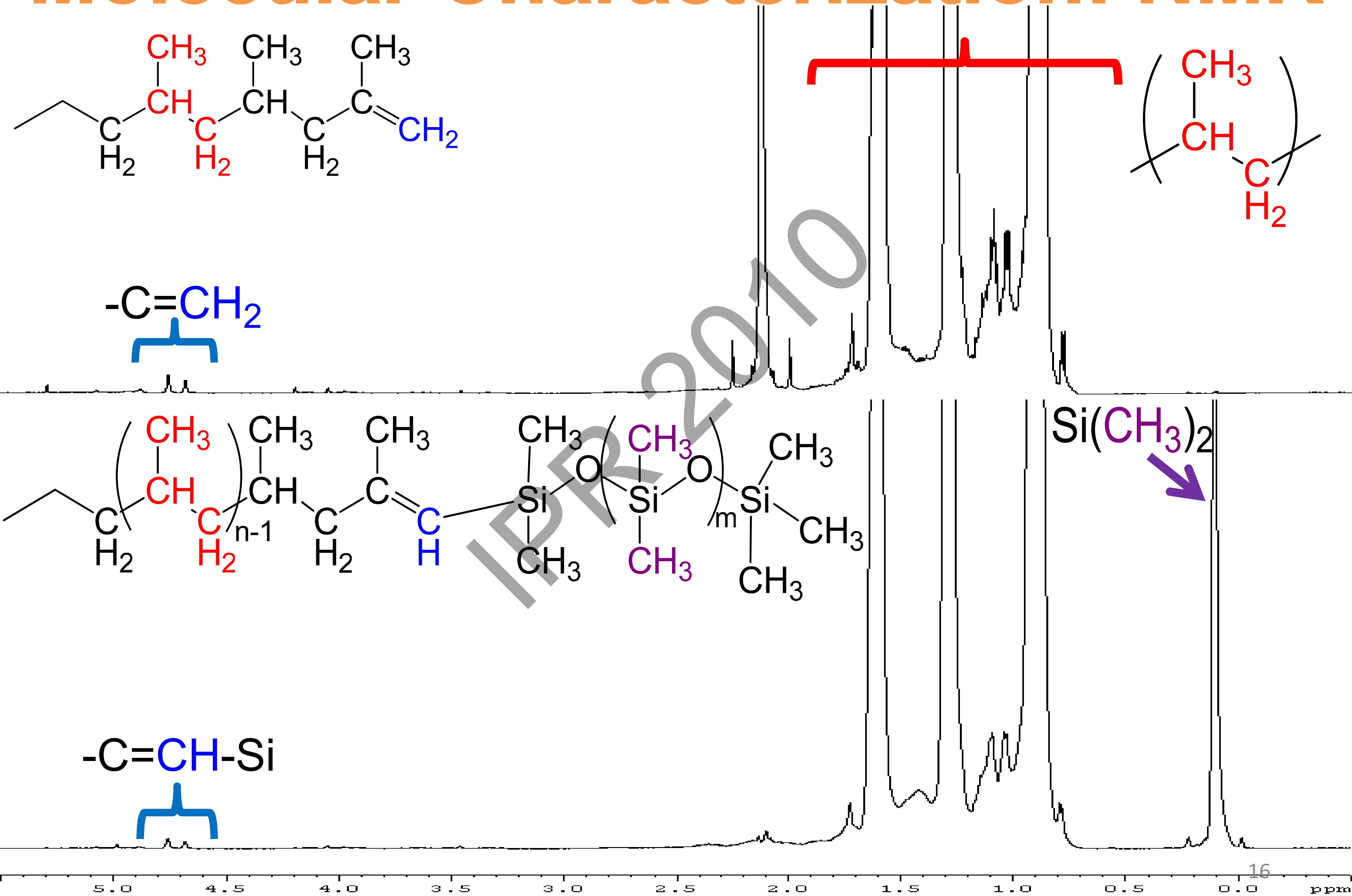
- ❑PP and PDMS react in **batch mixer**
- ❑Purified copolymers

Challenges in melt phase:

- ❑**Extreme condition for catalyst**
- ❑**Poor compatibility**



Molecular Characterization: NMR



Factorial Design

Factors	High	Low
Temperature (T, °C)	175	165
Catalyst Amount (C, mg)	140	60
PP/PDMS (M, mole ratio)	100:1	200:1

Factor	T	C	M
Run 1	175	140	200
2	175	140	100
3	175	60	200
4	175	60	100
5	165	140	200
6	165	140	100
7	165	60	200
8	165	60	100

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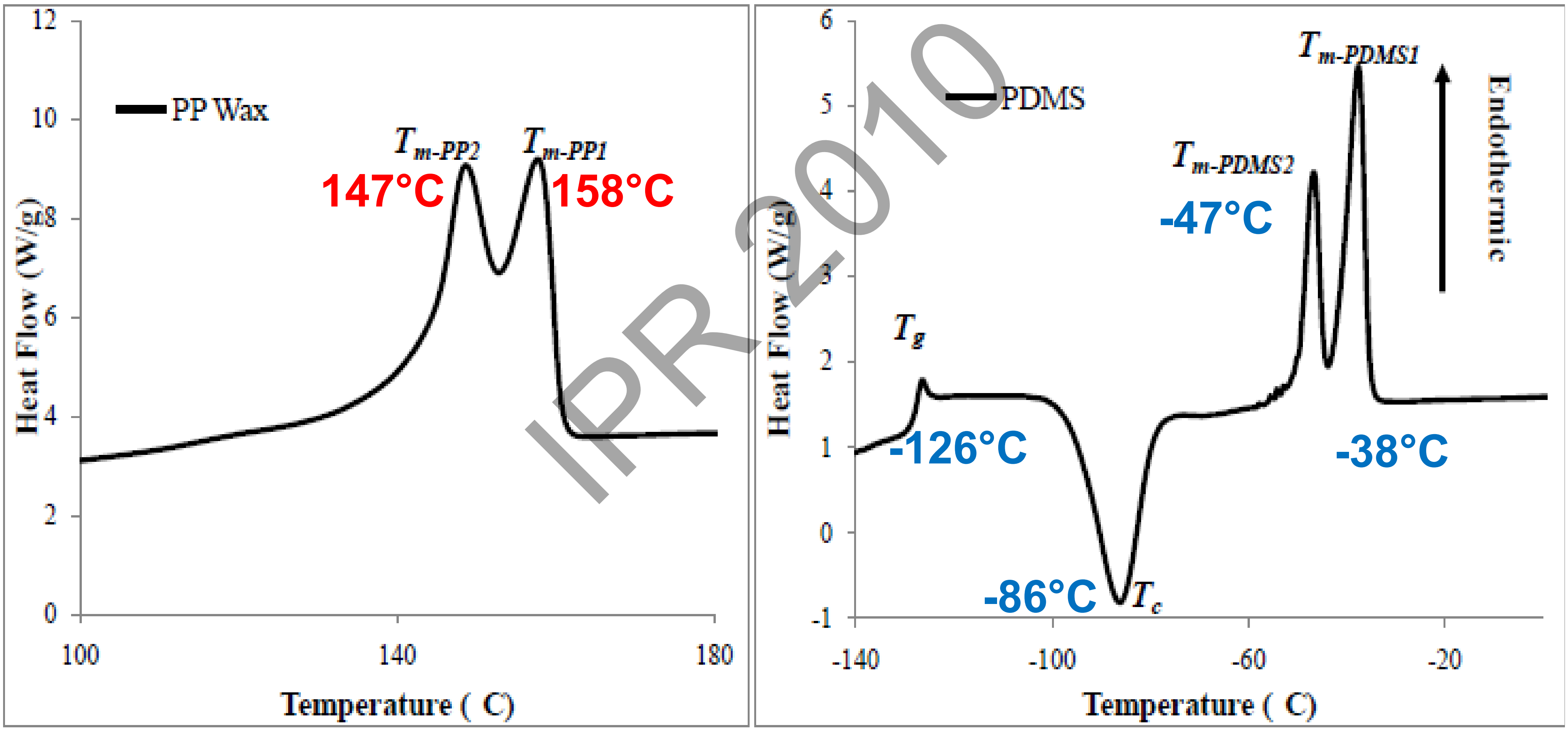
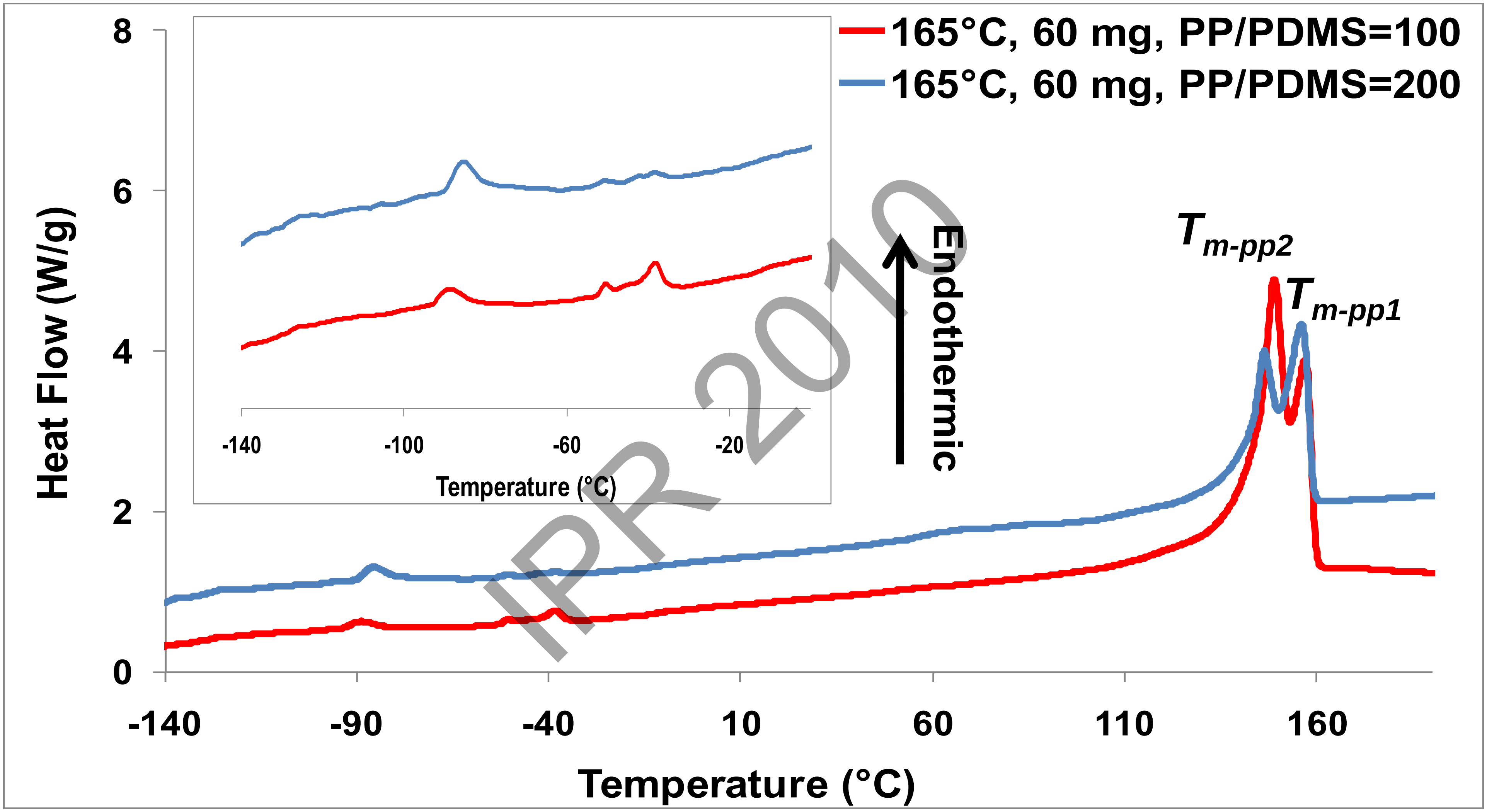
Thermal Properties- Differential Scanning Calorimetry (DSC)



Thermal Properties- DSC Cont'd



❑ **Confirm: (1) Presence of PDMS**

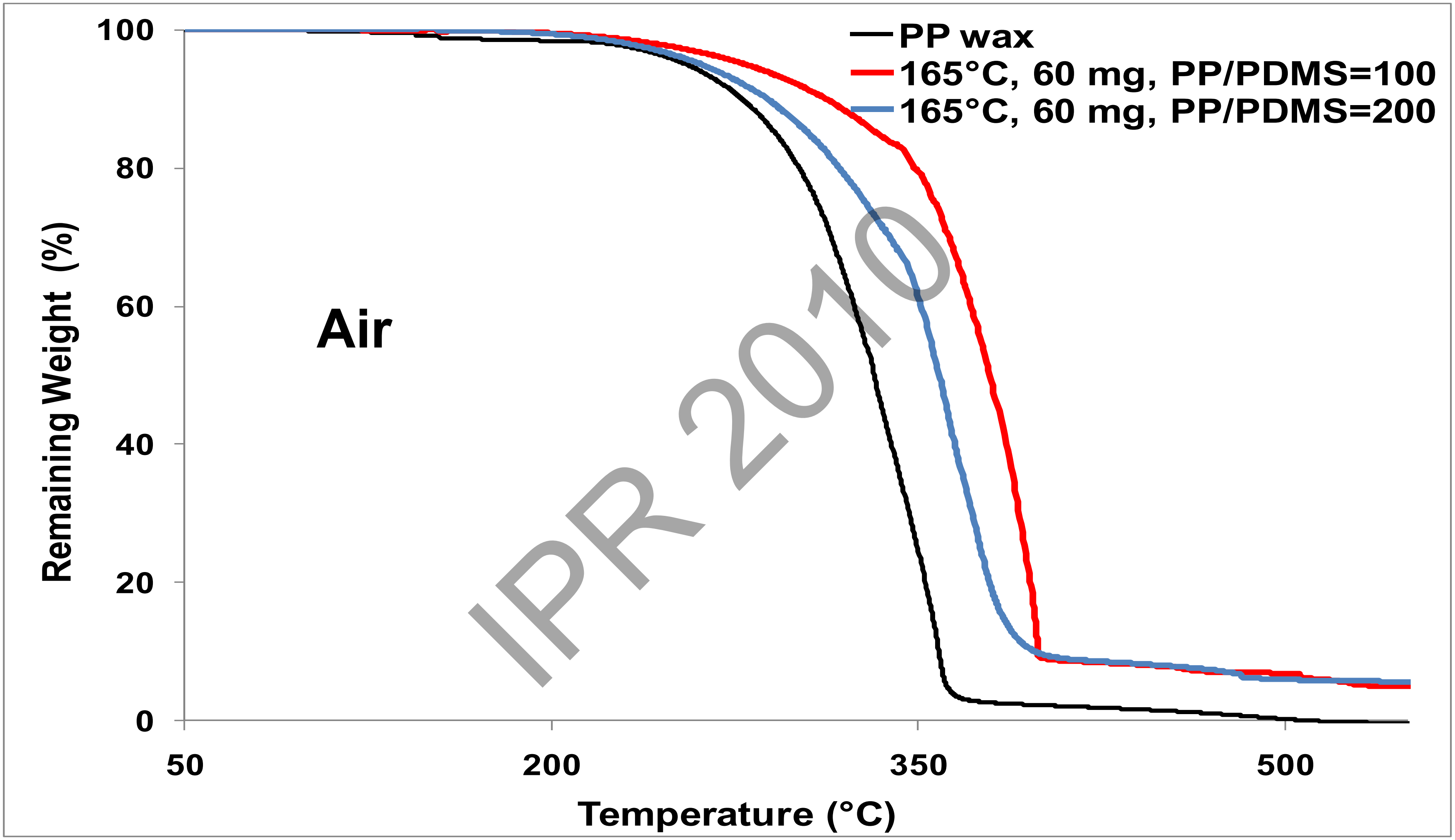
(2) Feasibility of CM in melt phase

Thermal Properties- DSC Cont'd

Run	$T_{m\text{-}pp1}$ (°C)	$\Delta H_{m\text{-}pp1}$ (J/g)	$T_{m\text{-}pp2}$ (°C)	$\Delta H_{m\text{-}pp2}$ (J/g)
165°C, 60mg, PP/PDMS =200	156	1005	146	870
165°C, 60mg, PP/PDMS =100	157	646	149	772
Pure PP wax	**158**	**1547**	**147**	**1116**

- **In copolymers, PP crystalline proportion is influenced by PDMS component**

Thermal Properties- TGA



- Thermal degradation beginning at :

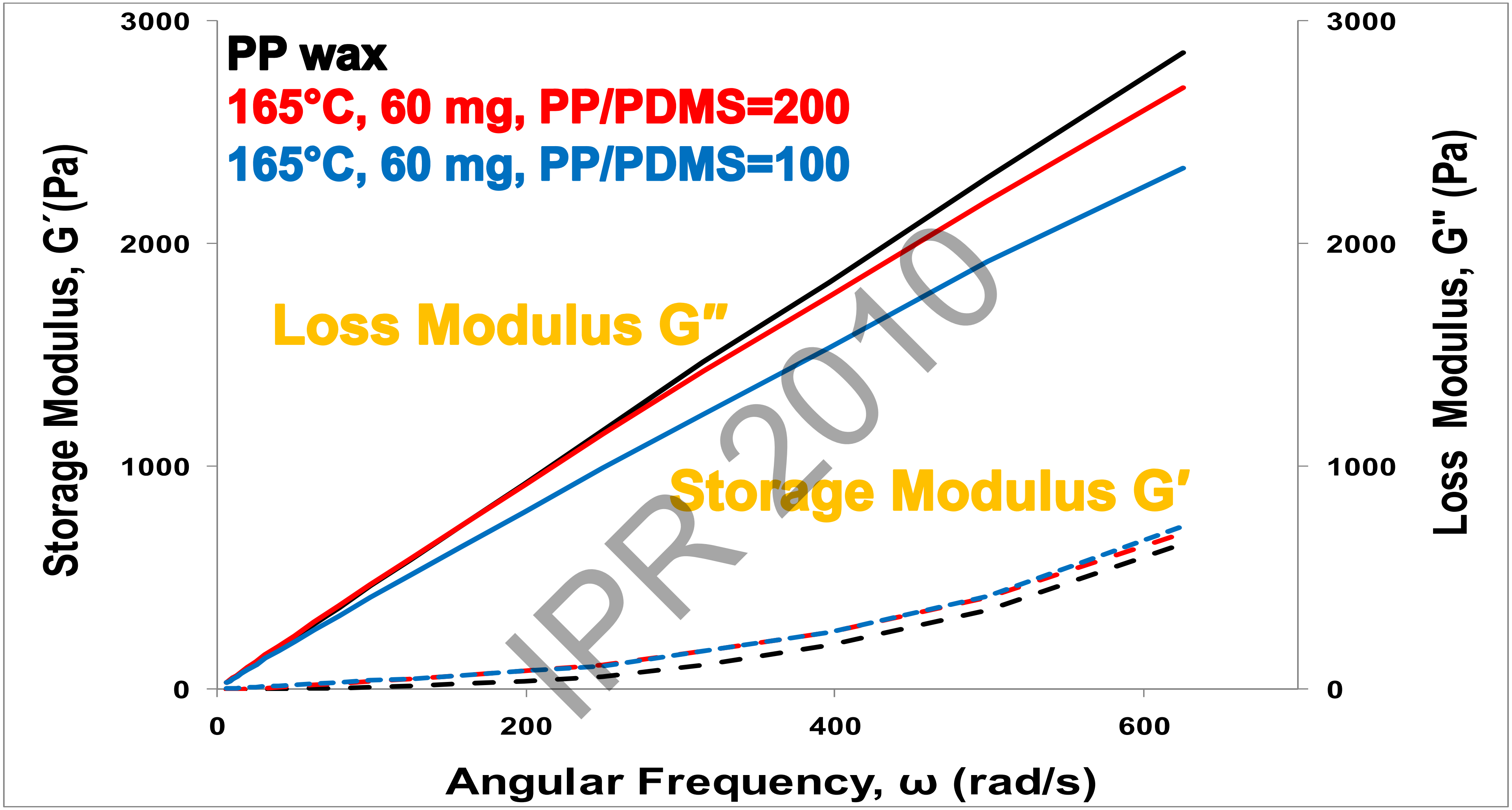
  309°C (PP); 368°C and 327°C (Copolymer)

Thermal Properties- TGA Cont'd

Run	Remaining Weight % at 350 °C	Remaining Weight % at 450 °C
165°C, 60mg, PP/PDMS =200	61.06	8.09
165°C, 60 mg, PP/PDMS =100	79.16	7.83
Pure PP Wax	**24.49**	**1.49**

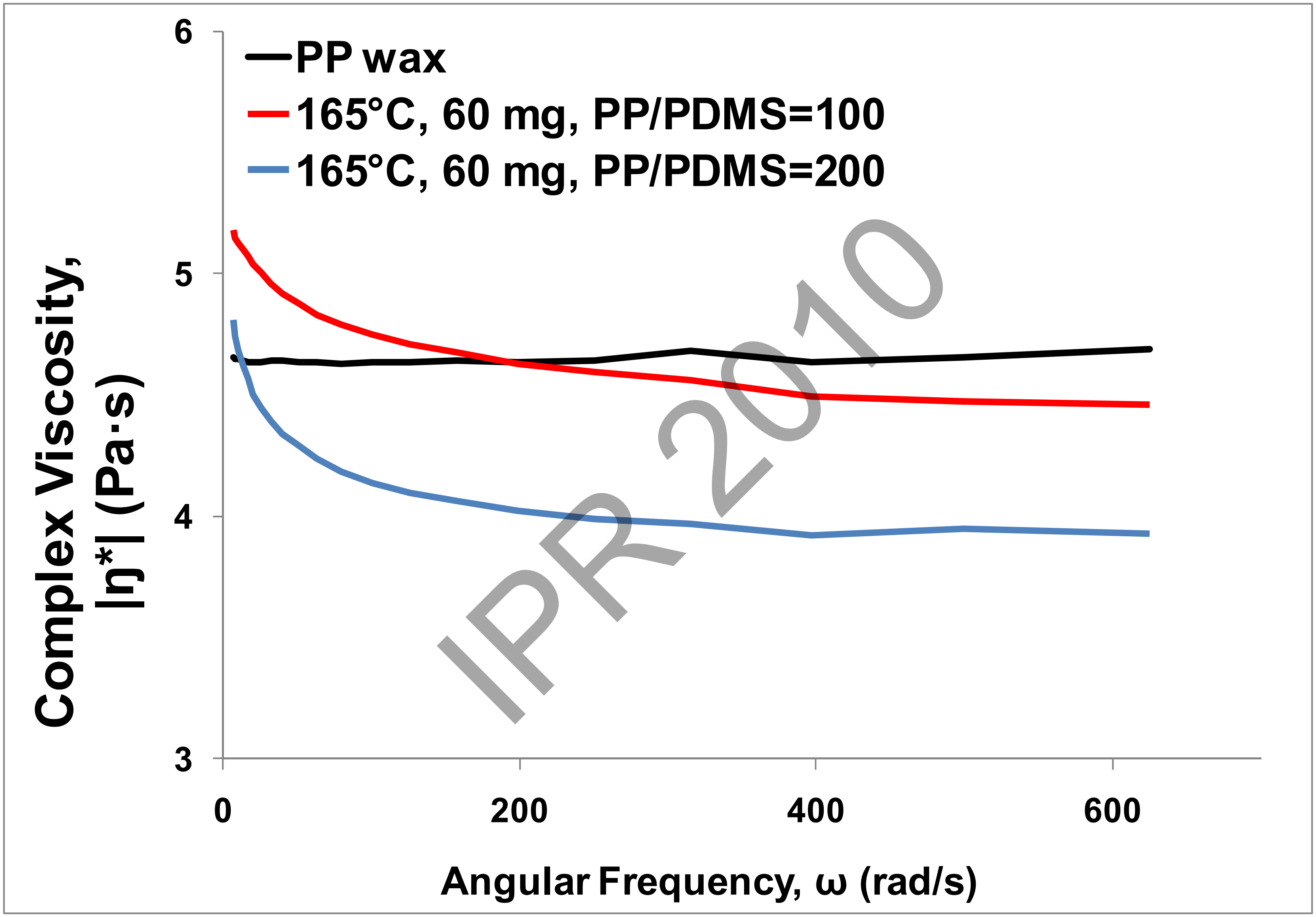
- ❑ **Higher thermal stability is observed in copolymers**
- ❑ **PDMS concentration ↑ Thermal stability ↑**

Viscoelastic Properties- Rheometer



- ❑ Viscous Component is dominant over elastic counterpart
- ❑ Improved G'; Decreased G"

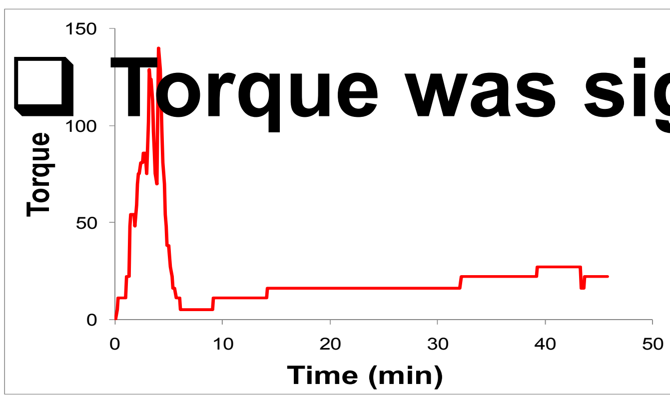
Viscoelastic Properties-Cont'd



❑At high frequency: |ŋ*| (Copolymers) < |ŋ*| (PP)

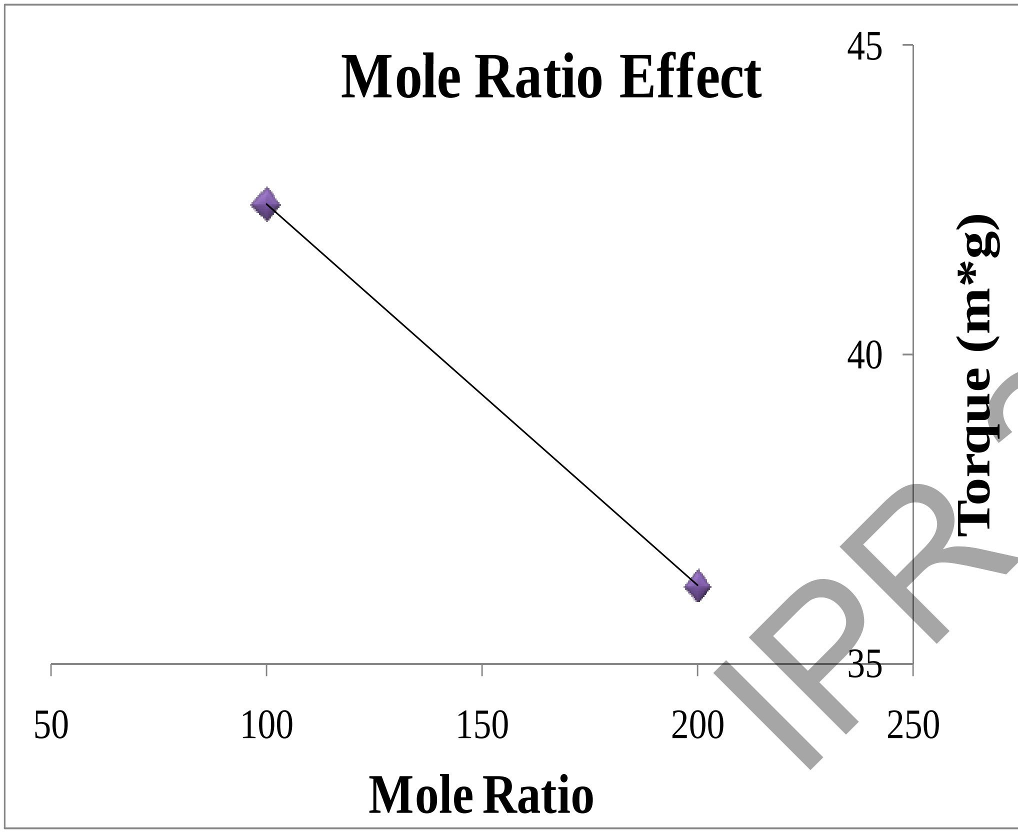
Statistical Analysis – Torque (TQ) Response

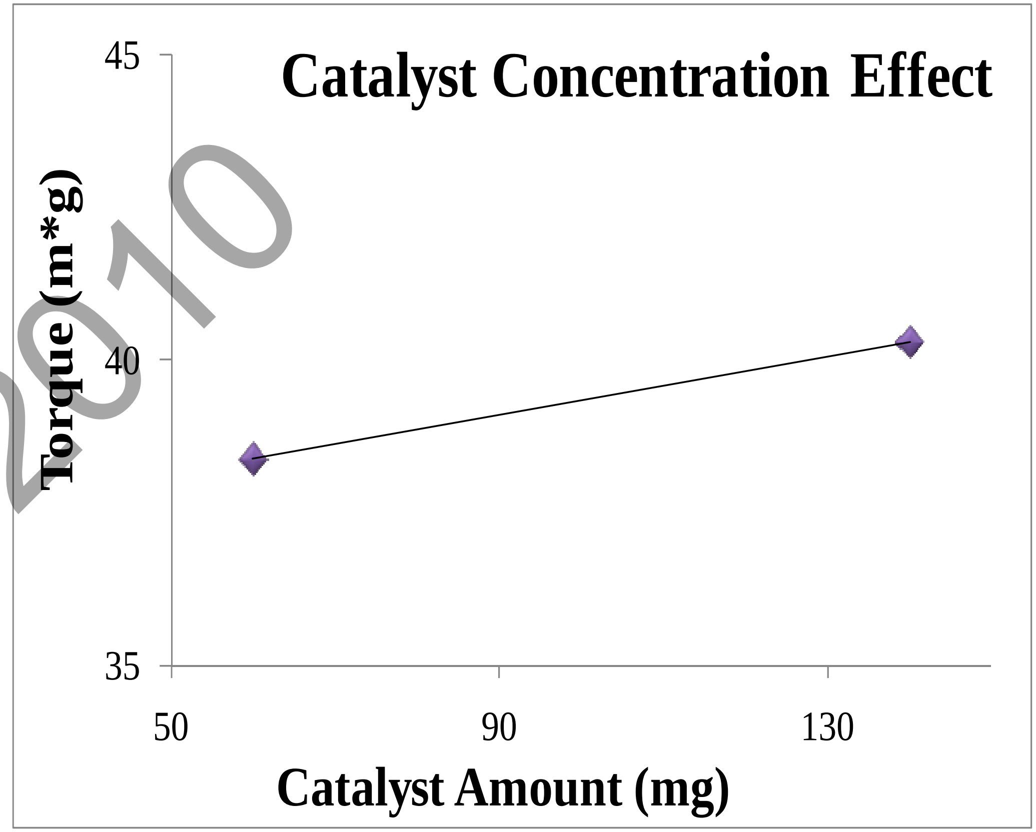
	Source of Variance	p-value
Main Effects:	**Temperature (T)**	0.00741
	Catalyst (C)	0.22161
	Mole Ratio (M)	0.00974
Interaction Effects:	**TxC**	0.00004
	TxM	0.25319
	CxM	0.73920
	TxCxM	0.52531



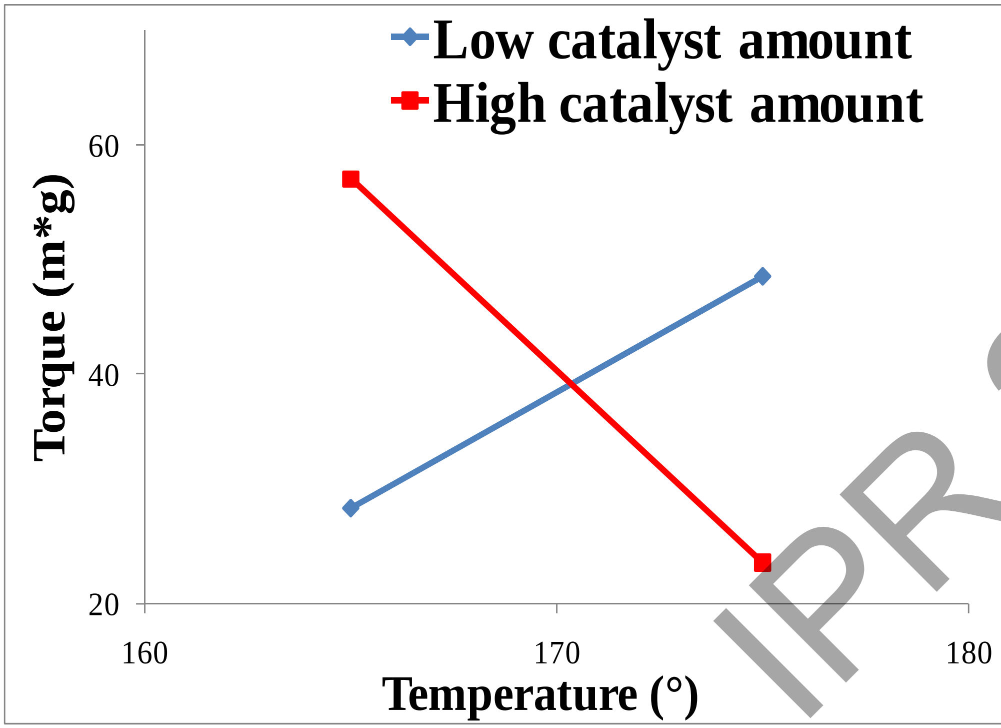
- **Torque was significantly affected by T, M and TxC**

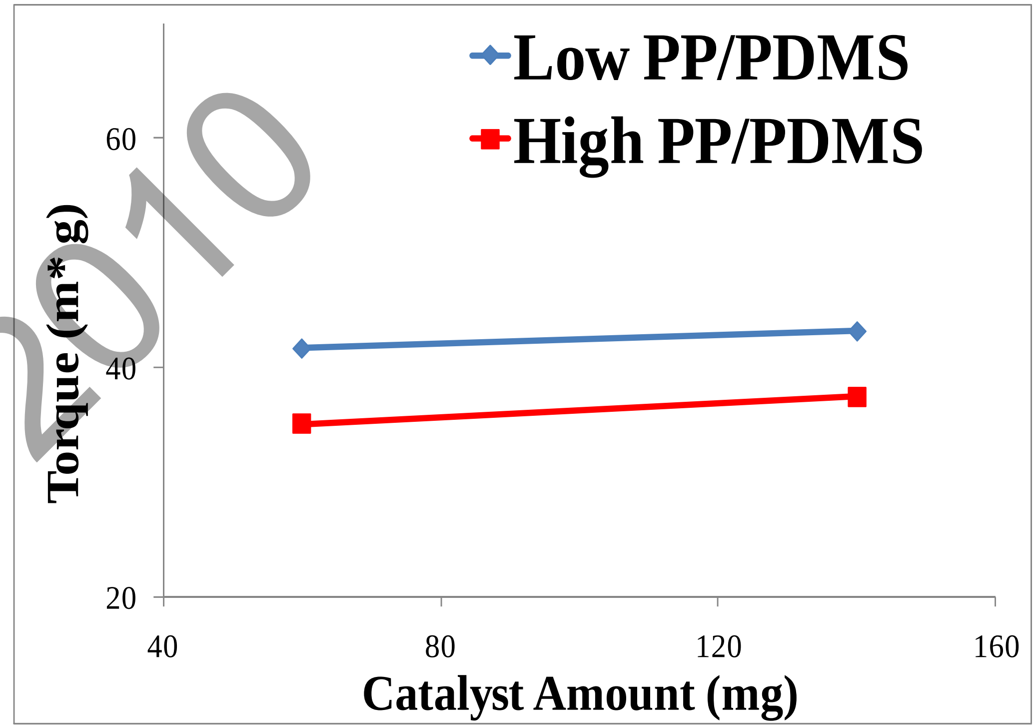
Statistical Analysis – Torque Response





Statistical Analysis – Torque Response





- **TQ = 39.3375-3.3375xT+0.9625xC-3.0875xM-13.4625xTxC**

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Conclusion

- ❑ Successfully syntheszied PP-PDMS copolymers through CM, in melt phase
- ❑ Characterization of copolymers:

↑ Thermal stability ↑ Elasticity ↓ Viscosity

- ❑ Factorial design: statistical analysis for torque response

Future Work

- Repeat all experiments: fully replicated factorial design
- Perform same polymerizations in extruder: better mixing, shorter reaction time
- Investigate other types of PDMS or polymers (PE, PB)

Acknowledgement

Supervisor: Dr. Costas Tzoganakis

Dr. Neil McManus

Dr. Ralph Dickhout

Colleagues in the Tzoganakis Lab

THANK YOU

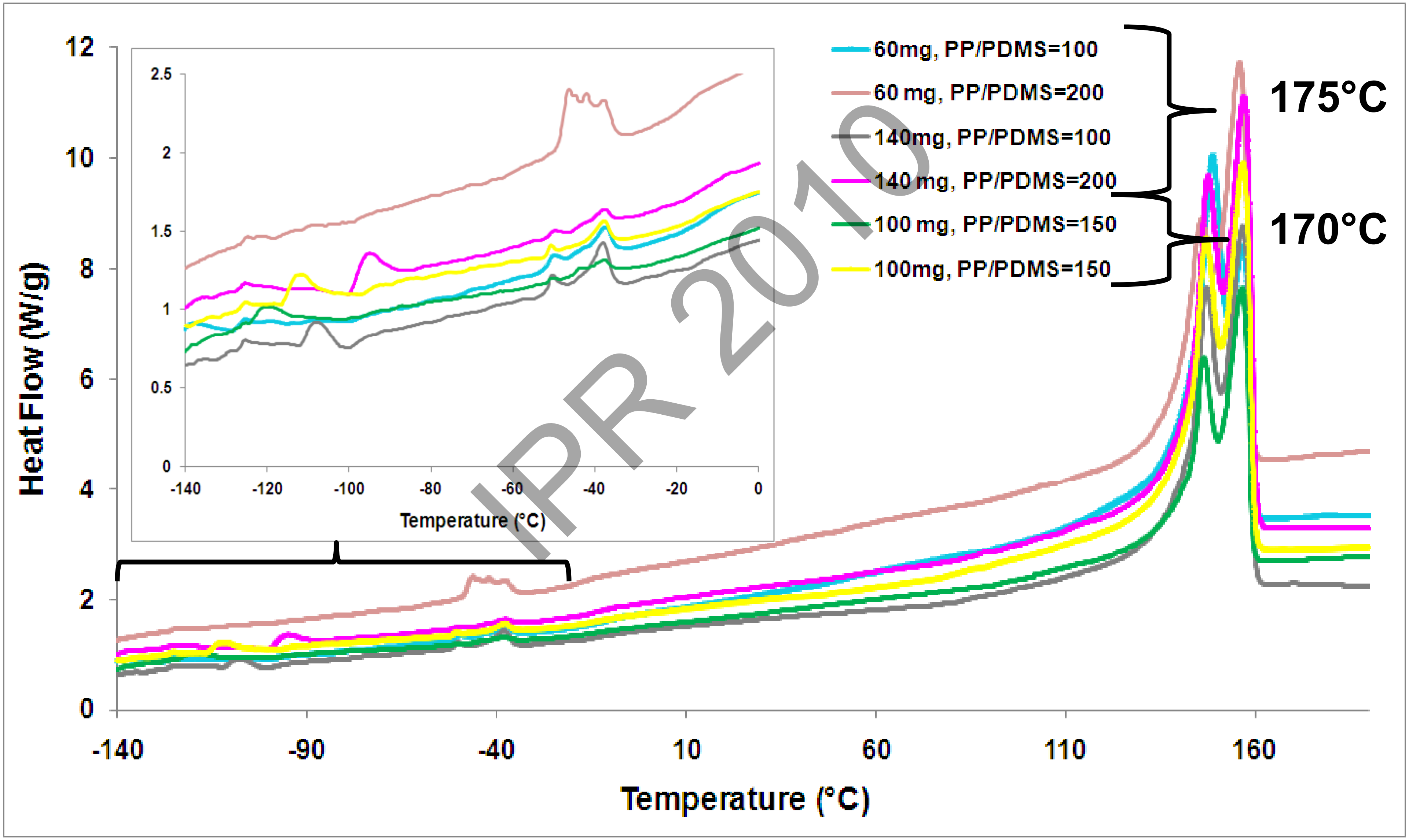
Factorial Design

Factor	**T**	**C**	**M**
Run 1	175	140	200
2	175	140	100
3	175	60	200
4	175	60	100
5	165	140	200
6	165	140	100
7	165	60	200
8	165	60	100
CP 1 and 2	**170**	**100**	**150**
BM 1, 2 and 3	**175**	**100**	**150**

NMR

Run	T (°C)	Catalyst (mg)	Initial mass ratio	5 min mass ratio	30 min mass ratio
1	175	140	329	488	408
2	175	140	329	348	362
3	175	60	329	514	447
4	175	60	329	647	357
5-2	165	140	329	601	315
6	165	140	329	353	327
7	165	60	329	1264	350
8	165	60	329	468	854

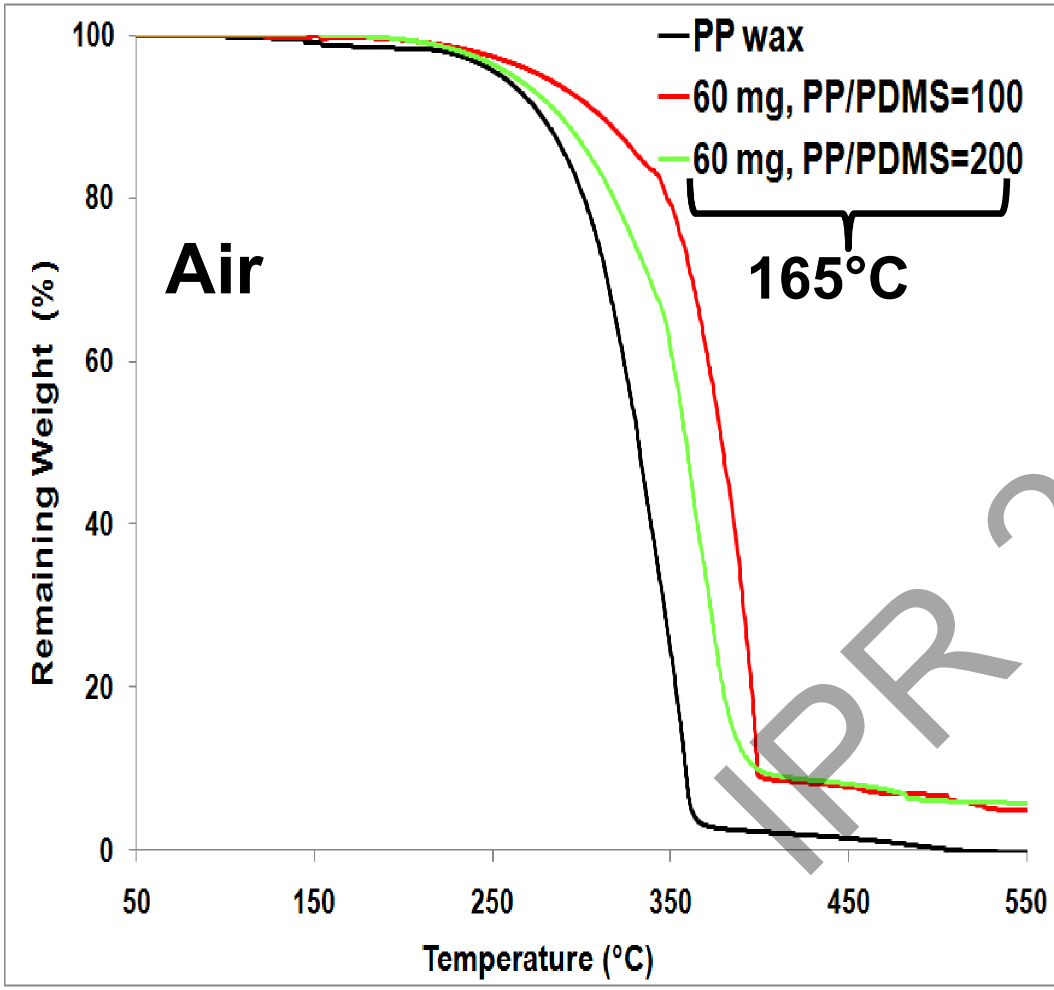
Thermal Properties- Investigated by DSC Cont'd

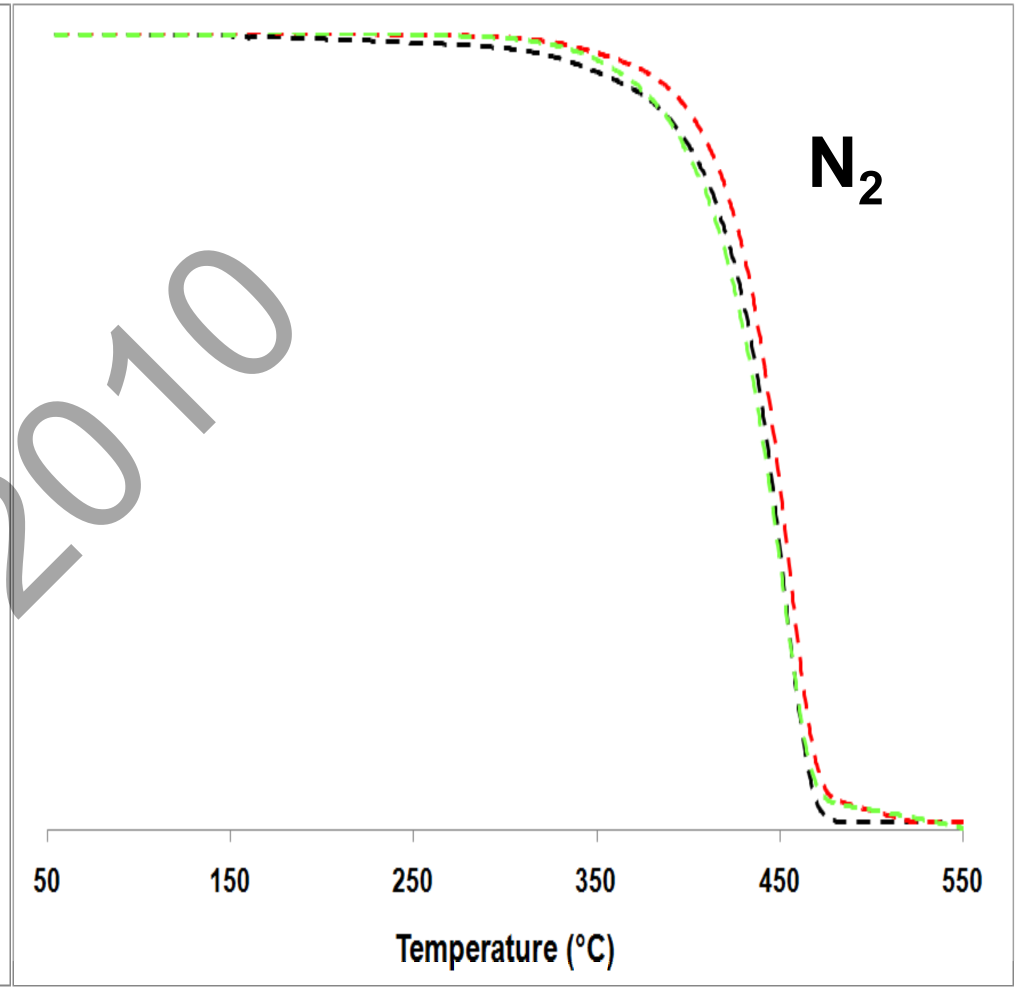


Thermal Properties- Investigated by DSC Cont'd

Run	$T_{g\text{-}1}$ (°C)	$T_{g\text{-}2}$ (°C)	$T_{m\text{-}PDMS2}$ (°C)	$T_{m\text{-}PDMS1}$ (°C)
1	-126	-99	-50	-38
2	-126	-111	-50	-38
3	-126	-110	-46	-38
4	-127	-89	-50	-37
5-2	-126	-95	-51	-38
6	-129	-98	-50	-38
7	-130	-88	-51	-38
8	—	-92	-51	-38
CP1	-123	—	-51	-38
CP2	—	-115	-51	-38
PDMS	**-126**	**-86 (T_c)**	**-47**	**-38**

Thermal Properties- TGA



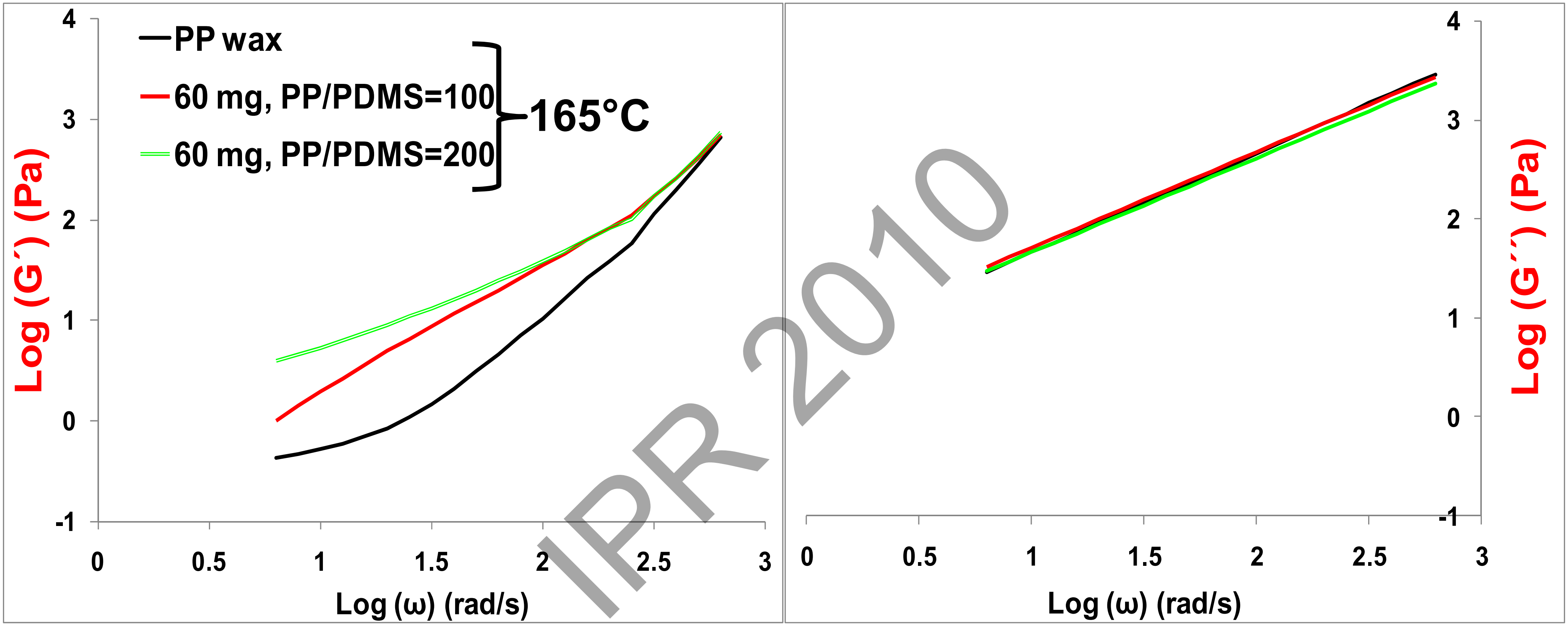


- T_d in air: 309°C (PP), 368°C (—) and 327°C (—)
- T_d in N_2: 419 °C (PP), 423°C (—) and 420°C (—)

Thermal Properties- TGA

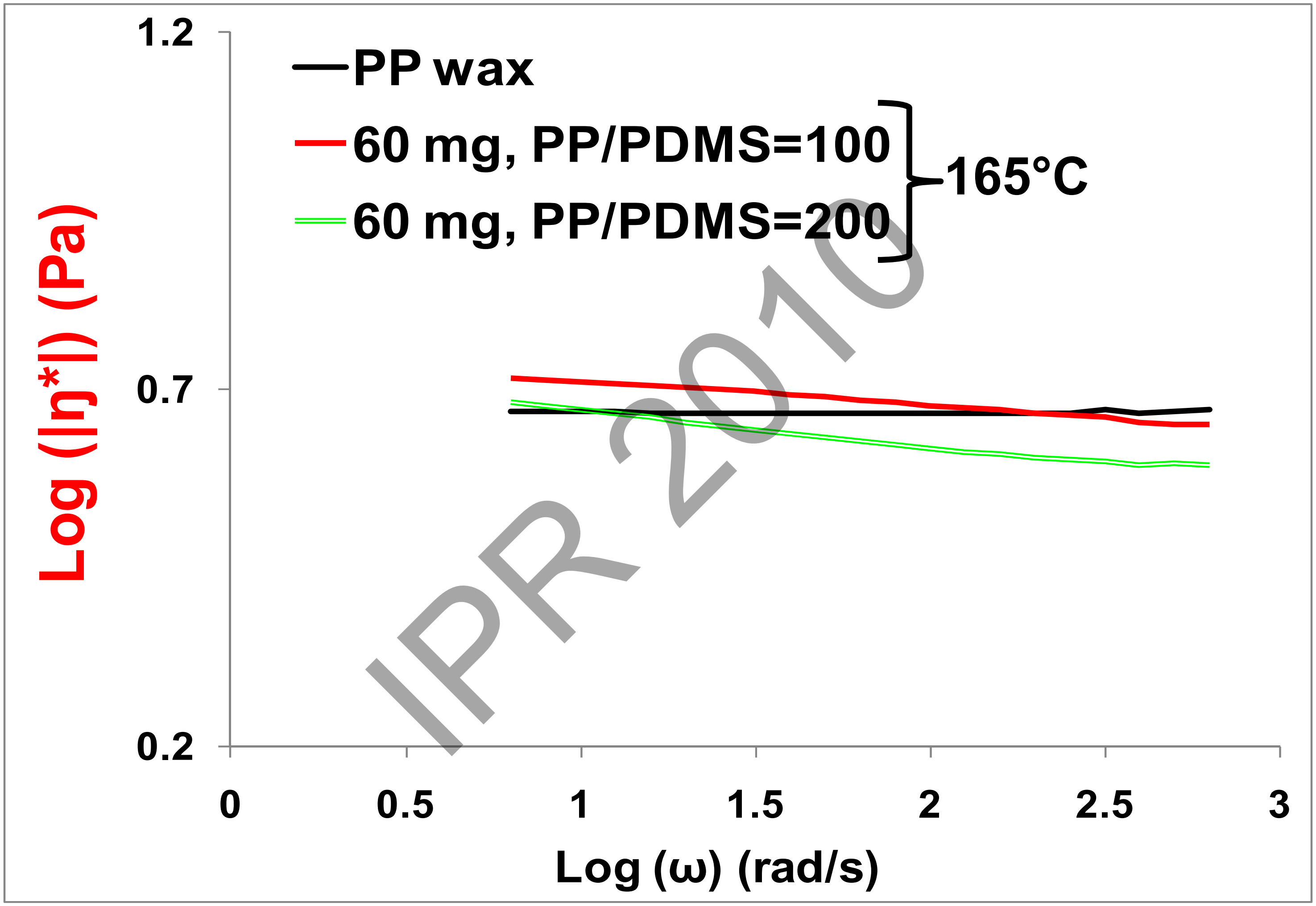
Run #	RW at 350 °C (%)	RW at 450 °C (%)
1	52.41	3.14
2	61.93	8.36
3	40.90	5.50
4	55.96	7.04
5-2	43.06	5.37
6	62.33	7.78
7	61.06	8.09
8	79.16	7.83
CP1	40.37	5.90
CP2	47.10	5.78
PP	**24.49**	**1.49**

Viscoelastic Properties-Cont'd



- ❑ **Improved elasticity: fiber spinning&thermoforming**
- ❑ **Effect of PDMS into PP on viscous modulus is less than elastic modulus**

Viscoelastic Properties- Rheometer

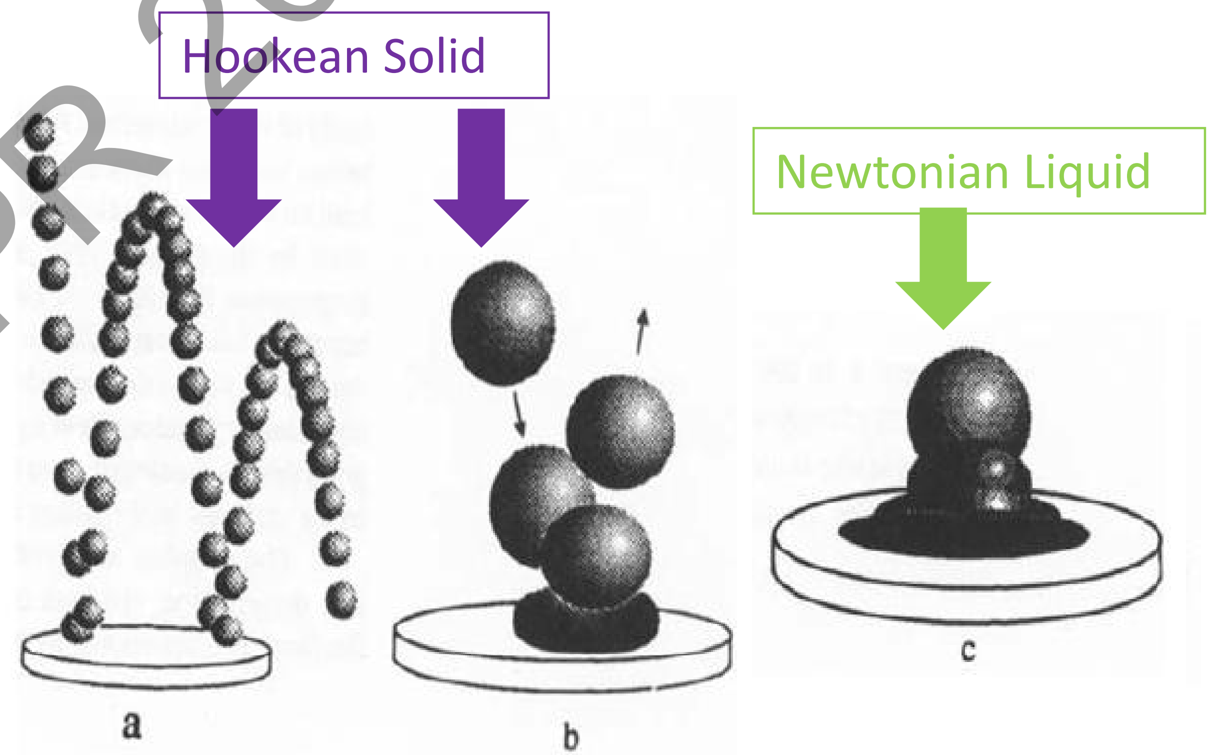


- |ŋ*| of copolymers < |ŋ*| of virgin PP at higher frequency

Rheology

- Rheology is defined as “ the study of the deformation and flow of matter” and the fundamental relations between force and deformation in materials is called constitutive relations.
- Most materials studied in rheology exhibit both liquid-like and solid-like properties.

Silly Putty behaves like a solid (a and b) and a liquid (c)



Macosko, C.W. *Rheology: Principles, Measurements, and Applications*; VCH Publisher, Inc.:New York, 1994

Rheometer

- Rheometers are instruments that measure both “stress and deformation history” on a material for which the constitutive relation is unknown.
- Rheometers can be categorized into two major classes by kinematics: Shear Rheometers and Extension Rheometers.

Malkin, A.Y.; Isayev, A.I. *Rheology: Concepts, Methods, and Applications*; Chem Tec Publishing: Toronto, 1994.

Sample Analysis

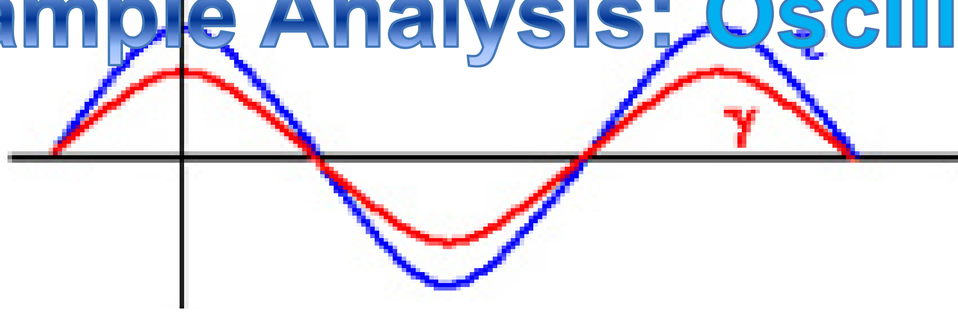
Rotational Measurement: a defined speed (shear rate) is used and the resultant torque (stress) is measured.

Oscillatory Measurement:

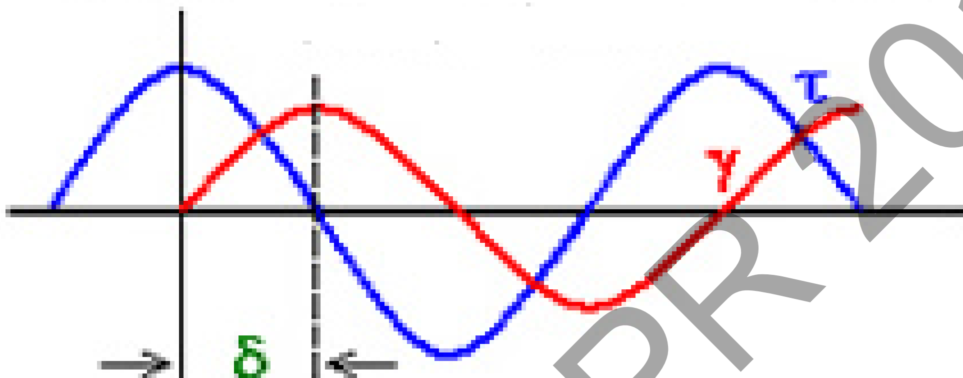
- Applied a sinusoidal oscillating stress wave and measure the resulting strain wave.
- Measurements are made over a range of frequencies.
- Complex viscosity **(η*)**, Phase angle (°) and Storage and Loss modulus (G' & G") as a function of frequency are determined.

Bird, R.Byron; Armstrong, Robert C.; Hassager, Ole. Dynamics of Polymeric Liquids V1: Fluid Mechanics; John Wiley & Sons Inc.: Toronto, 1977.

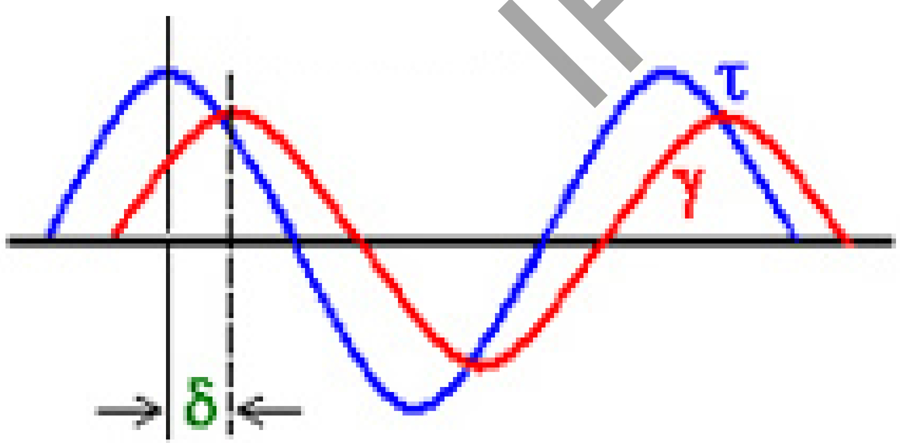
Sample Analysis: Oscillatory Measurements



Hook solid response with phase angle = 0 °.



Newtonian fluid response with phase angle = 90 °.



Viscoelastic materials response with phase angle in between 0 ° and 90 °

Rheology Advantage Data Analysis Manual. TA instruments, 2007.

Statistical Analysis – TQ Response Cont'd

Source of Variance	Effect	SS	DF	MS	F	p
Temperature (T)	-6.6750	89.1112	1	89.1112	25.1539	0.00741
Catalyst (C)	1.9250	7.4112	1	7.4112	2.0920	0.22161
Mole Ratio (M)	-6.1750	76.2612	1	76.2612	21.5267	0.00974
TxC	-26.9250	1449.9113	1	1449.9113	409.2745	0.00004
TxM	1.7750	6.3012	1	6.3012	1.7787	0.25319
CxM	0.4750	0.4513	1	0.4513	0.1274	0.73920
TxCxM	0.9250	1.7112	1	1.7112	0.4830	0.52531
Error			4	3.5426		
Total		1631.1588	11			