Polymer Processing Additives Based on Highly Branched (Arborescent) Graft Polymers

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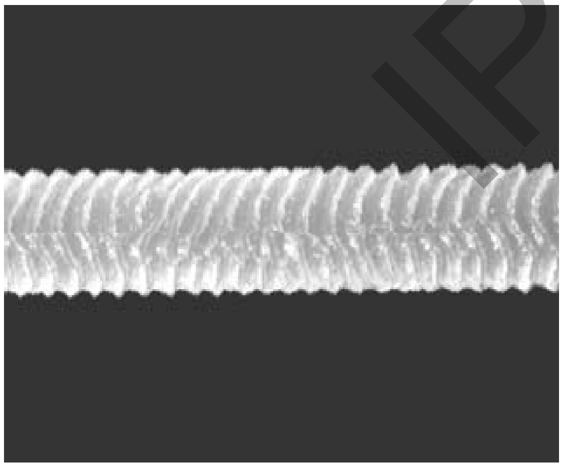
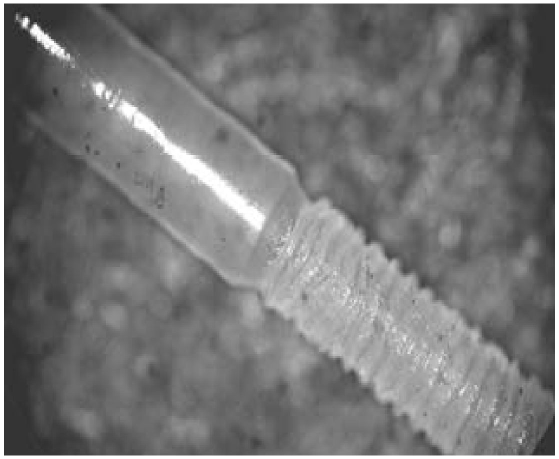
Outline

- Introduction to Polymer Processing Additives (PPA)
- Arborescent Polyisoprenes
  - Synthesis & Characterization
  - Capillary Rheometry Measurements
- Arborescent Polymers with Metal-binding Groups
  - Synthesis & Characterization
  - Capillary Rheometry Measurements
- Conclusions

Processing of Polyolefins

- Extrusion: Forming of molten polymer into various shapes by forcing through a die, e.g. Linear low density polyethylene (LLDPE) monofilament
- “Sharkskin” and cyclic melt fracture: Defects in extruded LLDPE visible as ridges perpendicular to the direction of flow





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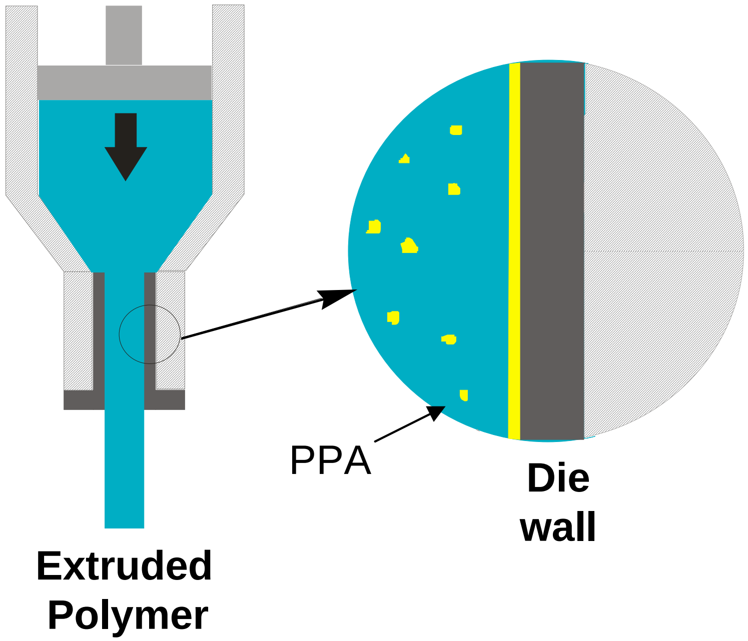
Polymer Processing Additives

- ❑ Fluorinated polymers added at low concentrations (< 0.1% w/w or 1000 ppm) to eliminate melt fracture and reduce extrusion backpressure

- ❑ Formation of droplets (0.1-20 μm) that migrate to the polymer-metal interface

- ❑ Low surface energy at the interface promotes slippage of the flowing polymer



Goal: Investigate the use of fluorinated arborescent polymers as PPA

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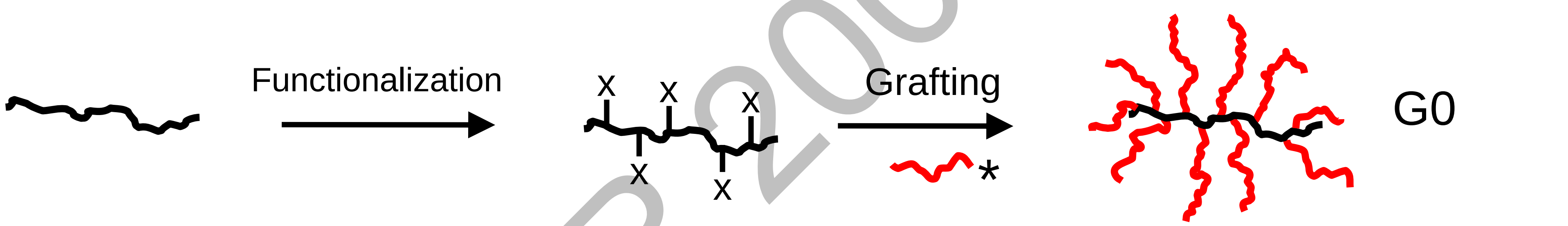
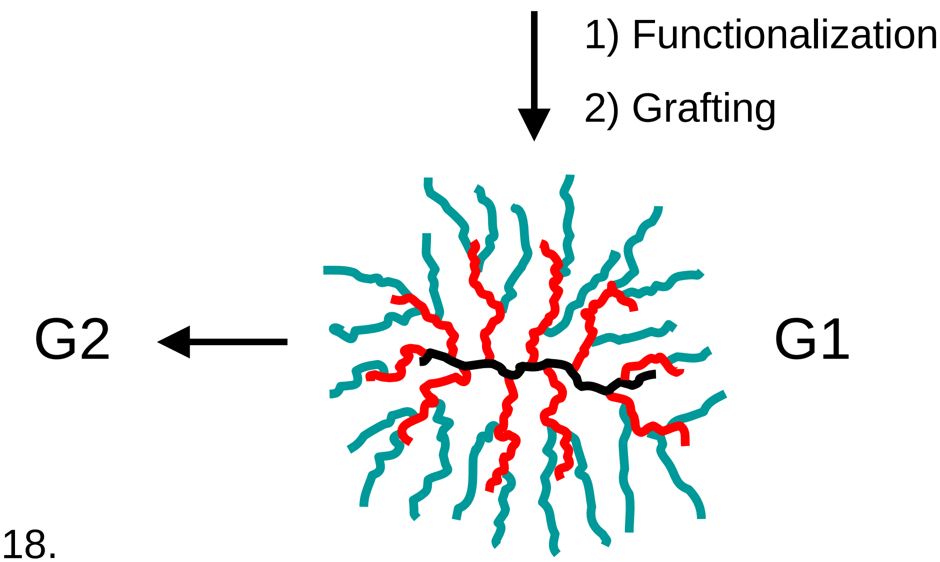
Arborescent Polymers

Branched structure obtained from successive grafting reactions



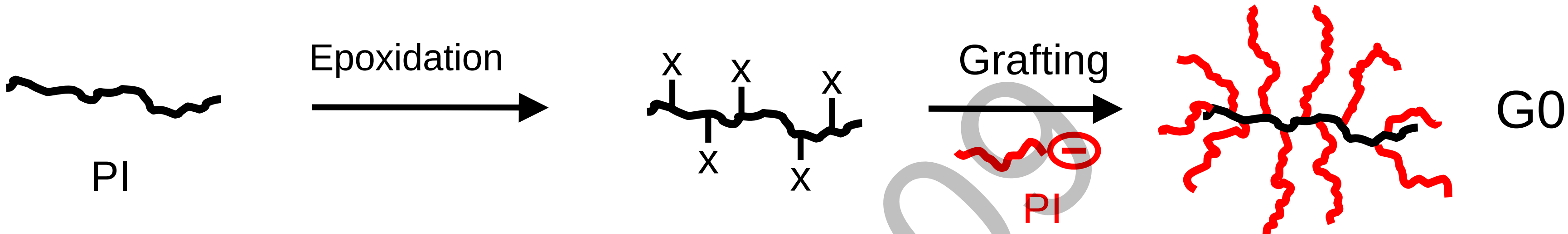


- ❑ Branching density and molecular weight of side chains fully controllable
- ❑ Narrow molecular weight distribution

- Li, J.; Gauthier, M. *Macromolecules* **2001**, *34*, 8918.
- Kee, R.A.; Gauthier, M. *Macromolecules* **1999**, *32*, 6478.

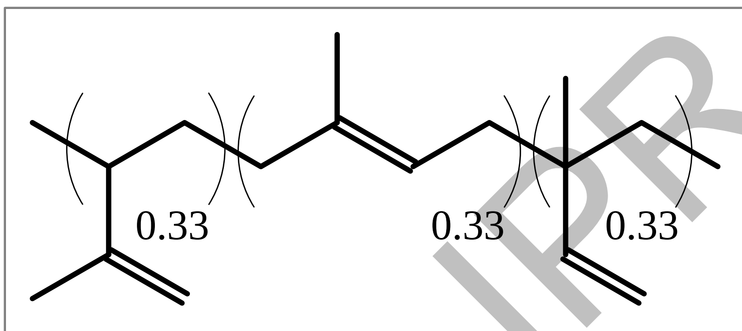
Project #1

Fluorinated Arborescent Polyisoprenes

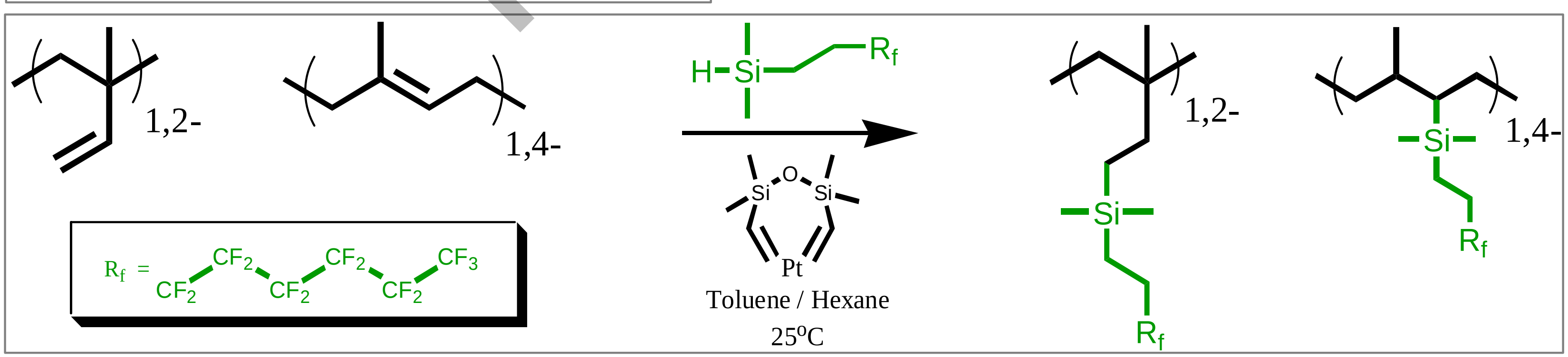


- Yuan, Z.; Gauthier, M. *Macromolecules* **2005**, *38*, 4124.

side chains

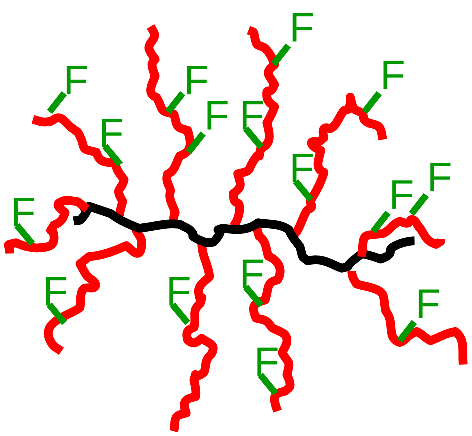


- Mixed microstructure by polymerization in THF
- Yields pendent vinyl groups for polymer modification with fluorinated reagents



Molecular Weight Characterization of PPA

PIG0[10]5-F29



sample	Before fluorination			After fluorination	
	M_w^{app}	M_w/M_n	f_w	M_w^{app}	M_w/M_n
PIG0[5]2.5-F35	41 200	1.05	15	41 000	1.13
PIG0[5]5-F9	73 000	1.02	14	55 000	1.08
PIG0[5]5-F16				63 000	1.09
PIG0[5]5-F28				71 000	1.09
PIG0[5]5-F41				insoluble	
PIG0[5]10-F37	119 000	1.04	11	100 000	1.09
PIG0[5]20-F34	195 000	1.06	10	170 000	1.13
PIG0[10]5-F29	113 000	1.04	23	92 000	1.14
PIG0[15]5-F24	241 000	1.02	40	150 000	1.11

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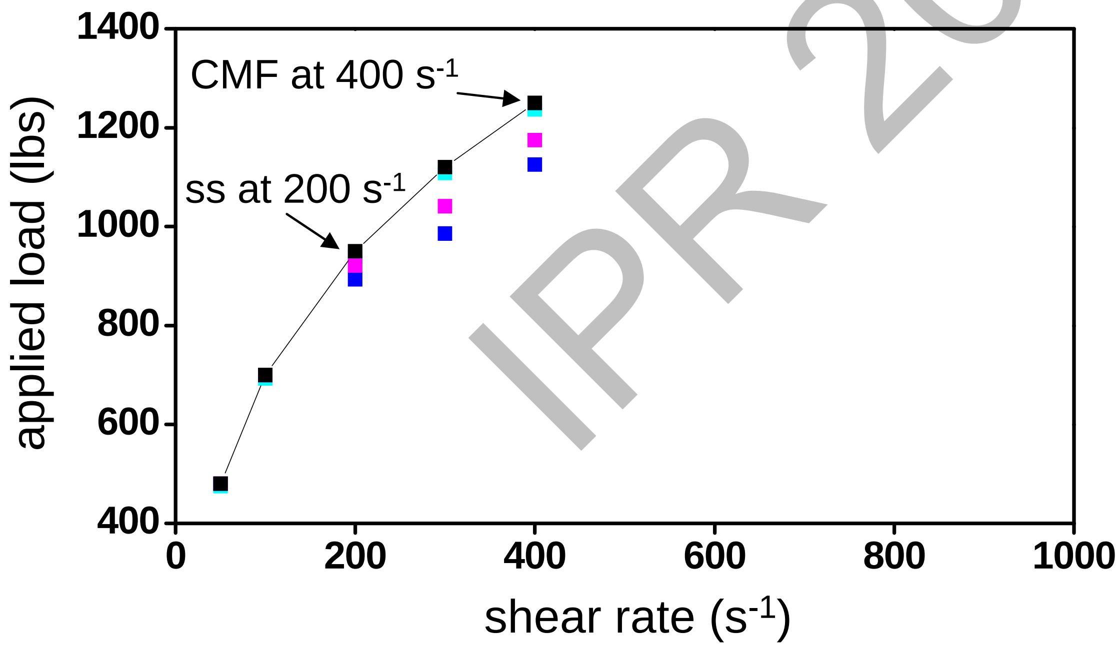
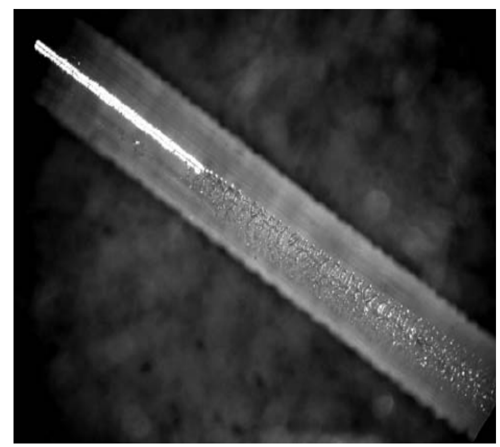
Extrusion Testing: Experimental Procedures

- Melt blending at 0.1% w/w (5 min at 190°C)
- Extrusion in a capillary rheometer at different shear rates (50 – 1000 s^{-1})
  (die length-to-diamater ratio 50/1; entrance angle 90°)
- Performances evaluated in terms of:
  - Backpressure drop observed (relative to LLDPE without PPA)
  - Appearance of the extrudate
- Low molecular weight poly(ethylene glycol) (PEG-3K) used as co-additive in some cases (3:2 ratio vs. PPA)
- Fluorinated linear isoprene homopolymers also tested as PPA
  → no improvement in processability

Extrusion Testing: Effect of Backbone Length

	M_w^{app} of the PPA	Extrudate appearance
no additive		ss 200 s^{-1} ; CMF 400 s^{-1}
PIG0[5]5-F28	190 000	mild CMF 200-400 s^{-1}
PIG0[10]5-F29	310 000	mild CMF 200-400 s^{-1}
PIG0[15]5-F24	590 000	mild CMF 200-400 s^{-1}

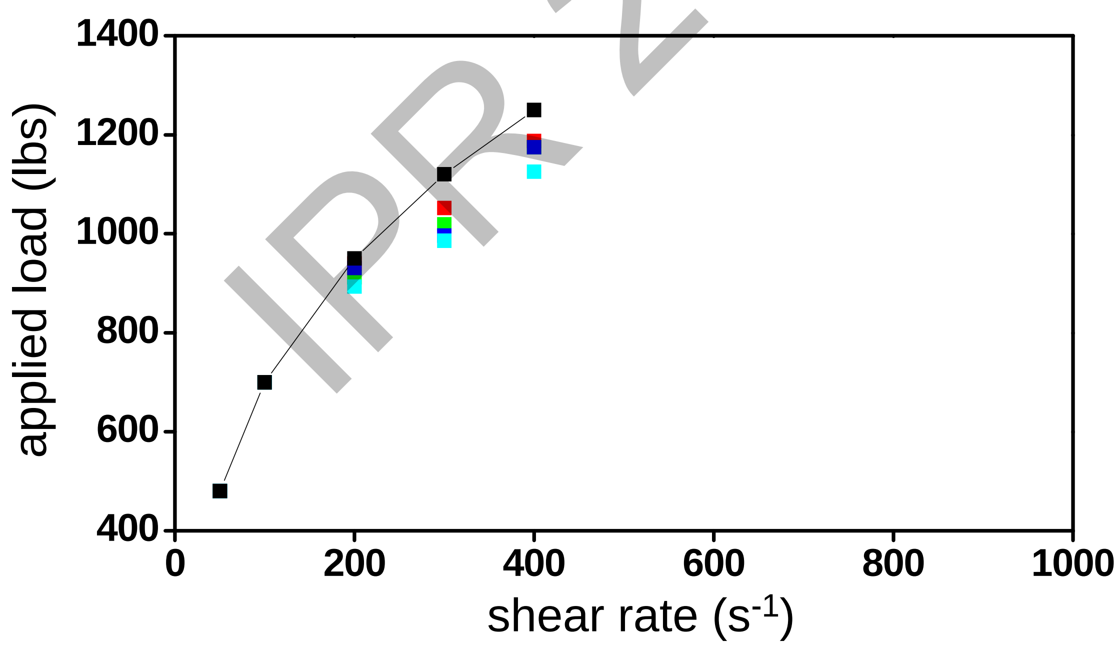




- Small improvement in appearance
- Largest pressure drops for shortest backbone, lowest M_w

Extrusion Testing: Effect of Side Chain Length

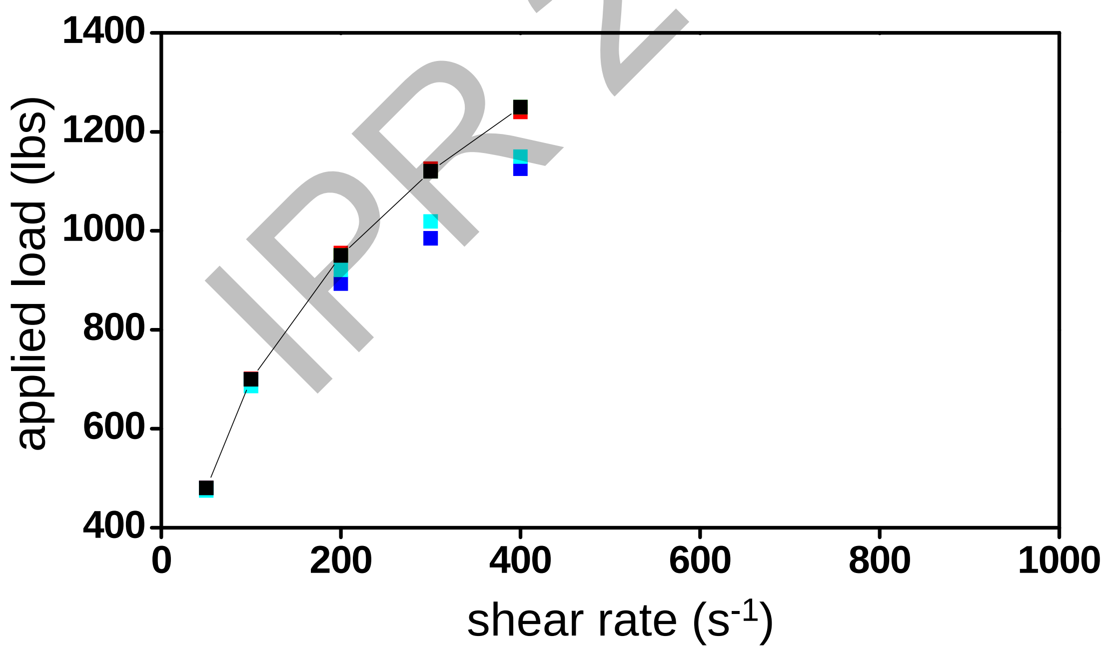
	M_w^{app} of the PPA	Extrudate appearance
no additive		ss 200 s^{-1} ; CMF 400 s^{-1}
PIG0[5]2.5-F35	130 000	mild CMF 200-400 s^{-1}
PIG0[5]5-F28	190 000	mild CMF 200-400 s^{-1}
PIG0[5]10-F37	380 000	mild CMF 200-400 s^{-1}
PIG0[5]20-F34	590 000	mild CMF 200-400 s^{-1}



- Best result for M_w side chains ~ M_w backbone

Extrusion Testing: Effect of Fluorine Content

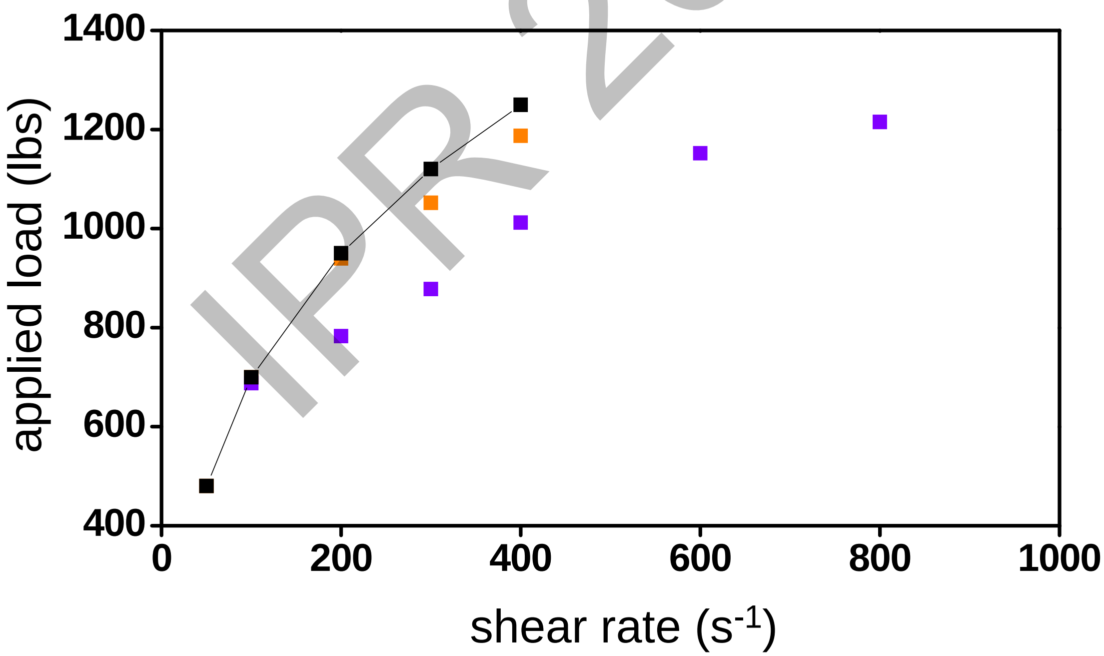
	M_w^{app} of the PPA	Extrudate appearance
no additive		ss 200 s^{-1} ; CMF 400 s^{-1}
PIG0[5]5-F9	110 000	ss 100-400 s^{-1}
PIG0[5]5-F28	190 000	mild CMF 200-400 s^{-1}
PIG0[5]5-F41	250 000	mild CMF 200-400 s^{-1}



- Intermediate fluorine content optimal

Extrusion Testing: Effect of PEG Co-additive

	co-additive	Extrudate appearance
no additive		ss 200 s^{-1} ; CMF 400 s^{-1}
PIG0[5]2.5-F35	none	mild CMF 200-400 s^{-1}
PIG0[5]2.5-F35	PEG 3K	glossy up to CMF (1000 s^{-1})

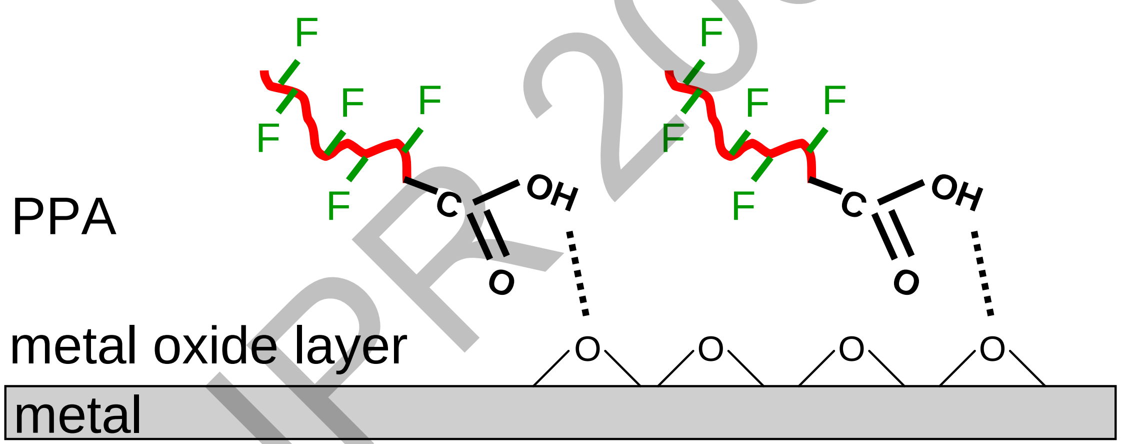


- Co-additive highly beneficial (partitioning agent)

Project #2

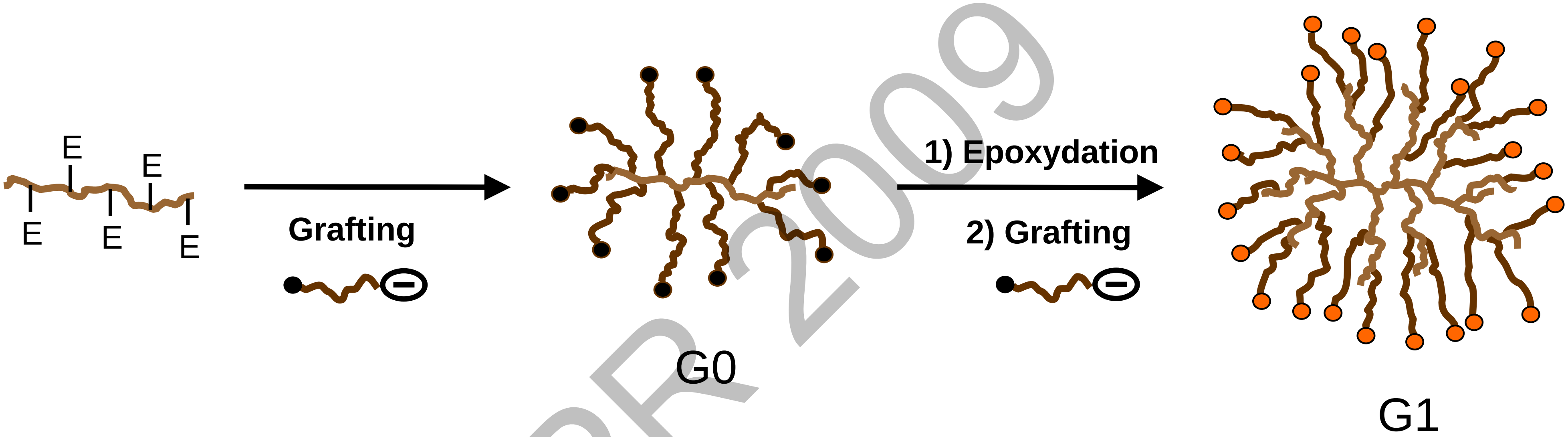
Fluorinated Arborescent Polyisoprenes with Metal-binding Polar Functionalities

Goal: Introduce specific interactions between the metallic surface of the processing equipment and the PPA layer

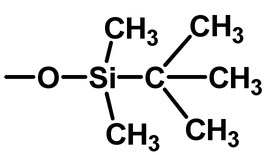


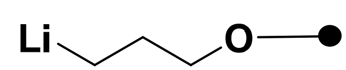
→Decrease the rate of desorption of the PPA during the extrusion

Synthetic Scheme (1)



E = epoxidized unit of PI

● = 

Key: use of a bi-functional initiator 

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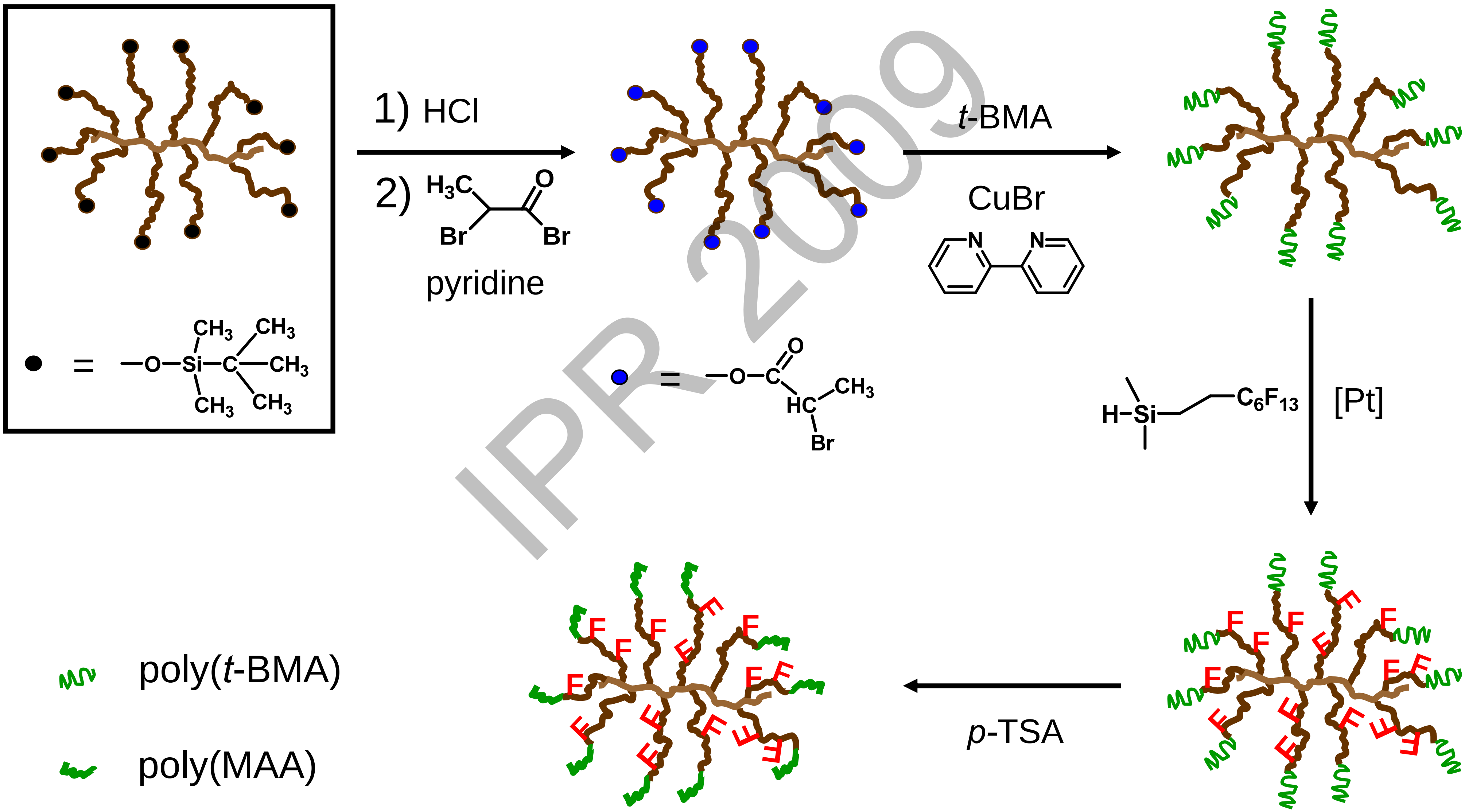
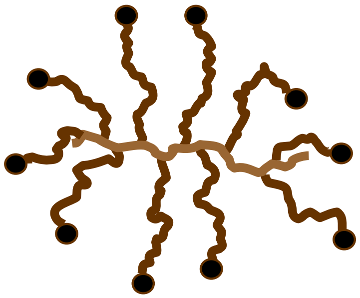
Synthetic Scheme (2) (e.g. G0 polymer)

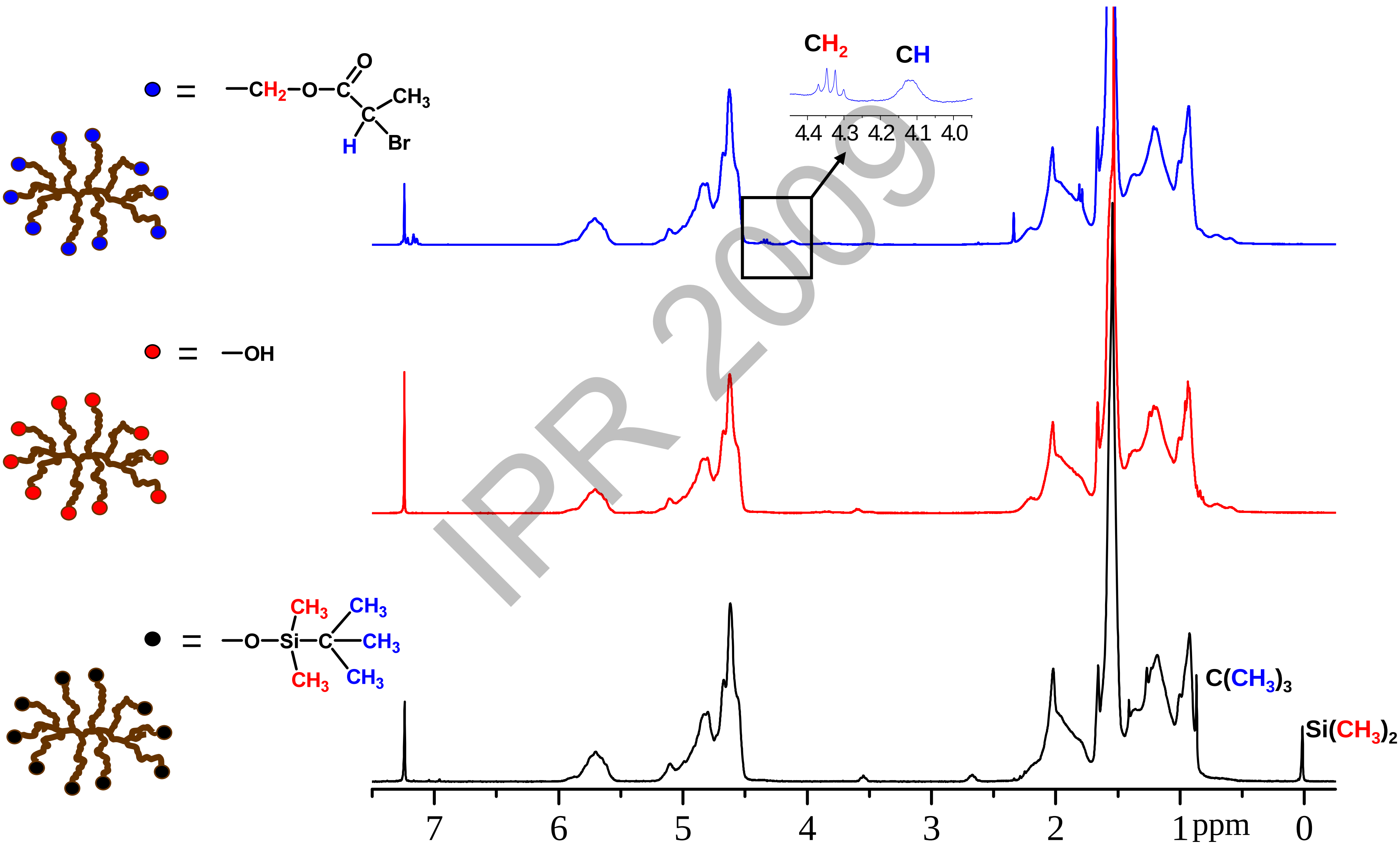




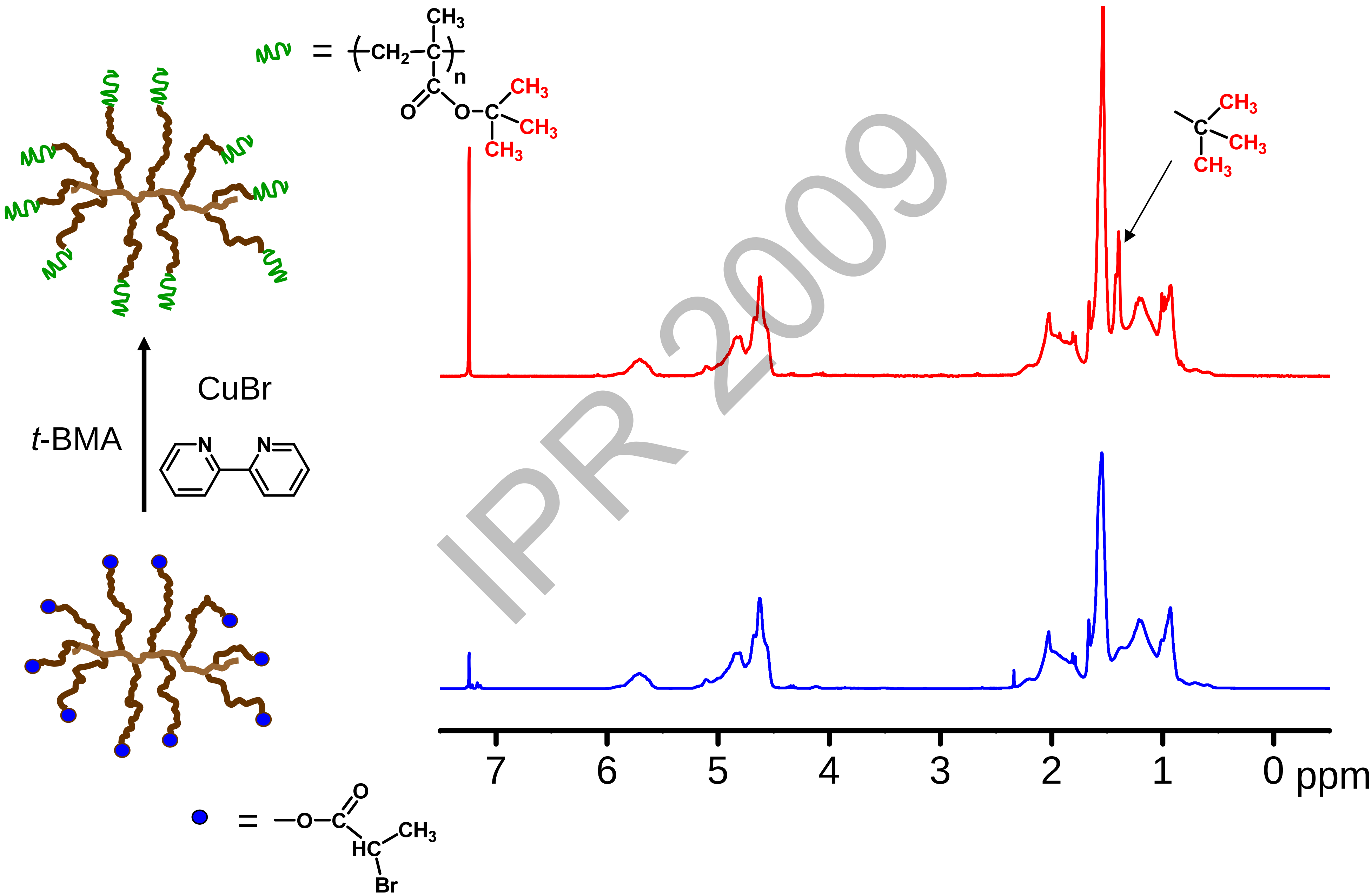
Graft homopolymers: Molecular weight data

	backbone		Side chains	Graft polymer		
	M_w	M_w/M_n	M_w	M_w	M_w/M_n	Arms
G0PI[5]-5	4900	1.08	5200	71000	1.07	13
G0PI[5]-10	4900	1.07	10500	99400	1.07	9
G0PI[7]-10	7100	1.07	10700	179000	1.08	16
G0PI[10]-7	11200	1.08	7200	160000	1.07	21
G0PI[10]-10	11200	1.08	8000	186900	1.09	22
G0PI-*g*-PI2.5	99400	1.07	2900	600900	1.04	176
G0PI-*g*-PI5			4700	722000	1.04	129

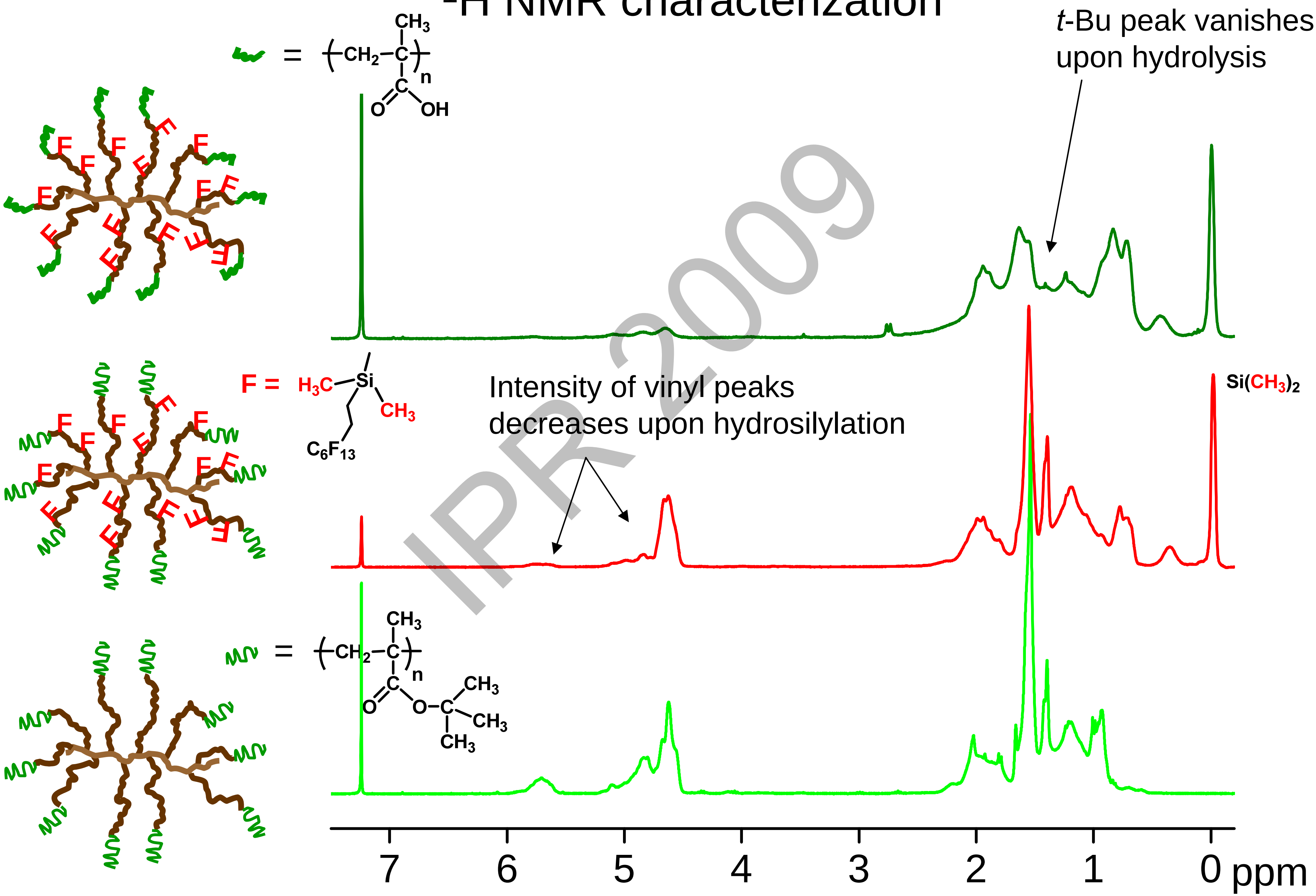
Molecular Characterization (^{1}H NMR)



Chain extension by ATRP: ^{1}H NMR characterization



Fluorination and hydrolysis: ^{1}H NMR characterization



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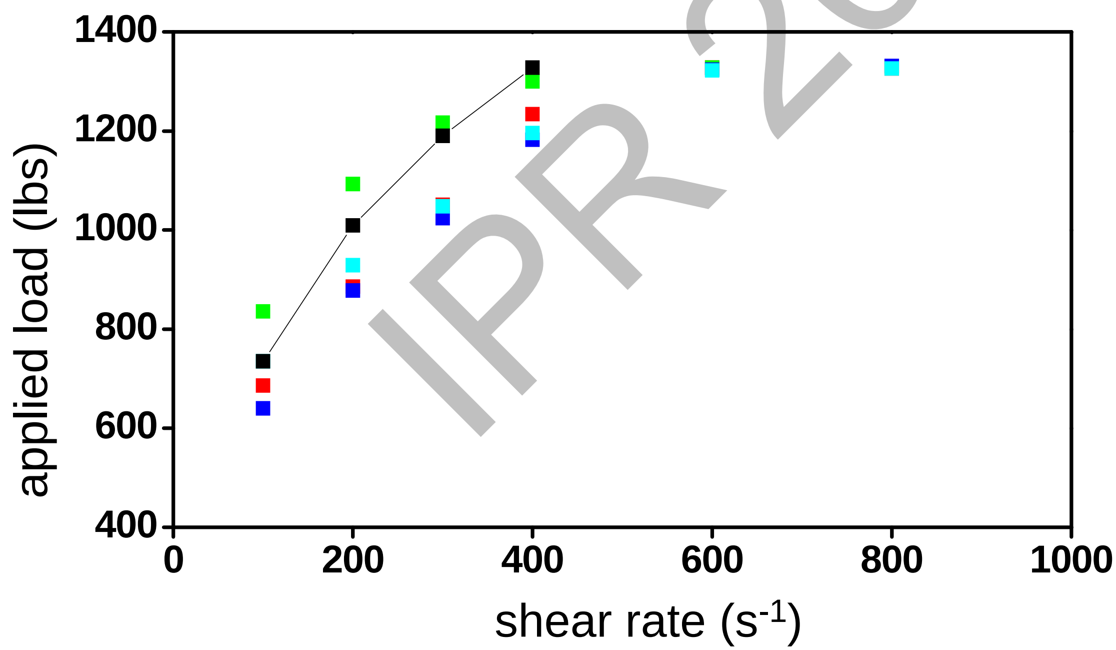
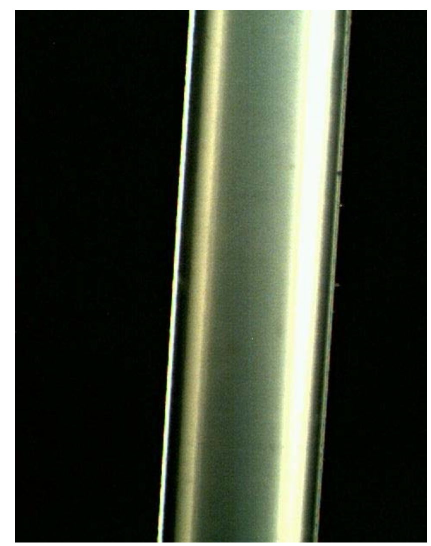
Graft copolymers: Molecular weight data

	After ATRP M_w	M_w/M_n	DP	Fluorination level (mol %)	Hydrolsyis level (mol %)
G0PI[5]10	105000	1.29	20	34	11
					19
G0PI[5]5	120900	1.96	20	24	13
G0PI[7]10	187000	1.73	20	24	35
					0
G0PI[10]7	123000	1.34	5	25	100
	95800	1.10	10	40	100
G0PI[10]10	108800	1.24	7	24	100
				30	100
				40	100
G0PI-*g*-PI5	370000	1.36	7	26	18
	441000	1.32	15	21	100
G0PI-*g*-PI2.5	376000	1.28	12	25	100

Extrusion Testing : G0 polymers

	Extrudate appearance
■ no additive	ss 200 s^{-1} ; CMF 400 s^{-1}
■ PIG0[5]8-F34-PtBMA(20)$_{11}$	glossy up to 400 s^{-1} ; CMF 600-800 s^{-1}
■ PIG0[5]8-F34-PtBMA(20)$_{19}$	glossy up to 400 s^{-1} ; CMF 600-800 s^{-1}
■ PIG0[7]10-F24-PtBMA(20)$_{0}$	ss 200 s^{-1} ; CMF 400 s^{-1}
■ PIG0[7]10-F24-PtBMA(20)$_{35}$	glossy up to 400 s^{-1} ; CMF at 600 s^{-1}





- Elimination of ss, CMF delayed to higher shear rates
- Modest decrease in backpressure

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Extrusion Testing : G1 polymers

	Extrudate appareance
G1PI2.5-F25-PtBMA(12)$_{100}$	ss @ 200 s^{-1}. CMF @ 600 s^{-1}
G1PI5-F26-PtBMA(7)$_{18}$	ss @ 200 s^{-1}. CMF @ 400 s^{-1}
G1PI5-F21-PtBMA(12)$_{100}$	ss @ 200 s^{-1}. CMF @ 400 s^{-1}
G1PI0-F17-PtBMA(37)$_{28}$	ss @ 200 s^{-1}. CMF @ 400 s^{-1}

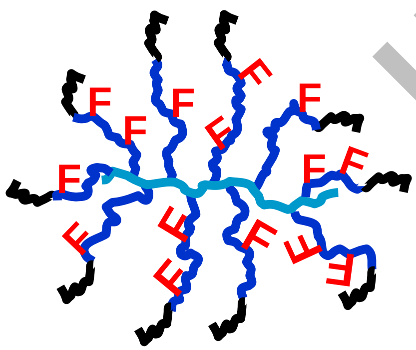
→ No improvement in term of backpressure reduction or extrudate appearance

→ Too many PMAA chains hindering the lubricating action of the PPA molecules?

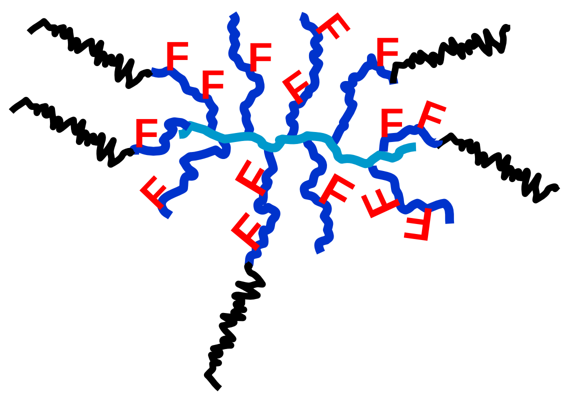
Mode of incorporation of the PMAA segments

Chain extension by ATRP performed with a different catalytic system
→ CuBr/PMDETA used instead of CuBr/2,2'-bipyridyl

Model experiments on linear substrates showed that more uniform poly(methacrylic acid) segments obtained



ATRP with CuBr/PMDETA



ATRP with CuBr/2,2'-bipyridyl

Extrusion Testing: G0 polymers (2)

	Extrudate appareance
G0PI[7]-5-F24-PtBMA$(20)_{13}$	ss @ 300 s^{-1}. CMF @ 600 s^{-1}
G0PI[10]7-F40-PtBMA$(10)_{100}$	Glossy up to 400 s^{-1} (up to 19% backpressure reduction at 300 s^{-1}), CMF @ 600 s^{-1}
G0PI[10]-10-F24-PtBMA$(7)_{100}$	ss @ 300 s^{-1}. CMF @ 400 s^{-1}
G0PI[10]-10-F30-PtBMA$(7)_{100}$	ss @ 200 s^{-1}. CMF @ 400 s^{-1}
GPI[10]-10-F40-PtBMA$(7)_{100}$	ss @ 200 s^{-1}. CMF @ 400 s^{-1}

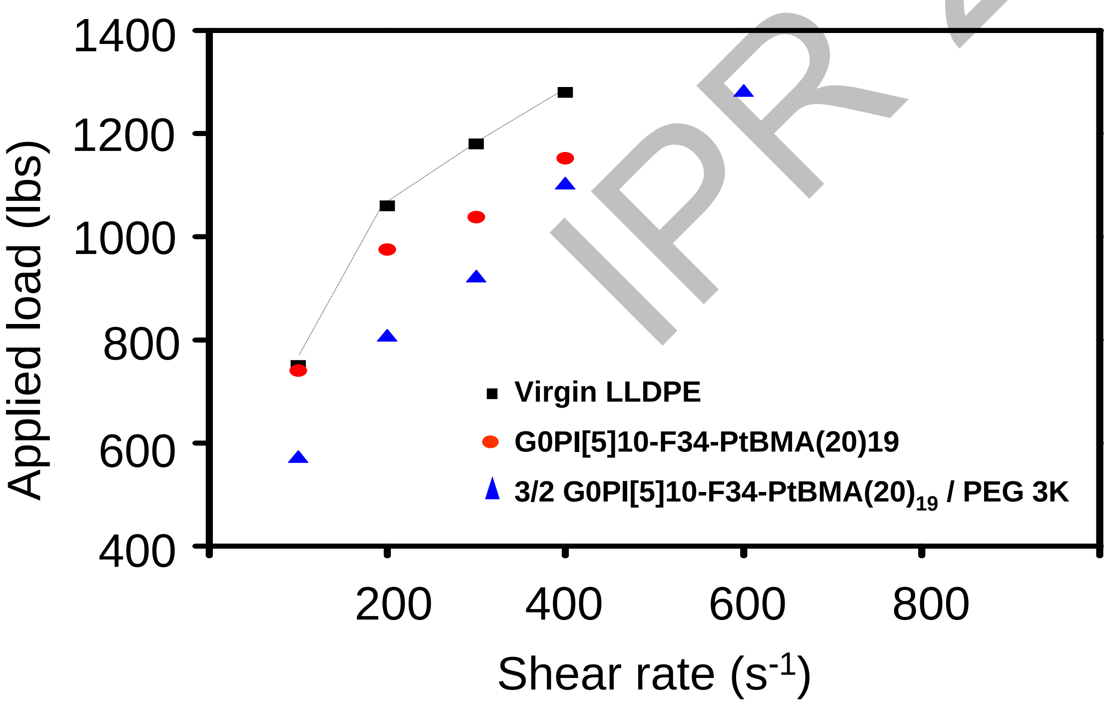
→ Backpressure reduction negligible for most of the samples

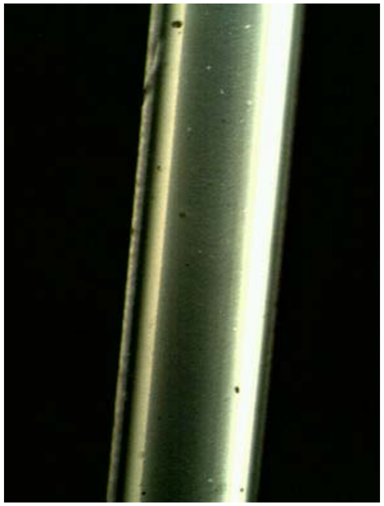
One sample: G0PI[10]7-F40-PtBMA$(10)_{100}$ yielded a higher load reduction and remained glossy up to 400 s^{-1}

→ Complete coverage of the macromolecule by PMAA segments inhibits its lubricating action?

Effect of PEG Co-additive

	Extrusion backpressure reduction				Extrudate appearance
	100 s^{-1}	200 s^{-1}	300 s^{-1}	400 s^{-1}	
G0PI[10]7-F25-PtBMA(5)$_{100}$	7	10	15	19	Glossy up to 400 s^{-1}; CMF @ 600-800 s^{-1}
G0PI[5]10-F34-PtBMA(20)$_{11}$	19	27	26	17	Glossy up to 400 s^{-1}; CMF @ 800 s^{-1}
▲ G0PI[5]10-F34-PtBMA(20)$_{19}$	24	24	22	14	Glossy up to 600 s^{-1}; CMF @ 800-1000 s^{-1}





- Co-additive beneficial (partitioning agent)

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Conclusions

- ❑ Fluorinated arborescent G0 and G1 isoprene homopolymers synthesized
  - Poor performance as PPA on their own
  - Some G0 structures very effective when combined with a low molecular weight poly(ethylene glycol) co-additive

- ❑ New class of fluorinated arborescent PPA with polar groups synthesized and characterized
  - More effective to eliminate sharkskin than non-binding PPA
  - Appearance improvements, moderate backpressure reductions
  - Heterogeneous distribution of PMMA leads to better performances
  - Best performance for G0 structures

Future work

- Optimize the structure (PMAA content, backbone length, side chain length,…)
- Investigate other polar groups (thiol, amine,...)
- Investigate higher generations of polymers
- Investigate action of fillers

Acknowledgements

Esso Imperial Oil

NSERC CRSNG

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