Understanding the Effect of the Microstructure of MPEG-PCEs on Ordinary Portland Cement (OPC)

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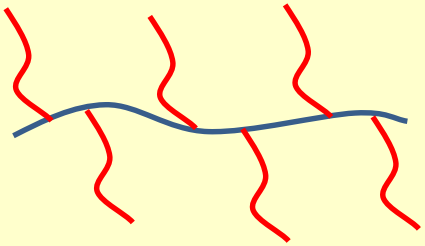
INTRODUCTION:

High Performance Concrete

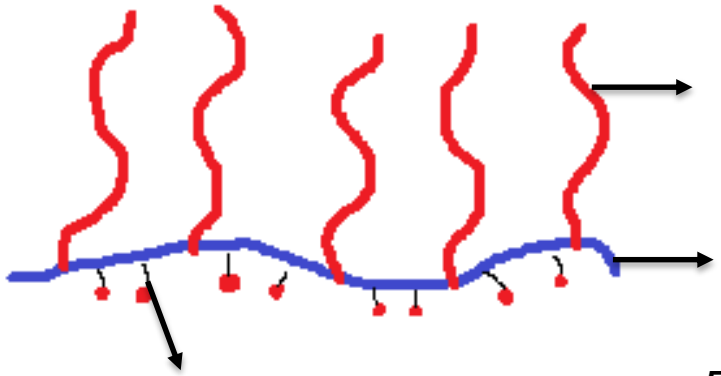
Concrete for special applications

SUPERPLASTICIZERS

PCE
Carboxylates

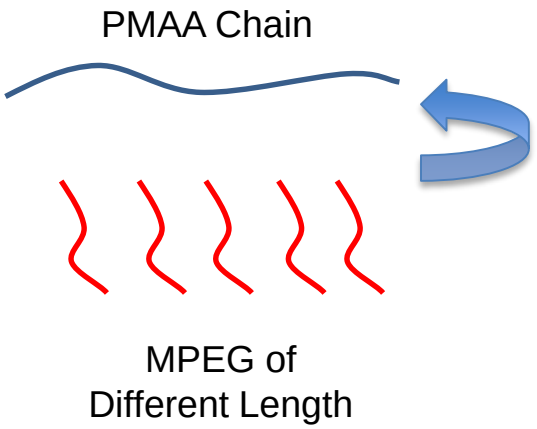


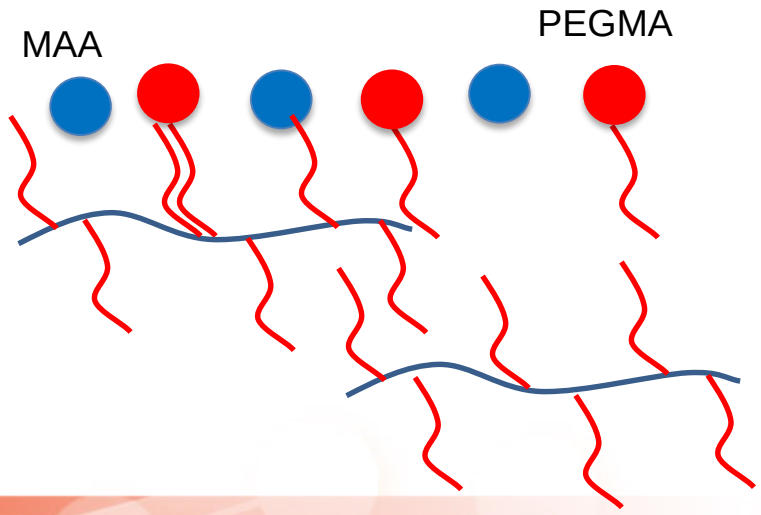
SYNTHESIS ROUTES OF (MPEG) PCE CARBOXYLATES



Partial Esterification of PMAA with MPEG

Free Radical Copolymerization of MAA and PEGMA



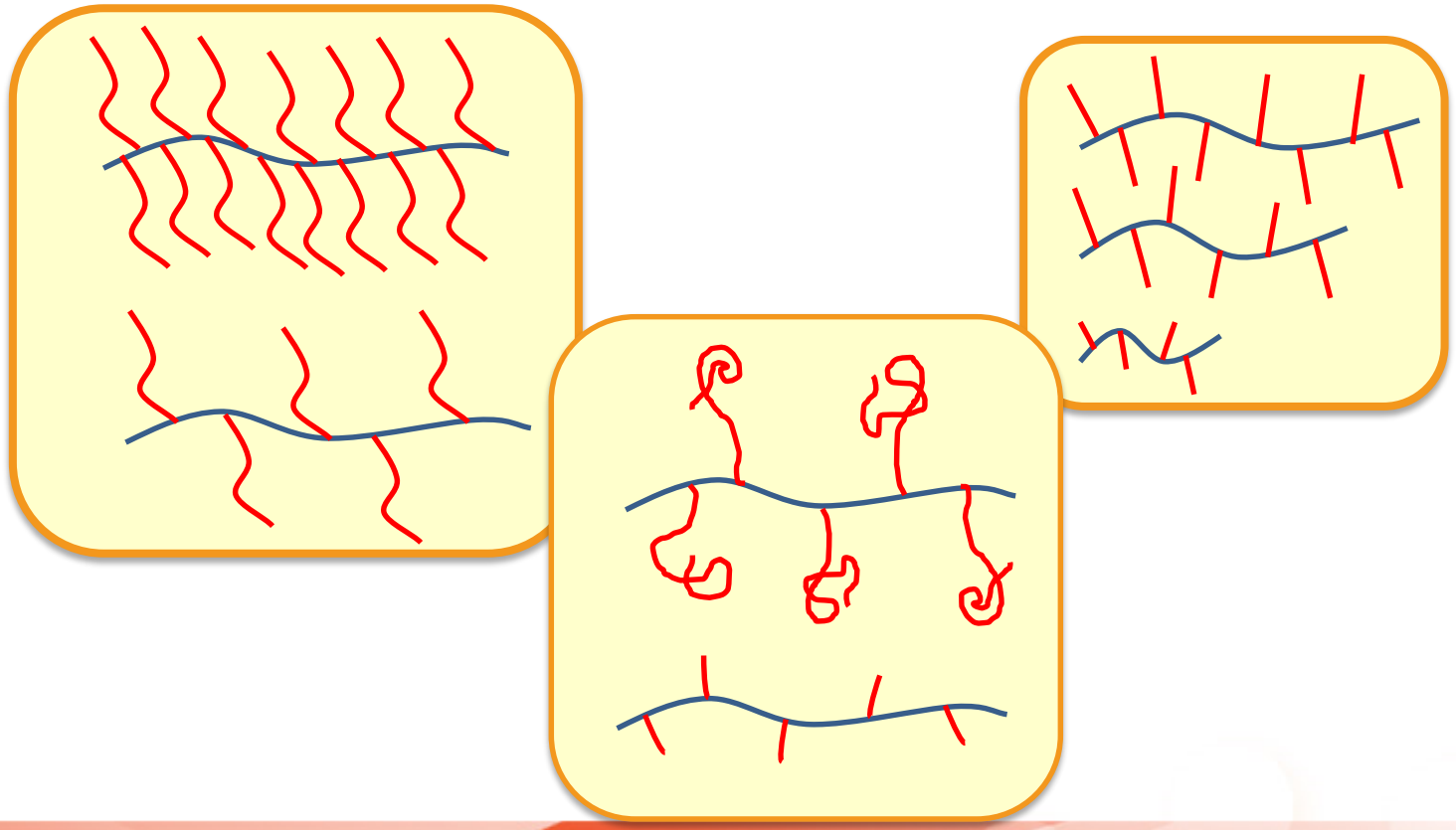


1. L. Lei, J. Plank. Ind. Eng. Chem. Res. 53 (2014) 1048-1055
2. J. Plank et al. Cem. Concr. Res. 78 (2015) 81-99
3. S. Pourchet et al. Cem. Concr. Res. 42 (2012) 431-439

FREE RADICAL COPOLYMERIZATION

Microstructure of the synthesized PCE can be controlled by:

- **Comonomer ratio**
- **Molar Mass of Chains**
- **PEGMA Side Chains Length**



OBJECTIVE and OUTLINE:

Understand the fundamentals of the effect of controlled microstructures of PCE superplasticizers on the hydration and rheology of ordinary Portland cements

1. **Controlled synthesis of comb-like macromolecules with desired microstructure**

   - Copolymerization of MAA and PEGMA of different lengths (Mn: 300 g/mol (5) – 950 g/mol (20) – 2000 g/mol (45))
   - Different molar masses
   - Diferent monomer ratios – charge densities

2. **Characterization of cement pastes**

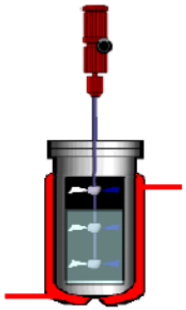
Calorimetry

Setting Time

Rheological Measurements

RESULTS:

Batch copolymerization of MAA-co-PEGMA 5 (Short side chain lengths)

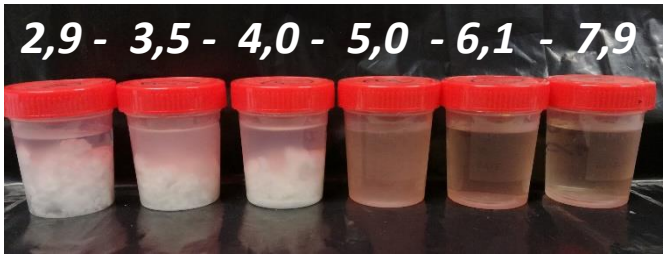


BATCH

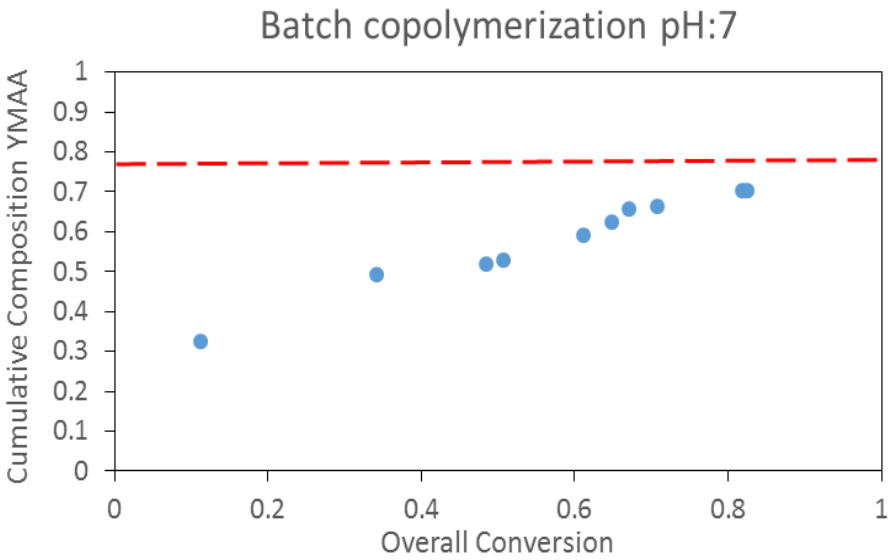
Starting Point

- Synthesis of MAA – PEGMA 5 (Short side chain length)
- Aqueous phase copolymerization
- pH of the medium affects the solubility of the copolymers

pH



- **pH = 7**
- T = 70 ºC
- SC = 5%
- Initiator = 1%

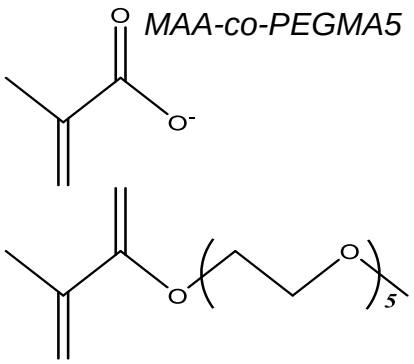


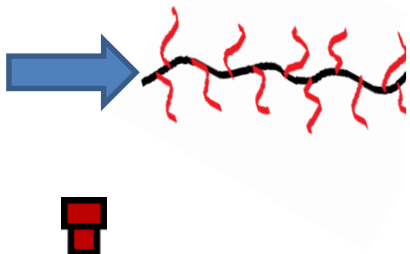
COMPOSITION DRIFT

- Big difference in reactivity ratios

RESULTS:

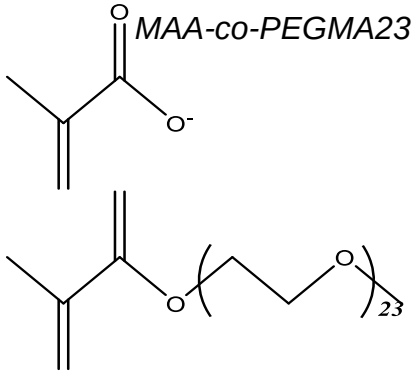
Kinetics of the copolymerization of MAA-co-PEGMA

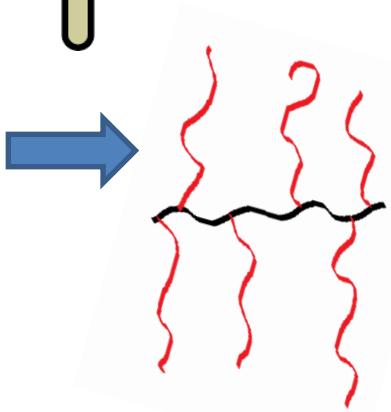




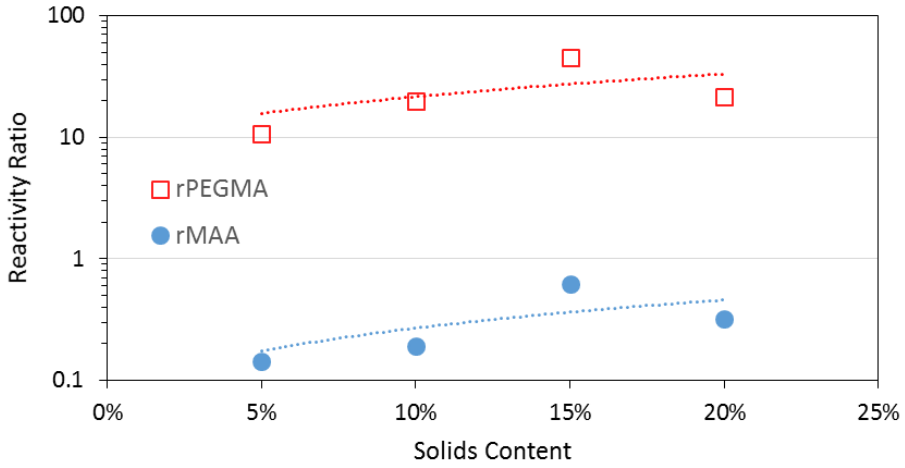
In-situ ^{1}H-NMR Aqueous Phase Copolymerization

pH = 7

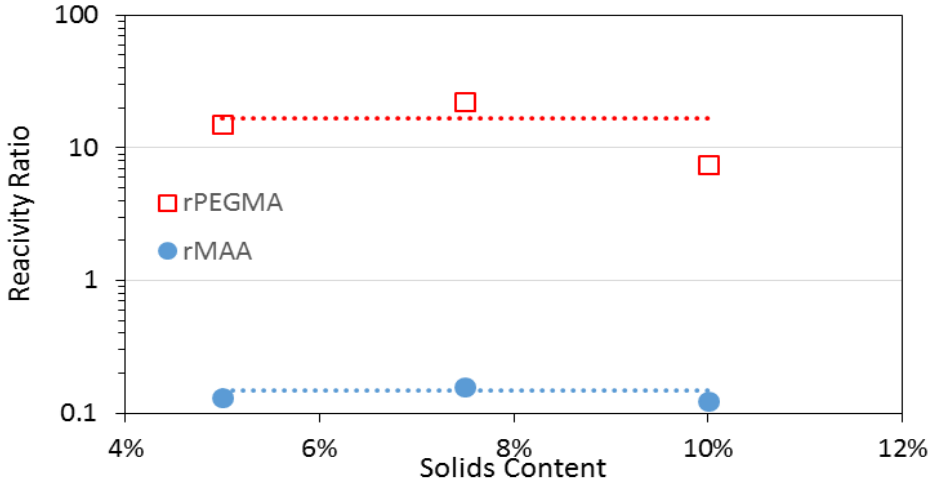




MAA-co-PEGMA5



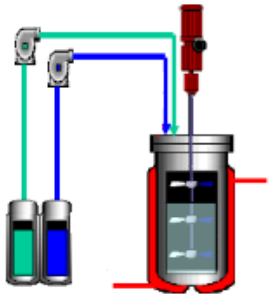
MAA-co-PEGMA23



5. I. Emaldi, S. Hamzehlou, J.S. Dolado, J.R. Leiza. Processes. 2017. 5 (2). 19 doi:10.3390/pr5020019

RESULTS:

Semibatch copolymerization of MAA-co-PEGMA 5

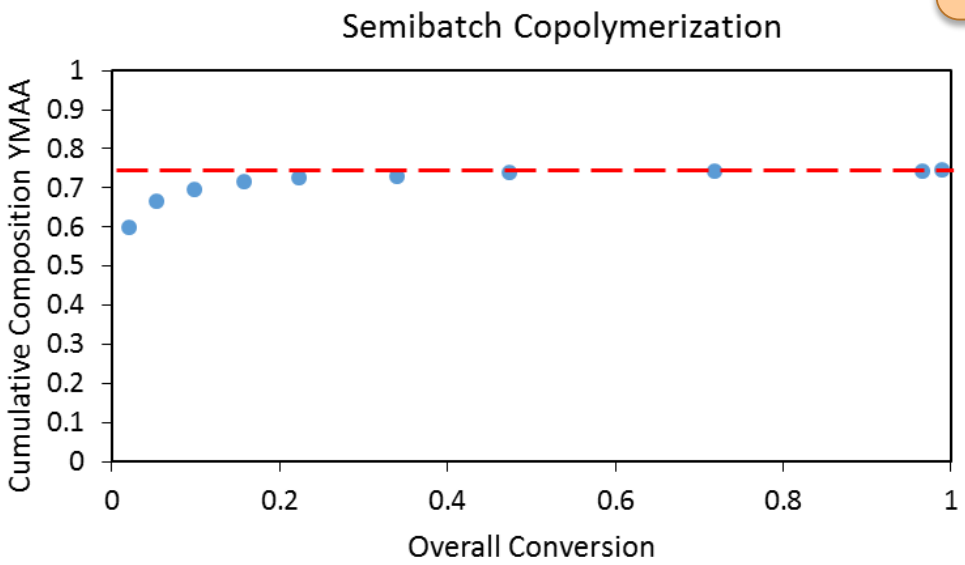


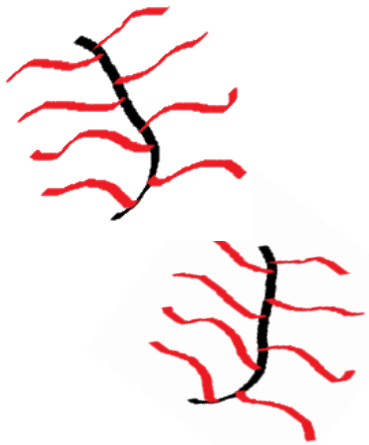
SEMIBATCH

- Starved semibatch copolymerizations
- Avoiding the reactivity ratio difference incovenient
- Slow feeding rates (8h)

- **pH = 7**
- T = 90 ºC
- SC = 30%
- Initiator = 2%
- Feed time = 8h

HOMOGENEOUS COMPOSITION



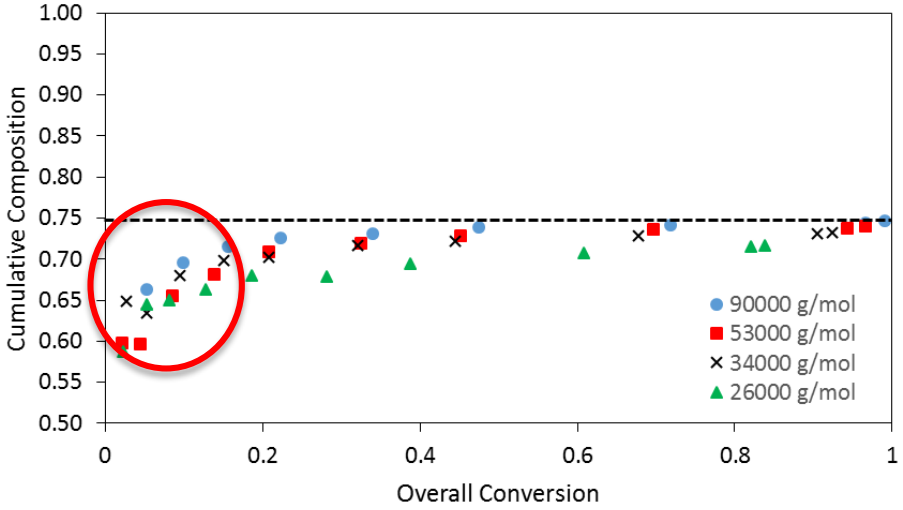


RESULTS:

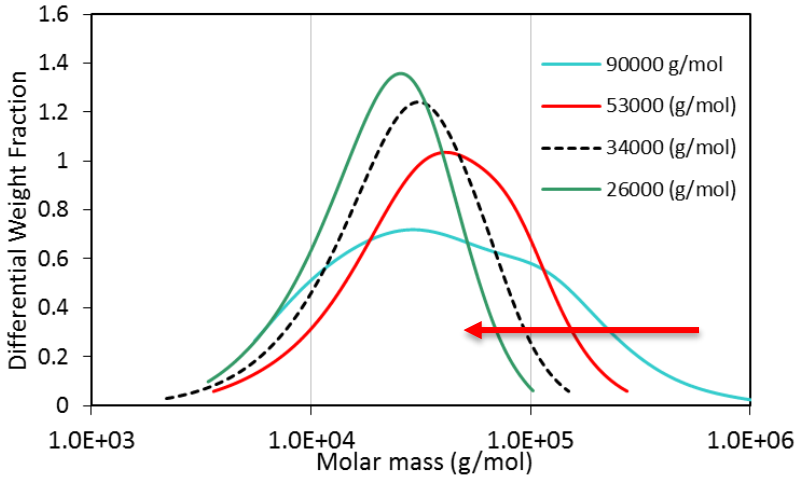
PCEs with Variable Molar Mass:

PCE	Monomer ratio	Mw (kg/mol)	Đ	DP	CTA % bmom	Solids Content	PEGMA Length (EGu)
S1	3:1	90.5	2.6	247	0	31.4%	5 (Short)
S2	3:1	53.4	1.7	222	0.5	31.4%	5 (Short)
S3	3:1	34.3	1.8	141	1	31.0%	5 (Short)
S4	3:1	26.7	1.7	111	1.5	31.0%	5 (Short)

CUMULATIVE COMPOSITION



MOLAR MASS DISTRIBUTION



*DP: Degree of Polymerization *CTA: Chain transfer Agent
*bmom: By mol of monomer *Đ: Polydispersity index

POLYMAT

RESULTS:

^{13}C-NMR

Distribution of the monomers in the chain

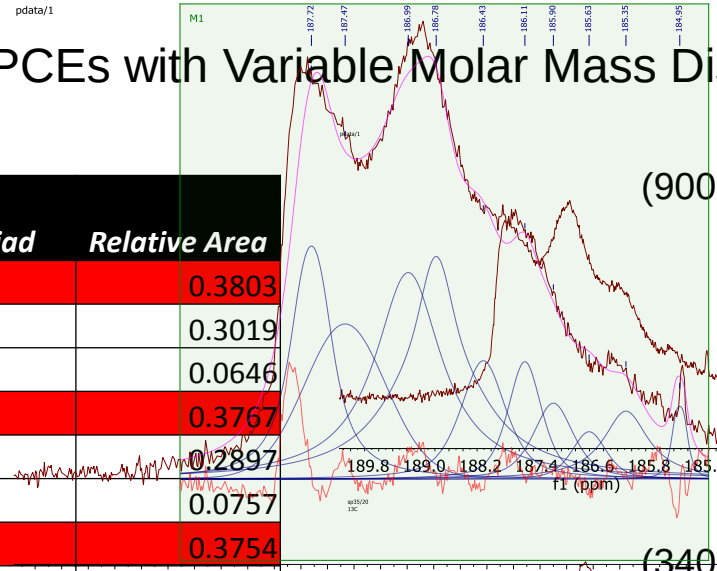
CHEMICAL COMPOSITION DISTRIBUTION

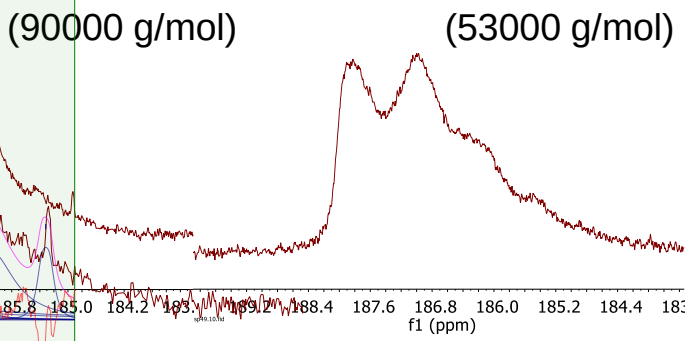
-*AAABBABABBABBAAABAAABBABBAAB*-

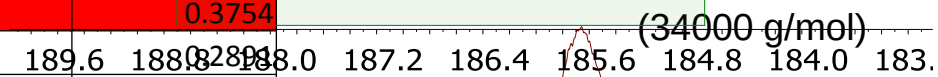
A: MAA
B: PEGMA

PCEs with Variable Molar Mass Distribution

Sample	*Mw*	*Triad*	*Relative Area*
S1	90000 g/mol	AAA	0.3803
		AAB	0.3019
		BAB	0.0646
S2	53000 g/mol	AAA	0.3767
		AAB	0.2897
		BAB	0.0757
S3	34000 g/mol	AAA	0.3754
		AAB	0.2851
		BAB	0.0679
S4	26000 g/mol	AAA	0.3548
		AAB	0.2799
		BAB	0.0823





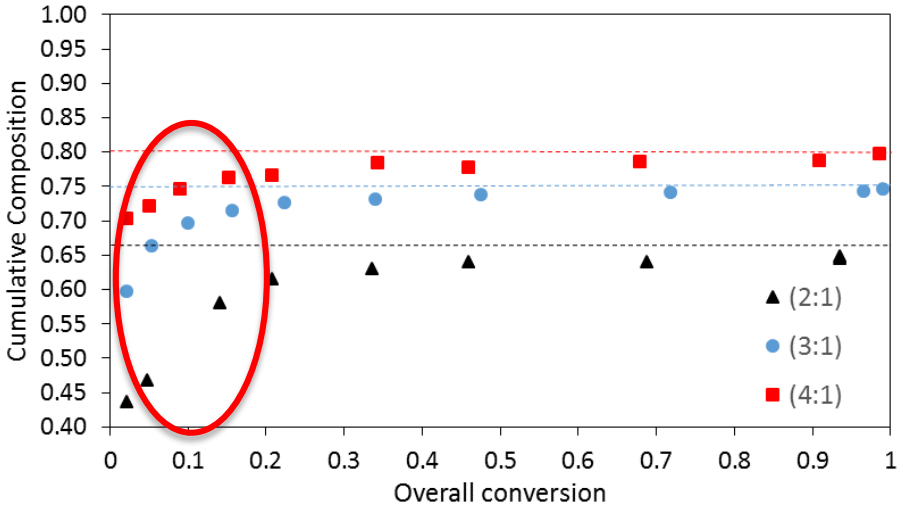


6. P. Borget et al. Col. Surf. 260 (2005) 173-182
7. B. Magny et al. Polymer 33 (1992) 3151-3154

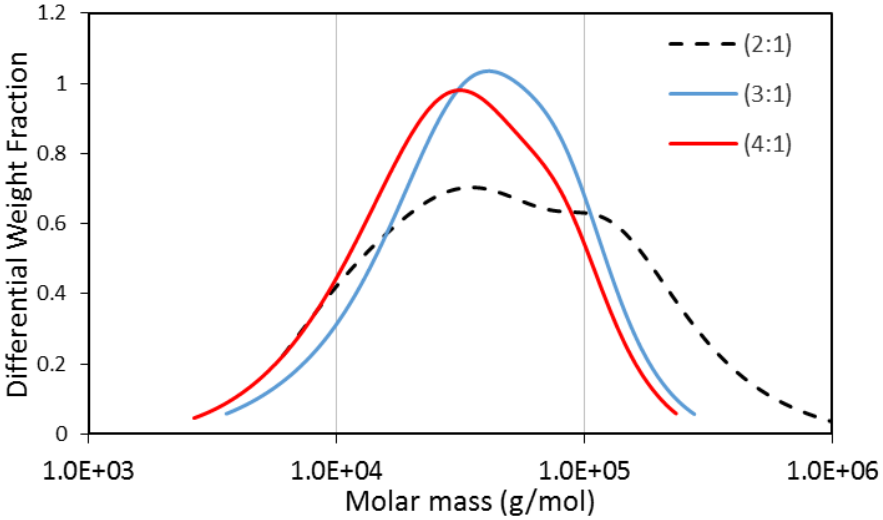
PCEs with Variable Monomer Ratio – Charge Density

PCE	Monomer ratio	Mw (kg/mol)	Đ	DP	CTA % bmom	PEGMA Length (EGu)
S5	2:1	98.0	3.1	185	0	5 (Short)
S2	3:1	53.4	1.7	222	0.5	5 (Short)
S6	4:1	44.4	1.8	195	0	5 (Short)

CUMULATIVE COMPOSITION



MOLAR MASS DISTRIBUTION



*DP: Degree of Polymerization *CTA: Chain transfer Agent
*bmom: By mol of monomer *Đ: Polydispersity index

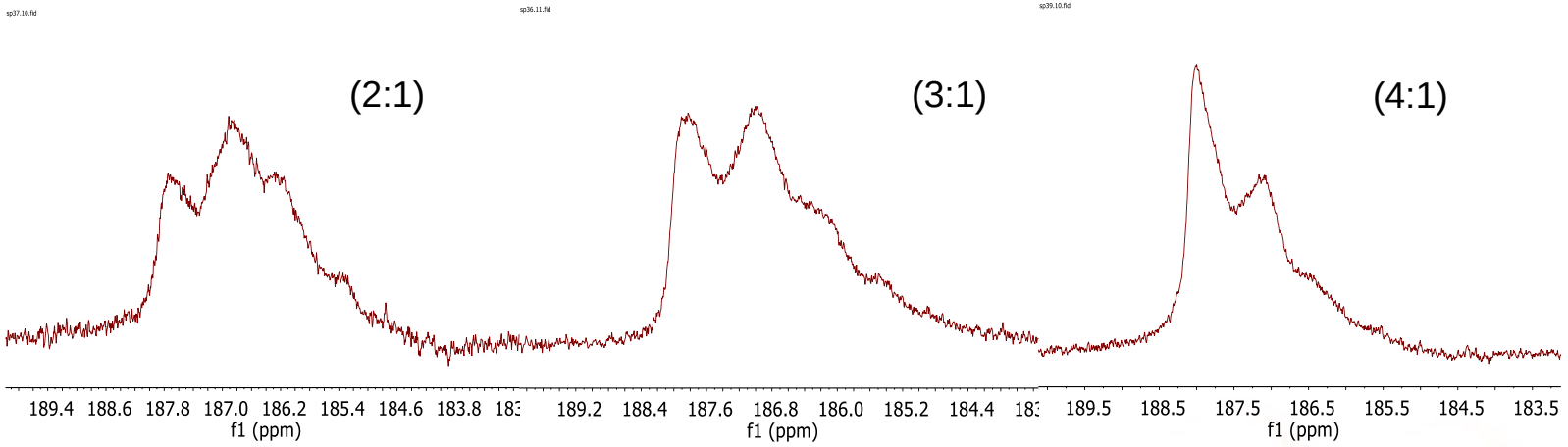
RESULTS:

CHEMICAL COMPOSITION DISTRIBUTION

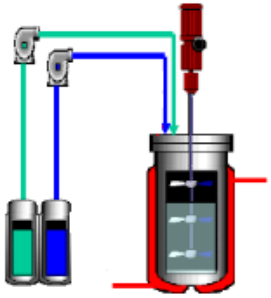
^{13}C-NMR

A: MAA
B: PEGMA

Sample	*Monomer Ratio*	*Triad*	*Relative Area*
S5	(2:1)	AAA	0.3134
		AAB	0.2694
		BAB	0.0657
S2	(3:1)	AAA	0.3767
		AAB	0.2897
		BAB	0.0757
S6	(4:1)	AAA	0.4165
		AAB	0.3115
		BAB	0.0691



RESULTS:



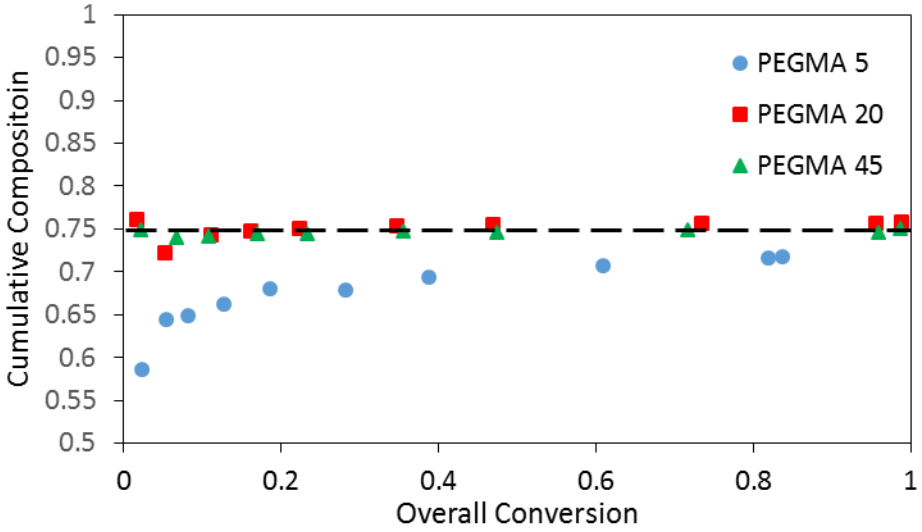
pH = 3
T = 90 °C
SC = 20%
Initiator = 2%
Feeding time = 8h

PCEs with Variable PEGMA Macromonomer

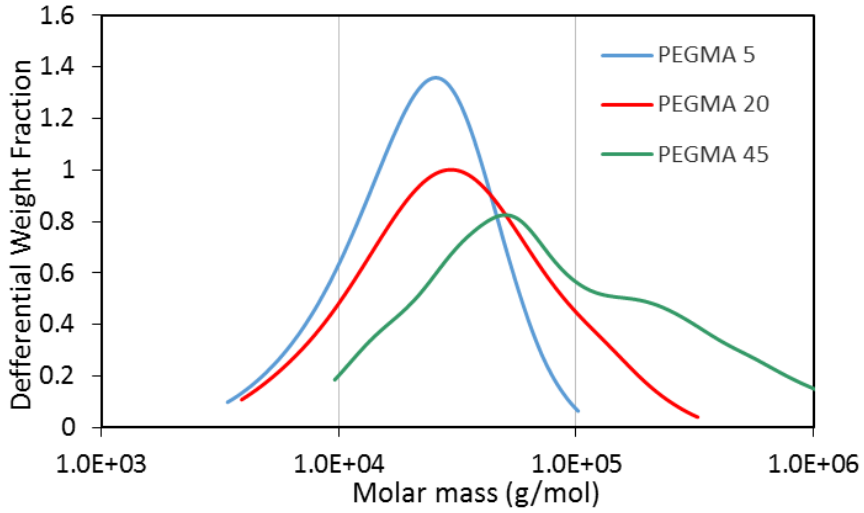
PCE	PEGMA length (EGu)	Monomer ratio	Mw (kg/mol)	Đ	DP	CTA % bmom	Solids Content	pH
S4	5	3:1	26.7	1.7	111	1.5	30.96%	7
M	20	3:1	47.1	1.9	83	0	20.26%	3
L	45	3:1	185.5	3.6	91	1	20.55%	3

*DP: Degree of Polymerization *CTA: Chain transfer Agent
*bmom: By mol of monomer *Đ: Polydispersity index

CUMULATIVE COMPOSITION



MOLAR MASS DISTRIBUTION



8. B. L. Smith, J. Klier. J. App. Pol. Sci. 68 (1998) 1019-1025

RESULTS:

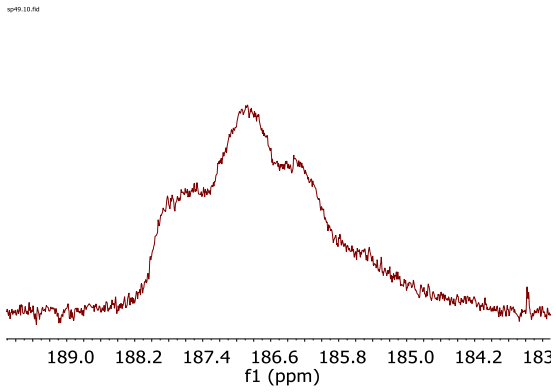
CHEMICAL COMPOSITION DISTRIBUTION

^{13}C-NMR

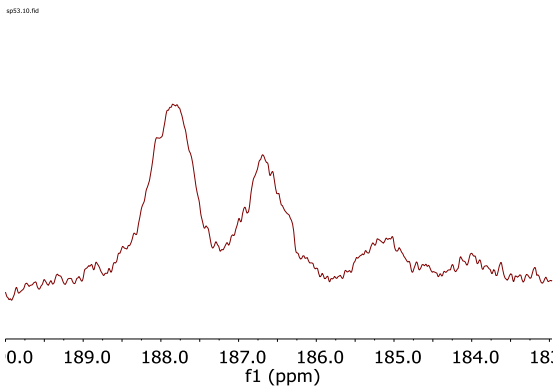
A: MAA
B: PEGMA

Sample	*PEGMA Length*	*Triad*	*Relative Area*
S4	5 EGu (300 g/mol)	AAA	0.3548
		AAE	0.2799
		EAE	0.0823
M	20 EGu (950 g/mol)	AAA	0.4071
		AAE	0.2351
		EAE	0.1161
L	45 EGu (2000 g/mol)	AAA	0.4015
		AAE	0.2244
		EAE	0.1242

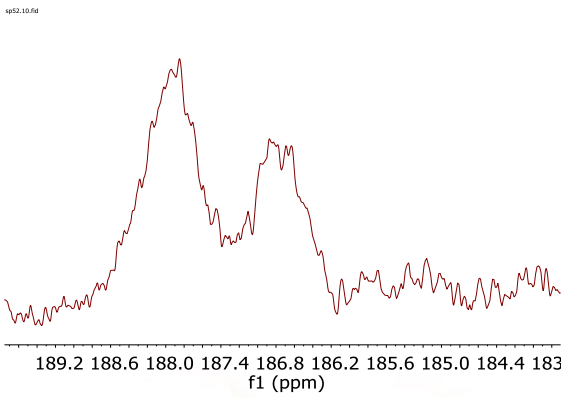
(PEGMA 5)



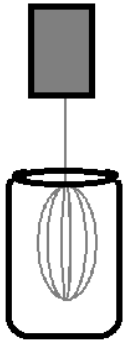
(PEGMA 20)



(PEGMA 45)



PREPARATION OF CEMENT PASTES



- W/C = 0.33
- PCE: 3 mg/ g CEM
- 90 s mix, 60 s rest, 90 s mix (750 rpm)
- CEM I 52.5 R

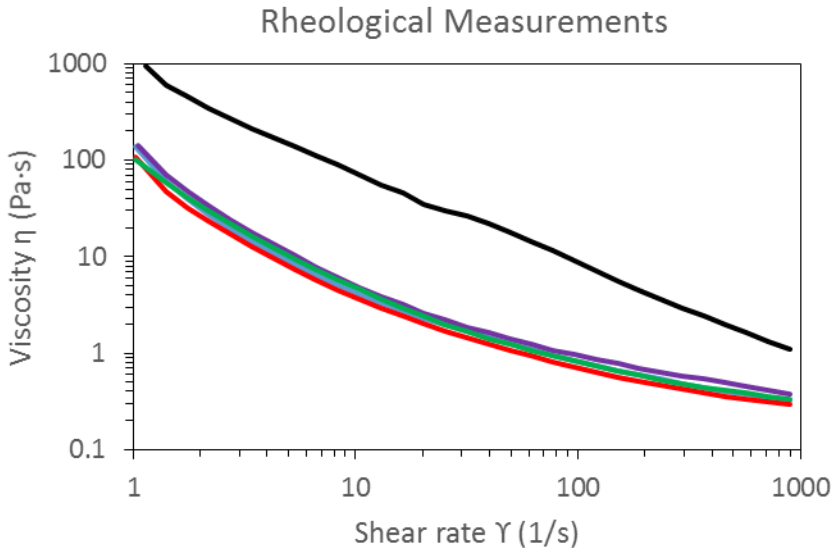
CHARACTERIZATION OF CEMENT PASTES

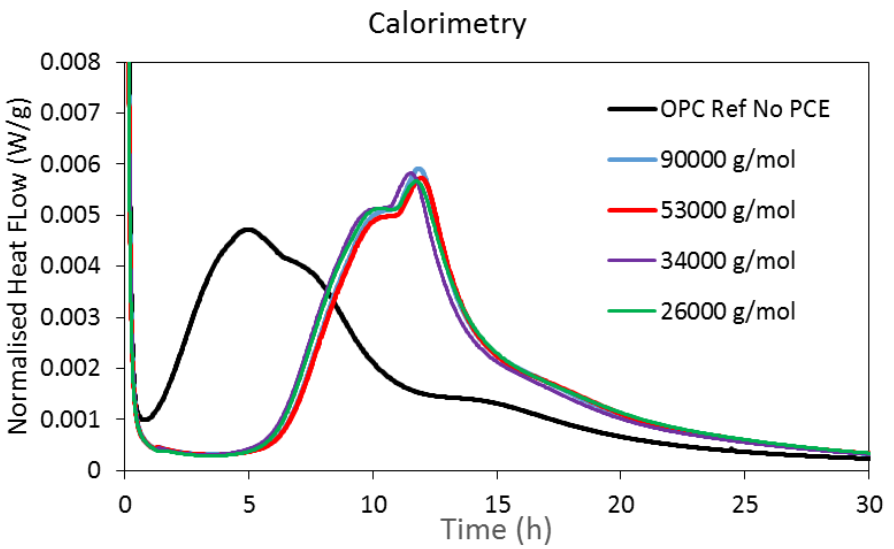
Calorimetry

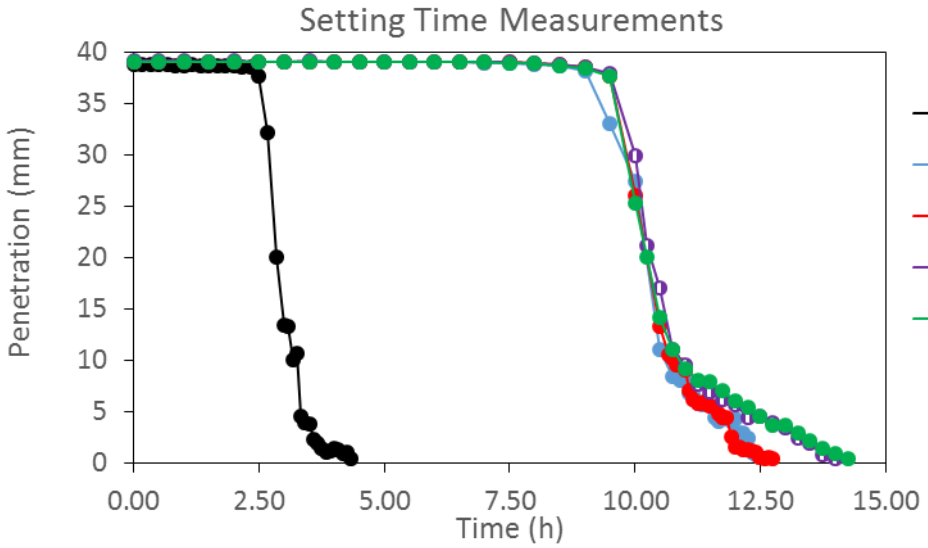
Setting Time

Rheological Measurements

EFFECT OF MOLAR MASS

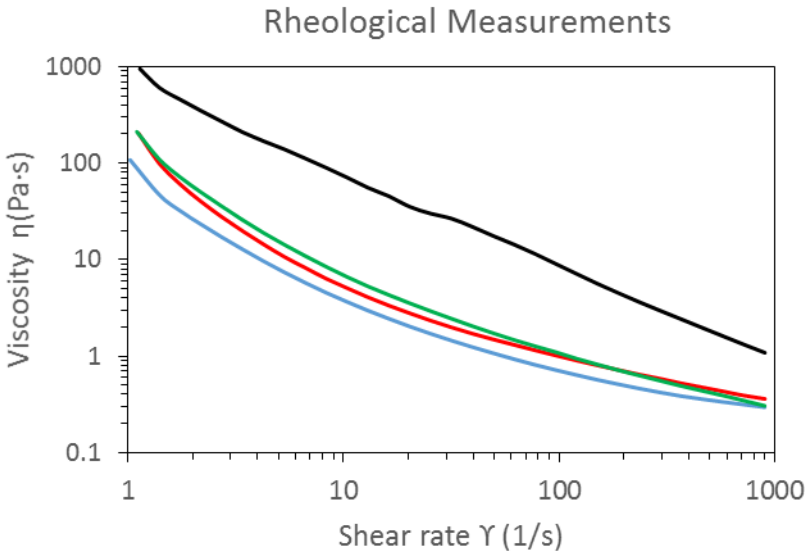


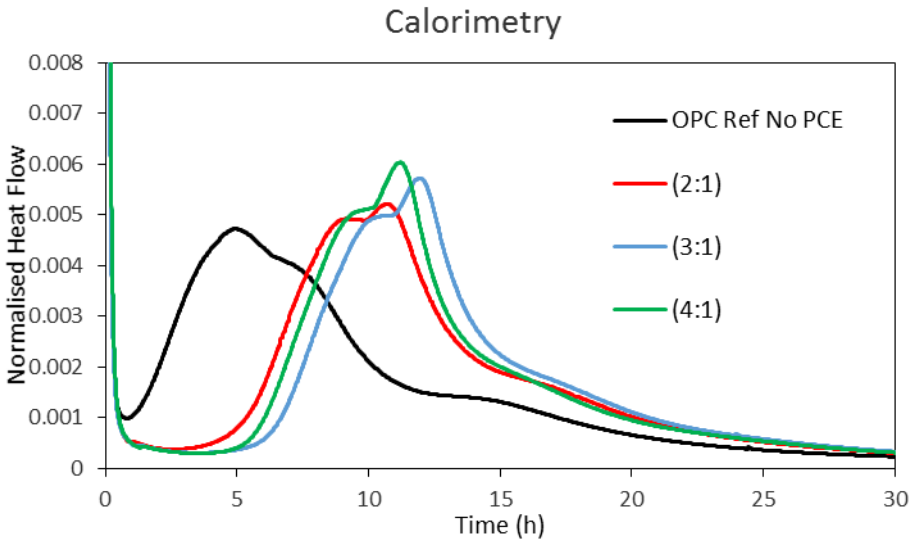


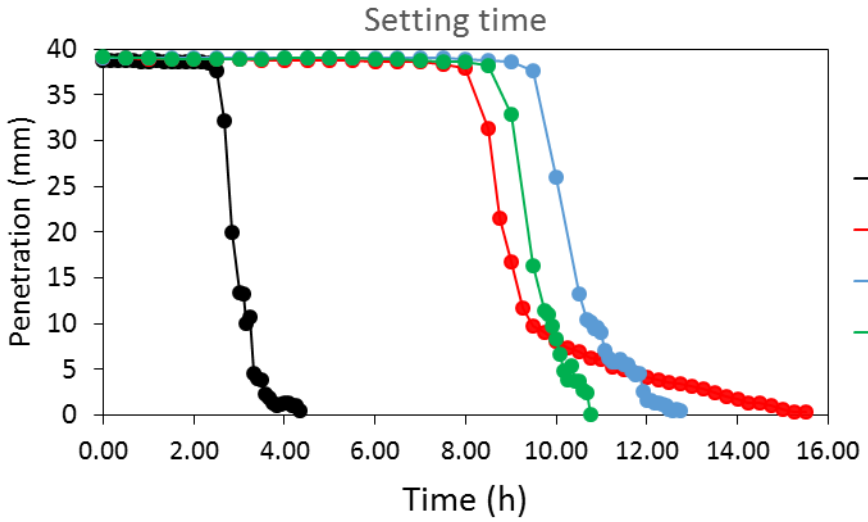


Sample	*Intial Setting (h)*	*Final Setting (h)*
OPC Ref No PCE	2.5	4.33
90000 g/mol	9.5	12.75
56000 g/mol	10.0	12.75
34000 g/mol	10.0	14.00
26000 g/mol	10.0	14.25

EFFECT OF CHARGE DENSITY

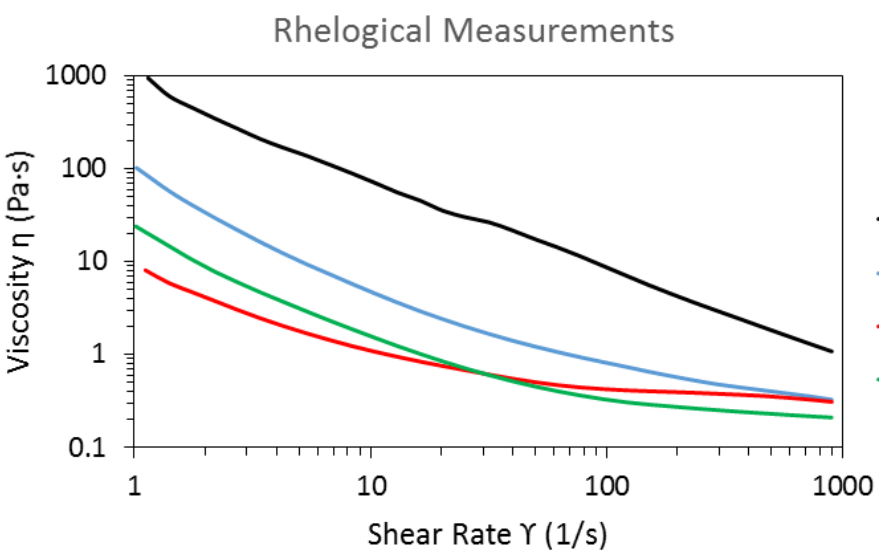


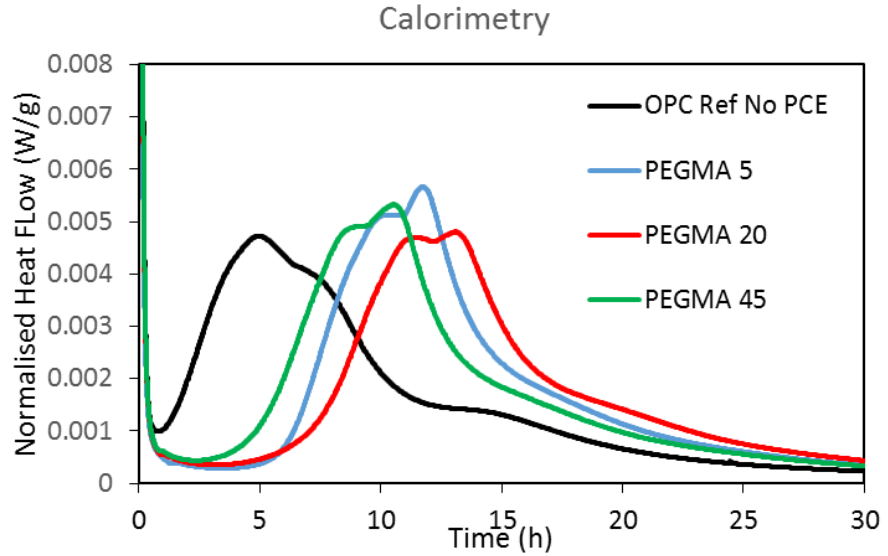


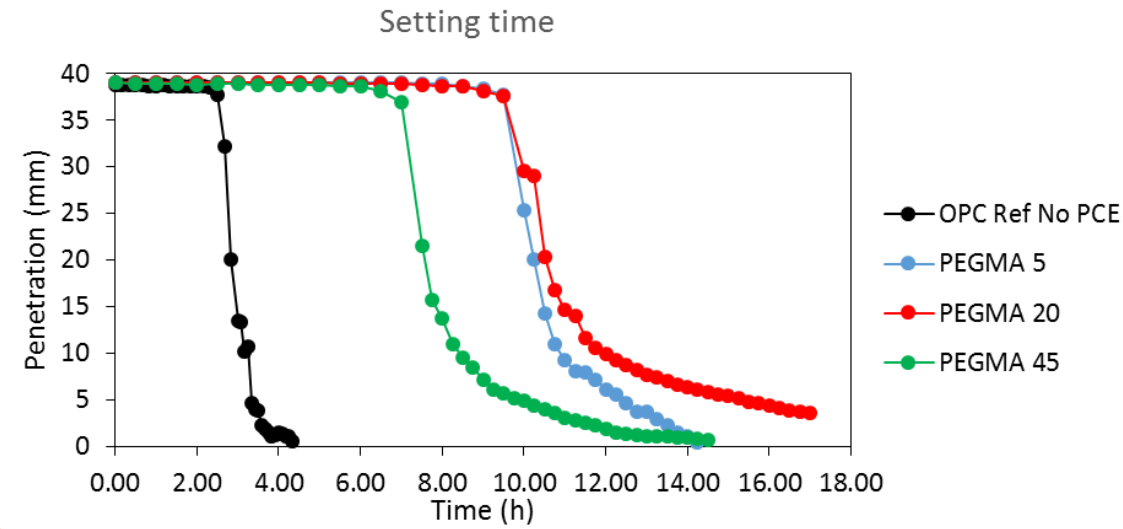


Sample	*Intial Setting (h)*	*Final Setting (h)*
OPC Ref No PCE	2.5	4.33
S5 (2:1)	8.5	15.50
S2 (3:1)	10.0	12.75
S6 (4:1)	9.0	10.75

PEGMA SIDE CHAIN LENGTH







Sample	*Intial Setting (h)*	*Final Setting (h)*
OPC Ref No PCE	2.5	4.33
S4 (PEGMA 5)	10.0	14.25
M (PEGMA 20)	10.0	17.00
L (PEGMA 45)	7.5	14.50

CONCLUSIONS:

1. *Synthesis of homogenous copolymers with variable properties*
   - *Molar mass*
   - *Monomer ratio – Charge density*
   - *Side Chain length*

2. *Molar mass:*
   - *Delayed final setting time with lower molar mass*

3. *Charge Density:*
   - *3:1 monomer ratio the highest viscosity reduction*
   - *Higher charge density bigger effect on aluminate phase*
   - *Higher charge density earlier final setting*

4. *PEGMA side chain length:*
   - *Medium and Long PEGMA higher viscosity reduction*
   - *Long PEGMA short retardation, early initial setting*
   - *Medium PEGMA long retardation, delayed final setting*

- Dr. S. Hamzehlou
- Dr. J.I. Miranda

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Ikerkuntzarako Zerbitzu Orokorrak
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Basque Country Initiative for Cement and Concrete Research

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Thank you for your kind attention

POLYMAT