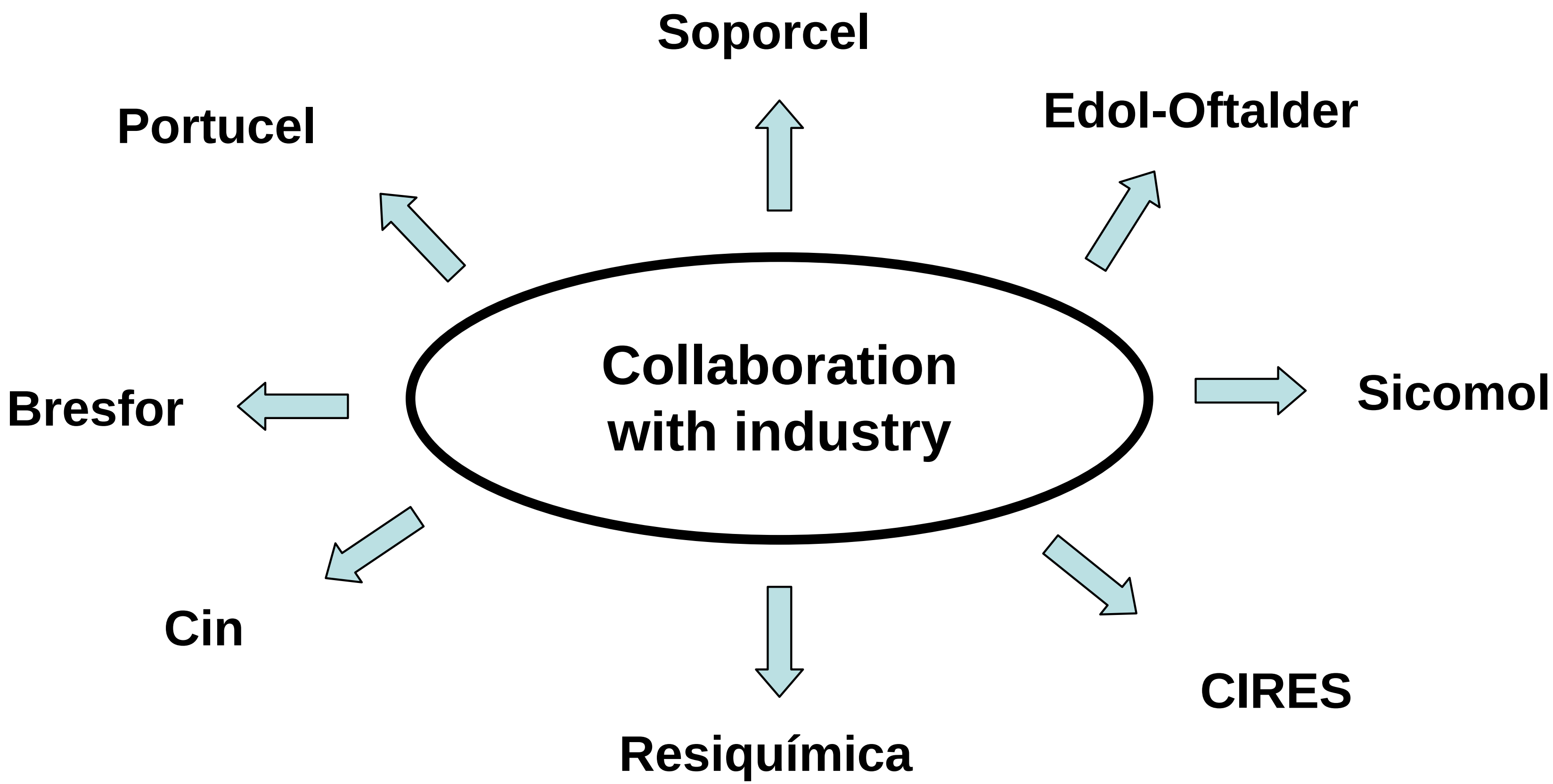
Polymeric Materials Group



Dia Aberto à Inovação e Transferência de Tecnologia

April 4th, 2006 **Case Study: PVC Industry**

CIRES

DEQ FCTUC

Departamento de Engenharia Química Faculdade de Ciências e Tecnologia Universidade de Coimbra

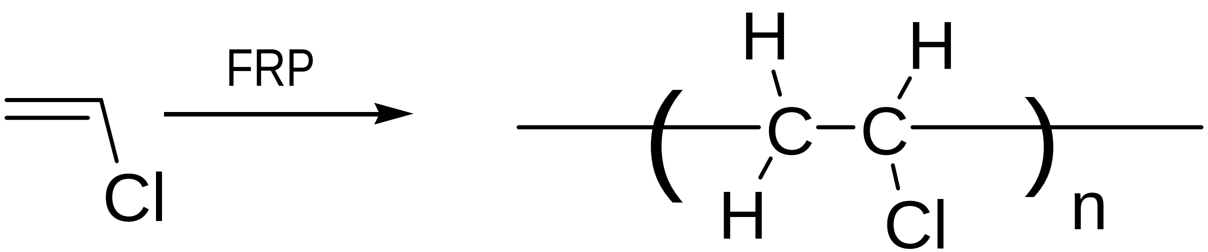
CIRES DEQ FCTUC PRO DEQ

Summary

Introduction

PVC

- Second largest (after polyethylene)
- Globally 25 million tonnes
- Very versatile
- Strength, transparency, low cost
- All from free radical reactions
- Most common is batchwise aqueous suspension process



Advantages

- Polymerization degree can be very high at low temperatures
- Does not require stringent purification of the reagent, except the elimination of the dissolved oxygen.
- Leads to high molar mass polymers under relatively mild conditions.
- Molecular weight increases rapidly
- Used in water system
- Enthalpically favorable

Easy to perform in industrial environment

(same since the beginning)

Free Radical Polymerization

Disadvantages

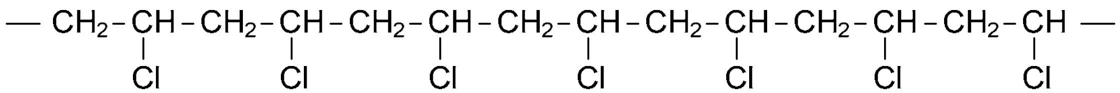
Lack of control over the molar mass / molar mass distribution

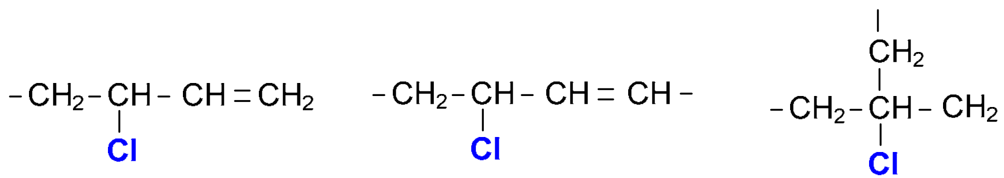
End functionalities. Dead chain. High level of structural defects (PVC). Limited possibilities of copolymerization.

Side Reactions

Chain Transfer Reactions

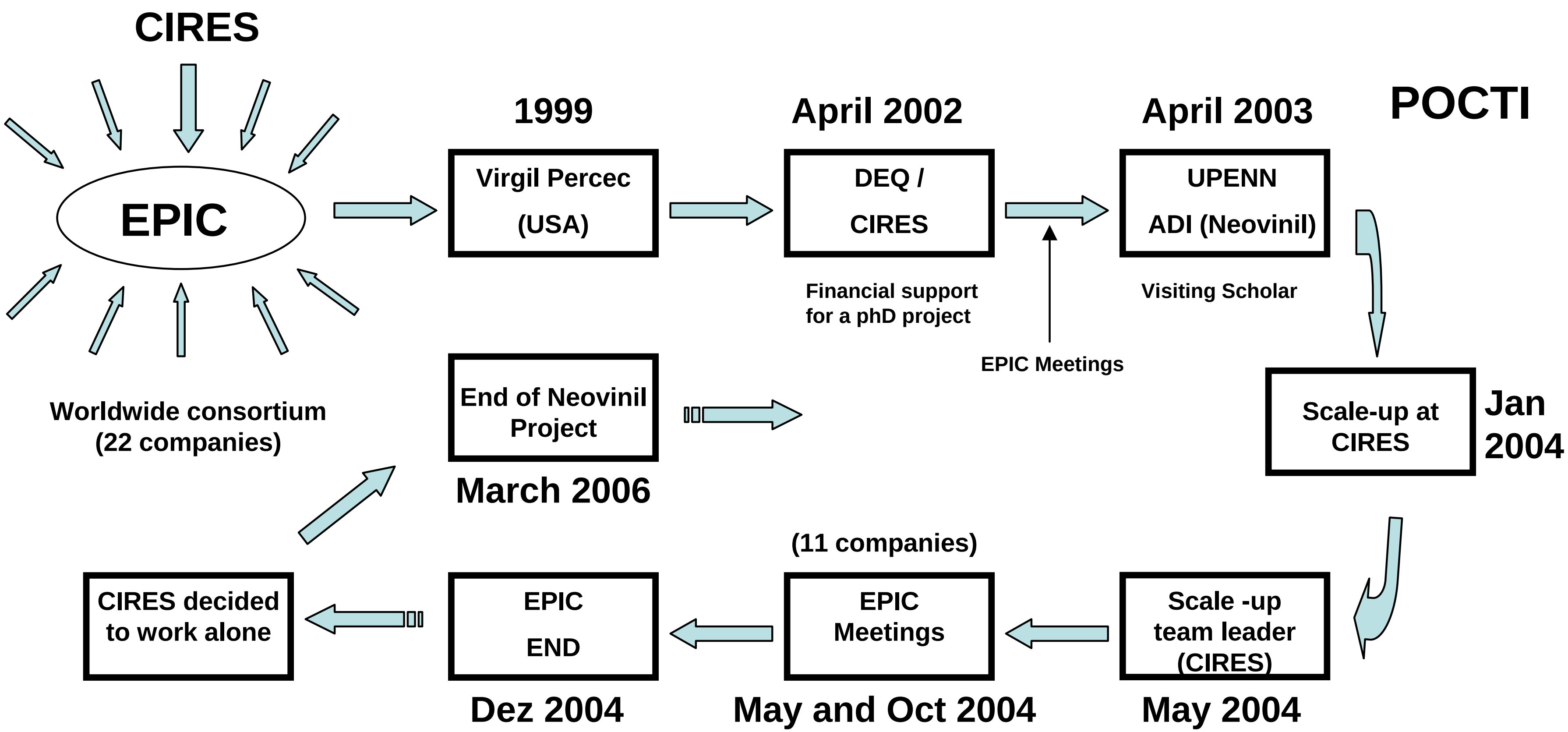
Structural defects





Solution ?

Project History



Main target:

Development of new polymerization mechanism able to polymerize VC in such way that could avoid **side reactions**

- Active chain ends
- No structural defects

1st time that something is done at molecular level

Neovinil

April 2002

UPENN

Scientific knowledge on new polymerization system for VC (1999-2003)

Visiting scholar

phD student

ULeeds

Consulting

January 2005

NEOVINIL

CIRES

Industrial experience

Commercial vision

Development Facilities

Desire for investments

DEQ

Strong Polymer background

Analytical Facilities

RESULTS

Own technology

Scale-up

Solution

Living Polymerization – Definition (1956)

"… Living polymers still able to grow whenever additional monomer is supplied".

And

"Ideally, living polymers propagate while their termination or chain transfer are rigorously prevented."

Living Radical Polymerization (1990s)

(3 main methodologies based on the reduction of active radical species)

Metal Catalyzed LRP

1999

Percec, V. et al J Polym Sci Part A: Polym Chem, 2001, 39, 3392-3418.

April 2002

(DEQ/CIRES)

Single Electron Transfer – Degenerative Chain Transfer

(SET-DTLRP)

2004

Percec, V. et al J Polym Sci Part A: Polym Chem, 2004, 42, 6267-6282.

LRP Features

- *Internal First-Order Kinetics with Respect to Monomer*
- *Linear Growth of Degree of Polymerization*
- *Narrow molar mass distribution*
- *Long-Lived Polmer Chains*
- *Low occurrence of irreversible bimolecular termination*
- *Does not require stringent conditions to be performed*

Controlled molecular weight

Controlled structure

Controlled architecture

Tailor made polymers

Introduction
FRP
Advantages
Disadvantages
Project History
Neovinil
LRP
Features
Industrial Adv
Academic vs Ind
Scale-up
Homopolymer
Low Tg
High Tg
Projects under study
Conclusions

Living Polymerization

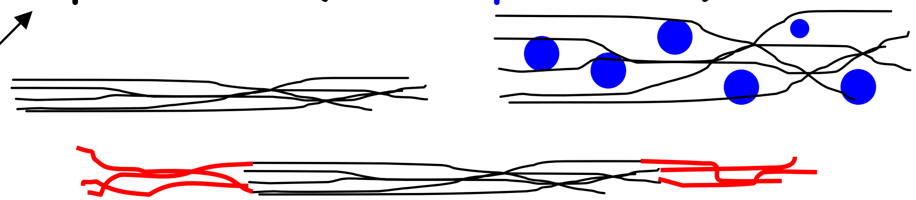
What does it mean from the industrial point of view ?

- PVC free of structural defects => Higher thermal stability

- Prepare PVC in a broad range of Mw with similiar thermal stability

- Possibility to prepare copolymers based on PVC

Low Tg - Flexible materials with internally plasticizers (without phthalates)



High Tg - High Heat Distortion temperature Polymers (new applications)

- Prepare PVC with new architectures

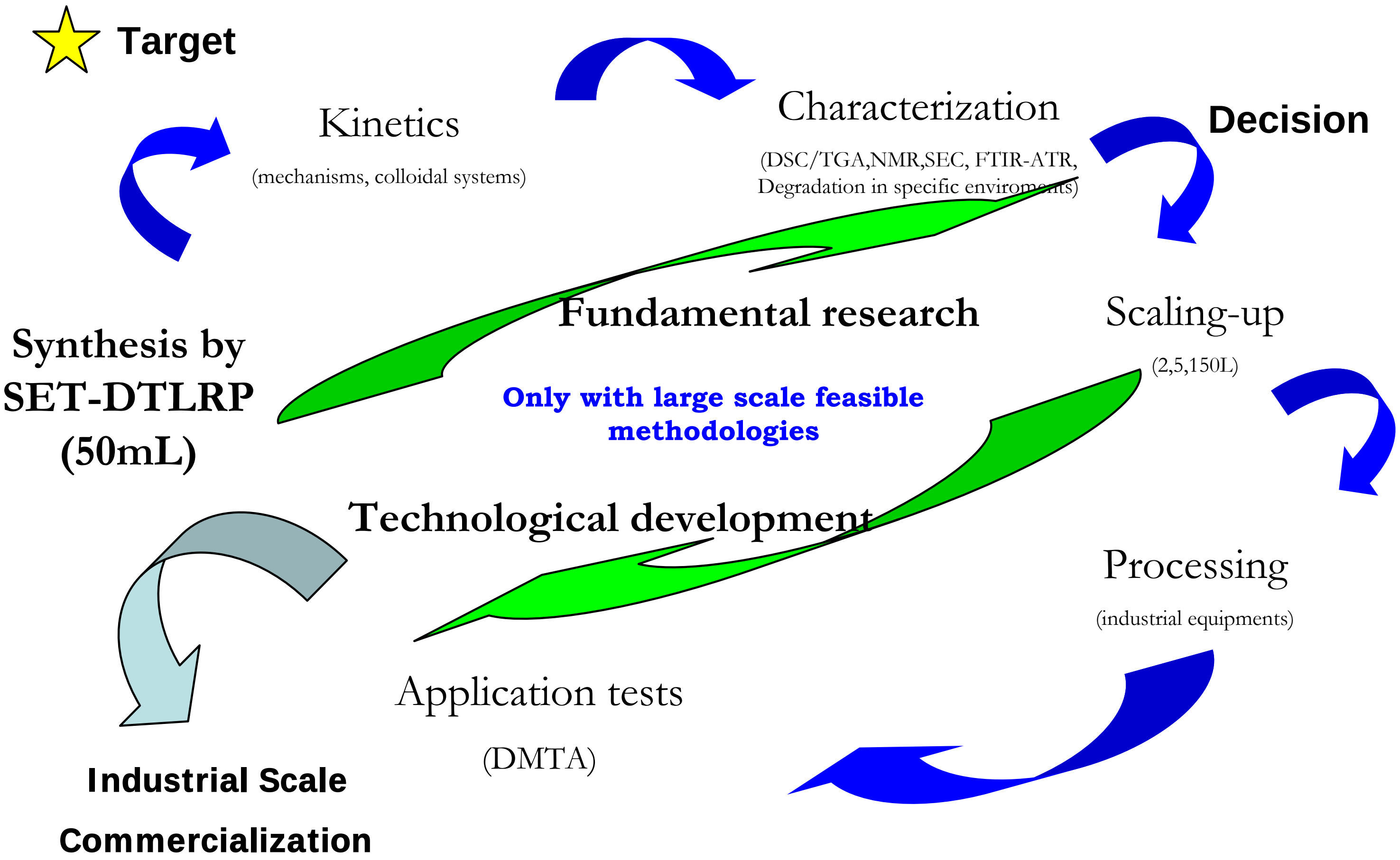
High Value Products

Academic vs Industrial

Academic	Industrial
Low Mw / High Mw	Low Mw / High Mw
Low Tg / High Tg	Low Tg / High Tg
Elastoromeric / HDT	Elastoromeric / HDT
	Similar or better than the commercial product
	Added value to pay the cost difference
	Reaction Time
	Reaction Temperature
	Reaction Medium
	Reaction Coumponds

LRP – Scale up

Steps involved in this project



Scale up – Standard Procedure

Four different scales

50 mL

(Glass reactors)

Mechanistics studies

Reaction kinetics

New ideas

2L and 5L

Processing Tests

150L

Reaction kinetics and Processing

Logistics

Processing

Resembles the industrial scale

??? m^3

Commercialization

Results

Homopolymerization and Copolymerization

PVC without structural defects
- **LMW** (Scale –up)
- **HMW**

New products based on PVC
- **Low Tg** (Research and development)
- **High Tg** (Own Technology and transfer to DEQ)

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Homopolymerization

The results obtained in small scale were sucessfully scaled up in 150L

AMOSTRA	0 min.	55 min.	60 min.	65 min.	70 min.	90 min.	110 min.	130 min.	150 min.	170 min.	190 min.	210 min.	230 min	250 min	270 min	290 min	310 min	RESULTADO
Refª Ca/Zn																		>60 <65
PAL-038 AMOSTRA C pH baixo																		>230 <250
PAL-038 Húmida																		>250 <270
PAL-038 AMOSTRA B																		[illegible]
PAL-038 Sêco a 30ºC																		>250 <270
PAL-038 AMOSTRA A																		>290 <310

[redacted]

Projecto Neovinil

[redacted]

although…

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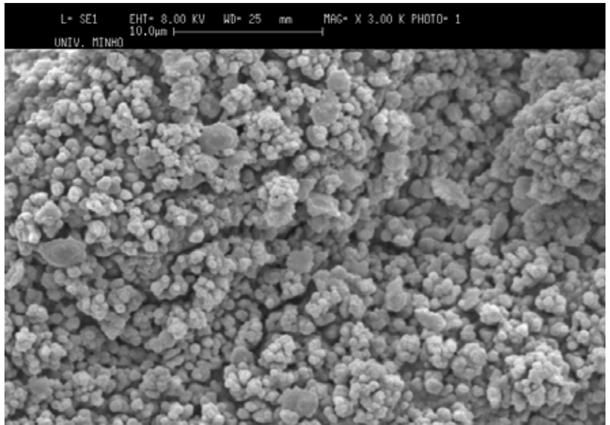
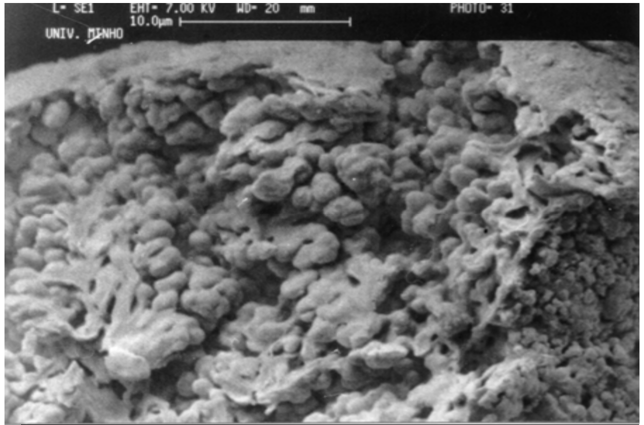
Homopolymerization

Morphology /Particle Size Distribution

LRP | **FRP**

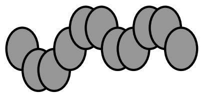


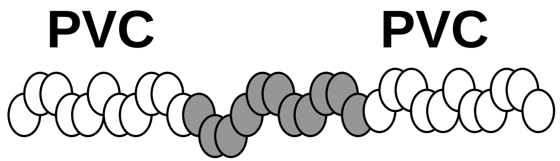


Development Costs

Block Copolymers (Low Tg)

Homopolymerization of the co-monomer

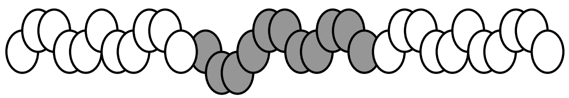




Acrilonitrile
2-Ethyl Hexyl Acrylate
Methyl Acrylate
Ethyl Acrylate
n-Butyl Acrylate
tert-Butyl Acrylate
….

Polymer

Tg
Mechanical Properties
Price
Active Chain Ends
Compatibility with PVC
Range of temperatures



Block Copolymers (Low Tg)

Research Steps

n-butyl acrylate

1 SET-DTLRP

PBA

50 mL

1 Characterization

LRP features

(Active Chain Ends)

2

Synthesis of PVC-b-PBA-b-PVC

50mL

2

Tg

Miscibility

3

Scale-up (2L, 5L)

3

Characterization and Processing

4

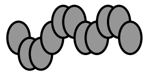
Comparison to commercial product

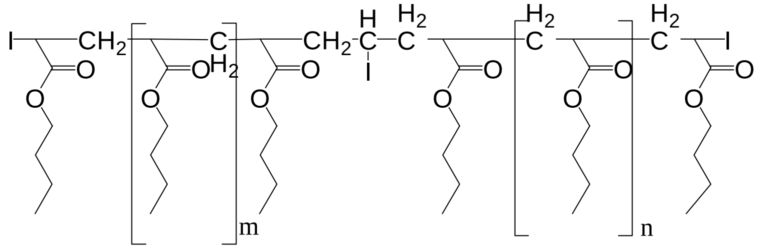
1) Coelho JFJ et al, J Polym Sci Part A: Polym Chem, 2006, 44, 2809-2825.
2) Coelho JFJ et al, J Polym Sci Part A: Polym Chem, 2006, 44, 3001-3008.
3) Coelho JFJ et al, Polymer, 2006, submitted.
4) Coelho JFJ et al, J Vinyl Addit Techn, 2006, submitted.

Block Copolymers (Low Tg)

1st Stage

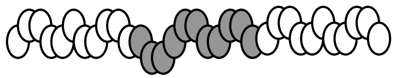
I-PBA-I



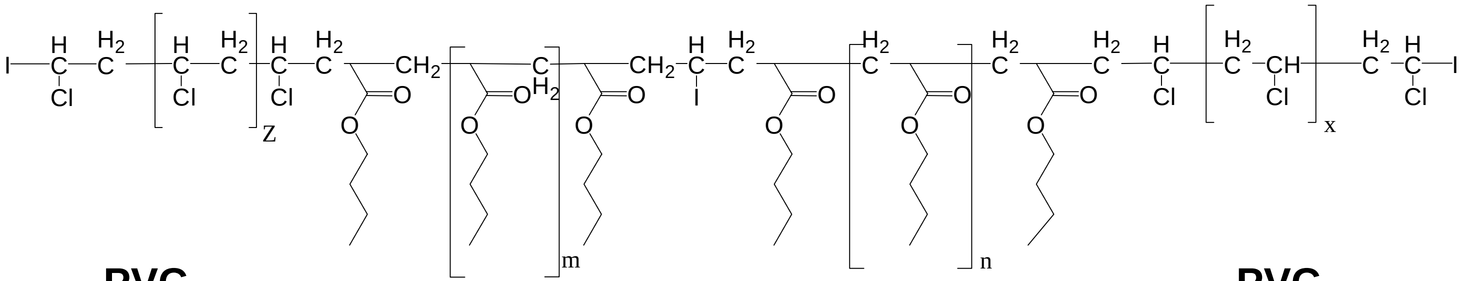


+ VCM

2nd Stage



I-PVC-PBA-PVC-I



PVC

PBA

PVC

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Neovinil

LRP

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Academic vs Ind

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Homopolymer

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High Tg

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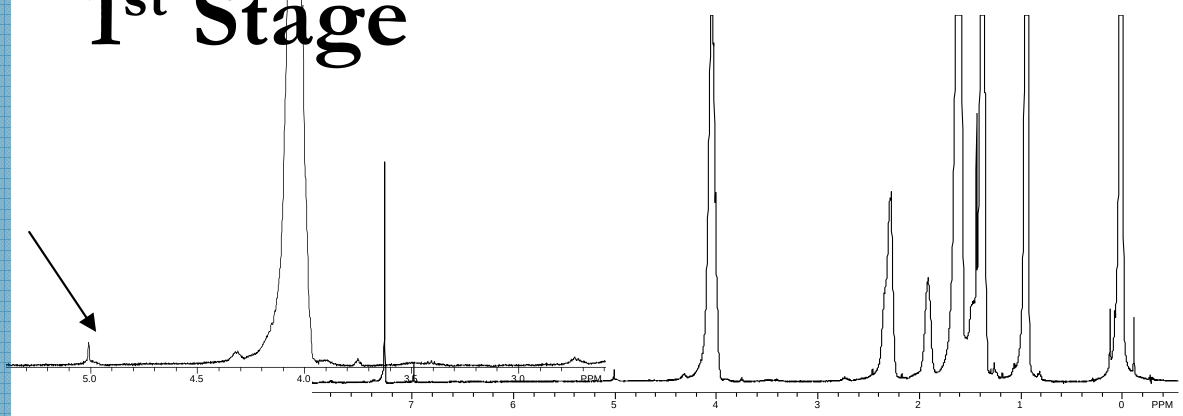
Block Copolymers (Low Tg)

1st Stage

I-PBA-I



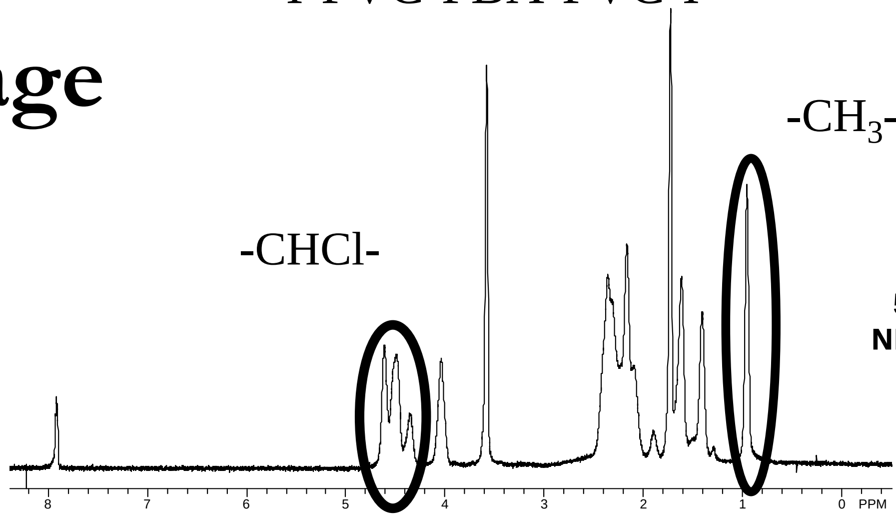
500 MHZ NMR $CDCl_3$

2nd Stage

I-PVC-PBA-PVC-I

-CH_3-

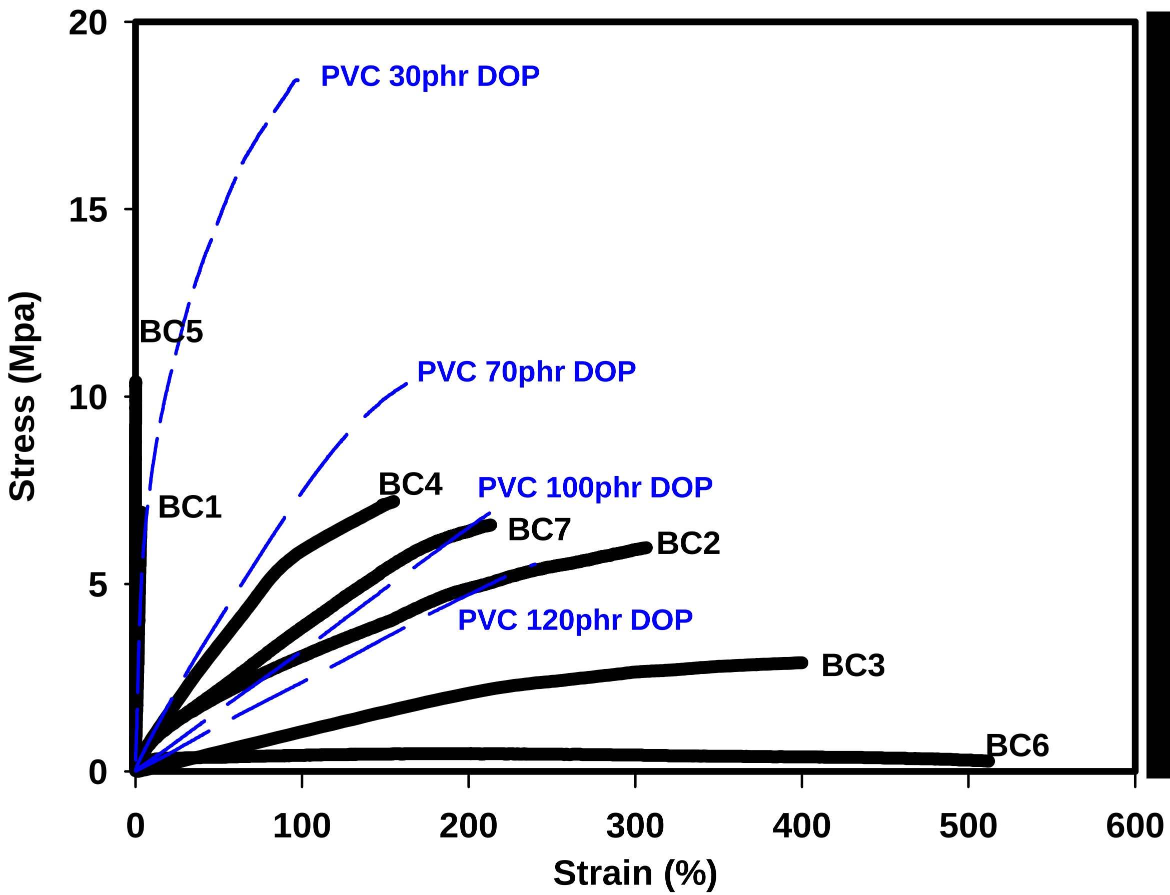
-CHCl-



500 MHZ NMR THF-d_8

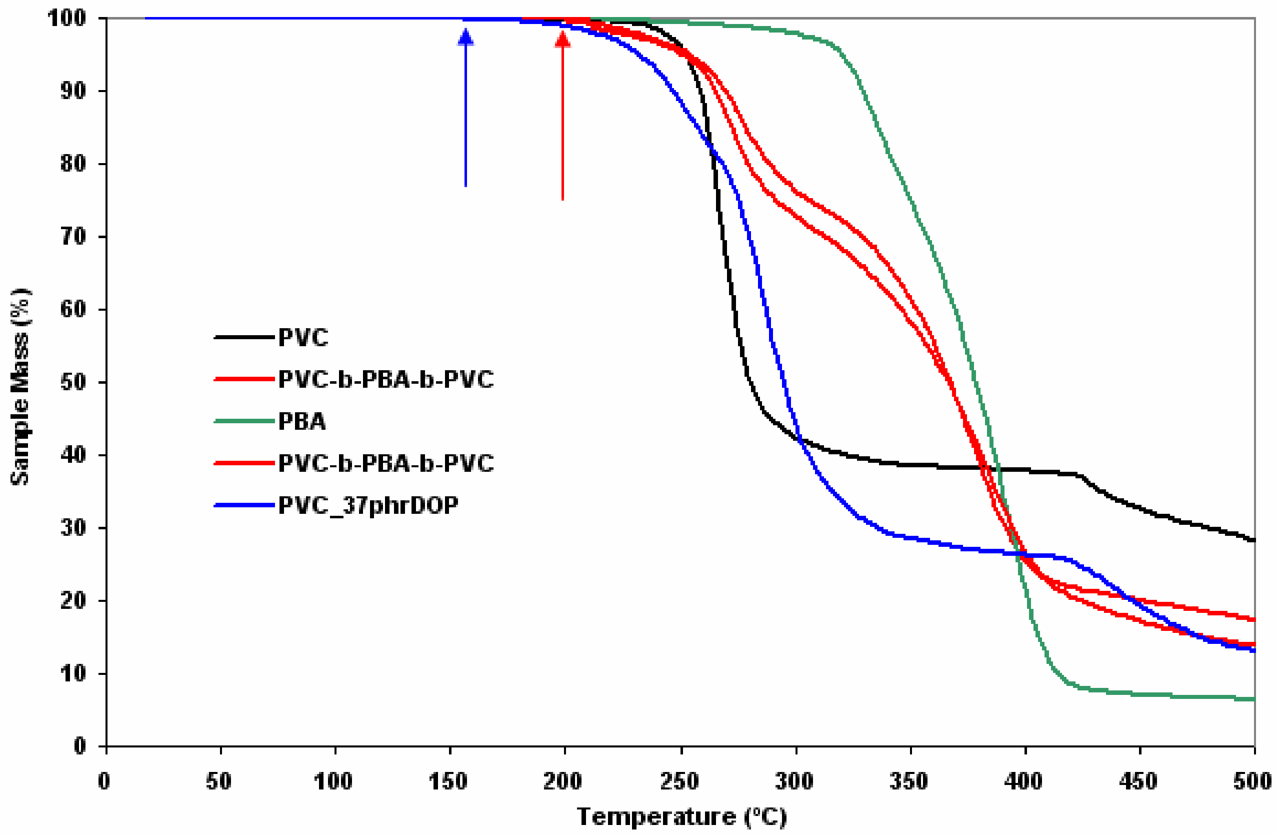
Block Copolymers (Low Tg)

Tensile Tests



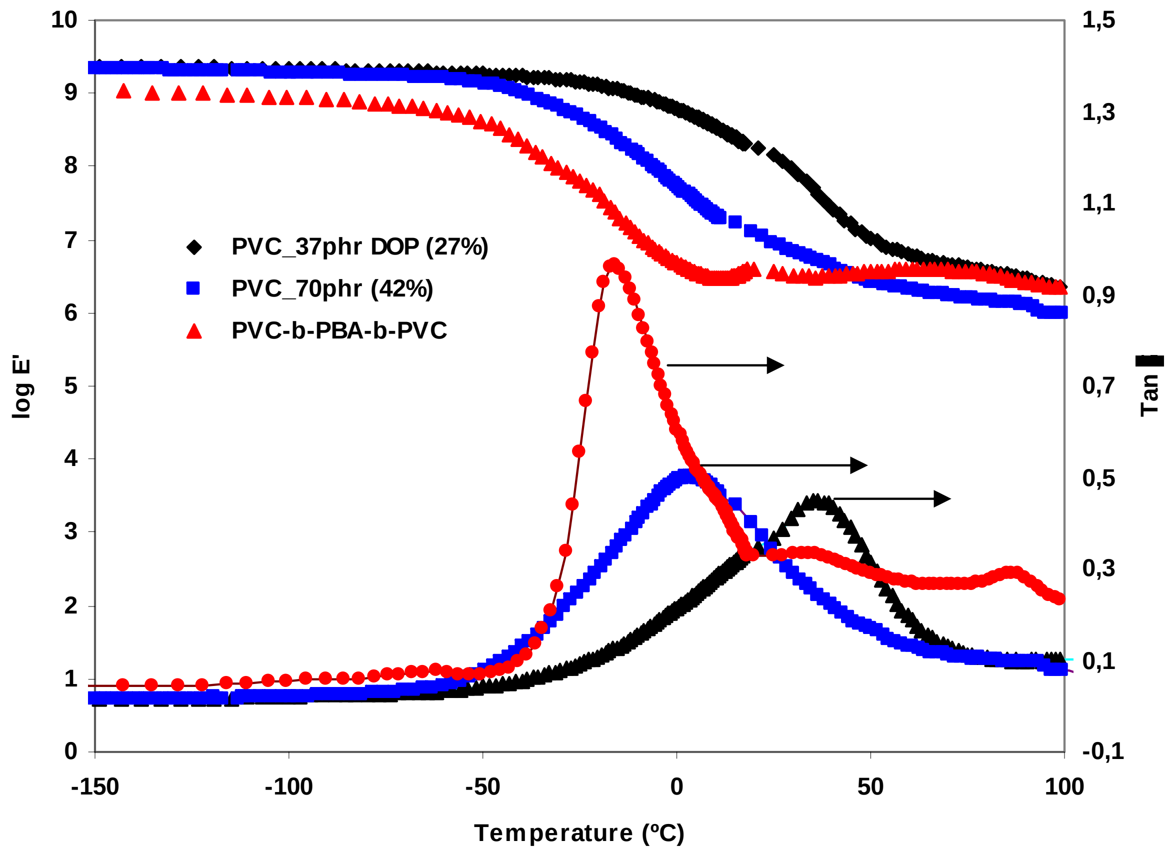
Block Copolymers (Low Tg)

Thermogravimetric Analysis



Block Copolymers (Low Tg)

Dynamic Mechanical Thermal Analysis



Block Copolymers (High Tg)

Tg (PVC) ≈ 80ºC → Tg (…) ≈ 105ºC (for hot water pipes)

Percec

2004

$$I - PVC - I + MMA \xrightarrow{\quad} \text{PMMA-b-PVC-b-PMMA}$$

→ DMSO

→ 90ºC

→ CuCl

PMMA-b-PVC-b-PMMA

(105ºC < Tg < 110ºC)

Percec, V. et al J Polym Sci Part A: Polym Chem, 2004, 43, 1478-1486.

Limited / Impossible to implement this technology in large scale production tipically used for PVC

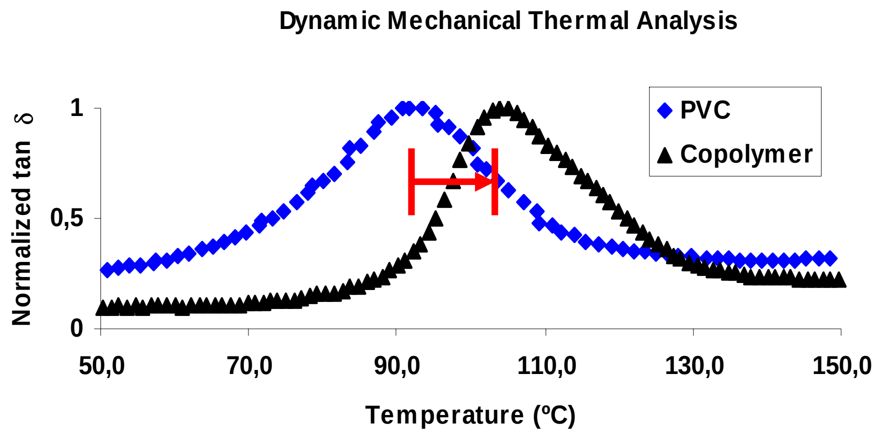
Block Copolymers (High Tg)

- I – PVC – I $\xrightarrow{UV}$ PMMA-b-PVC-b-PMMA (Tg ≈ 105ºC)

Alves, P. Seminário 2005

- PVC – Polymer (?) – PVC (Tg ≈ 108ºC)

(Based on the same technology used for low Tg)



- New strategy (it will allow to increase the Tg until 140ºC)

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Projects under study

Kinetic determinations (structure of monomer vs rate of polymerization) => DEQ (Carvalho, E. Seminário 2006)

Different initiator systems (structure of initiatior vs rate of polymerization)

New polymeric architectures => DEQ (Marques, D. Seminário 2006)

New products made of PVC with different properties (hydrophilicity)

Increase the mechanical resistance of the PBA

Scale-up of copolymers to the 150L (know how developed for the homopolymerization)

New materials based on multiblocks (ABCBA) kinetic and compatibility advantages)

Economical evaluation of our products

Conclusions

- The SET-DTLRP allows the synthesis of well controlled structures
- Works with industrial available compounds
- Possible to perform in large scale reactors
- Low cost when compared with other LRP systems
- Open the possibilty of using PVC in macromolecular engineering

.... only LRP method for VCM polymerization so far

Conclusions

A cooperação universidade/indústria é possível, desejável, todos os participantes são essenciais dado que possuem valências totalmente distintas e acabam sempre por beneficiar de alguma forma

Conclusions

3 alunos de pós-doc

12 publicações em revistas

3 patentes

Invenção do SET-DTLRP

NEOVINIL

Lidera um projecto inovador na sua área de negócio (autonomia)

Progressão exterior

Possibilidade de estabelecer parcerias estratégicas

Competências na área de investigação fundamental

2 Patentes em perspectiva

Adquiriu competências na área onde mais se investiga (LRP)

Dow, Ciba, IBM, Dupont, PPG, Arkema, Polymer Laboratories……

Aluno de doutoramento

Equipamento / Optimização

Inúmeras publicações

Pólo de investigação em SET-DTLRP

Acknowledgements : Cires for supporting my phD scholarship

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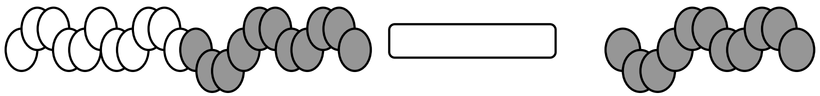
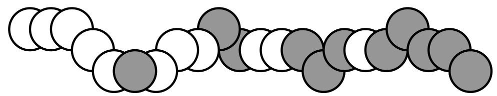
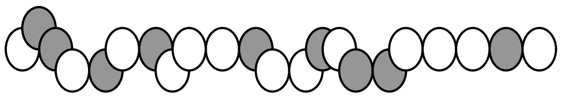
Living Radical Polymerization



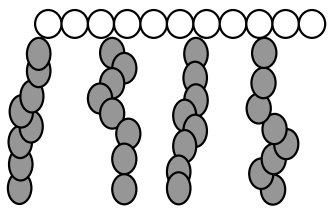
Block Copolymer



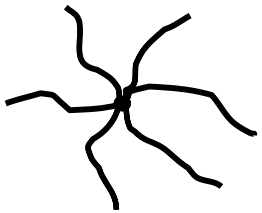
Gradient Copolymer



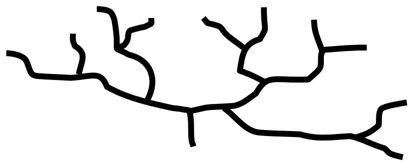
Random Copolymer



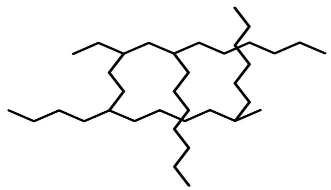
Graft Copolymer



Star (Co)polymer



Hyperbranched (Co)polymer



Network