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Novel trialkylsilyl methacrylate block copolymers as self-polishing binders for chemically active antifouling paints

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Outline

I- Aim of the study

II- Synthesis of silylated-based diblock copolymers

III- Polishing properties in sea water

IV- Conclusions

I - Aim of the study

Synthesis of poly(meth)acrylic copolymers bearing sea water hydrolyzable side groups

Hydrophobic/hydrolyzable copolymer

(insoluble in water)

Hydrolysis/Saponification reaction

Sea water
(pH=8.2 – 8.3)

Hydrophobic/hydrophilic copolymer which could become soluble in sea water

Requirements for self-polishing binders

- Tin-free systems
- Control of the polishing rate

I - Aim of the study

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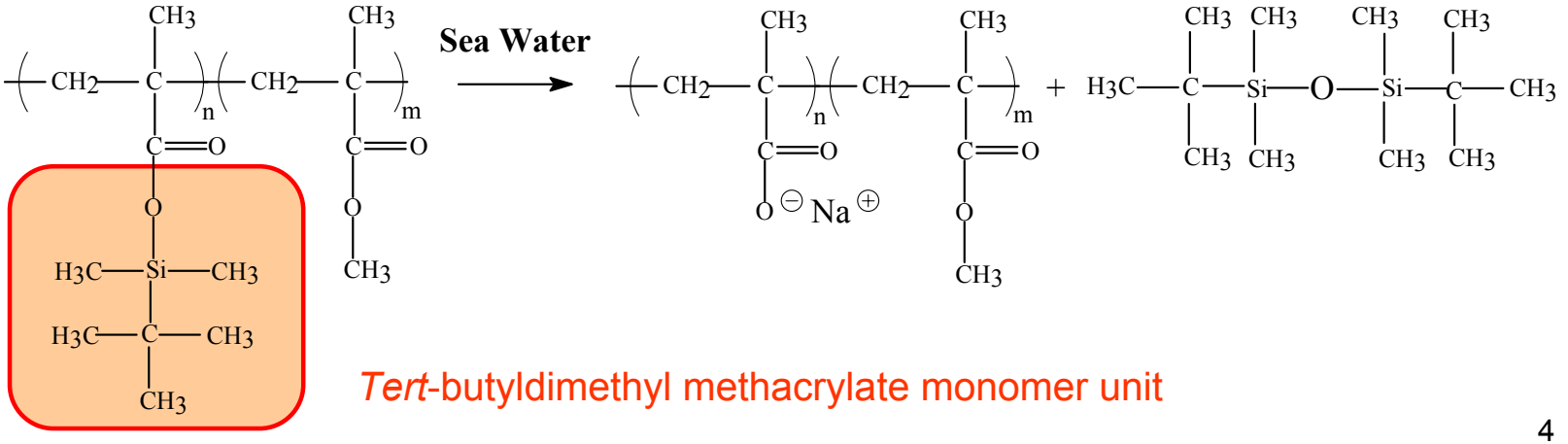
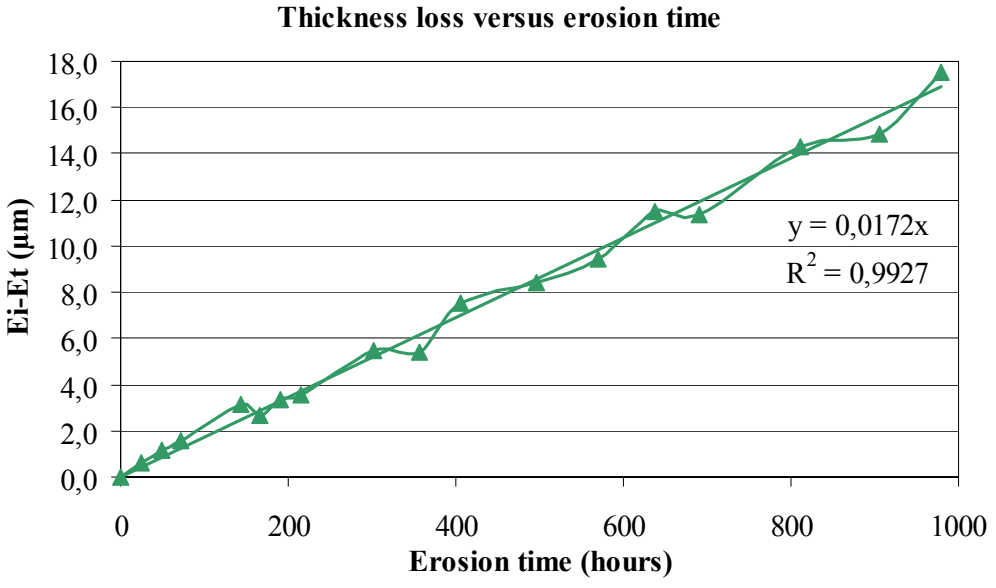


Tert-butyldimethyl methacrylate monomer unit

I - Aim of the study



Constant polishing rate (µm/d)

Zero order release rate of biocides

Polishing rate (µm/d) of trialkylsilyl ester-based polymers depends on[1,2]:

- Molar proportions of hydrolyzable side groups
- Molecular weights (Mw range = 25,000 to 130,000 g.mol^{-1})
- Type of alkyl groups linked to the silicon atom

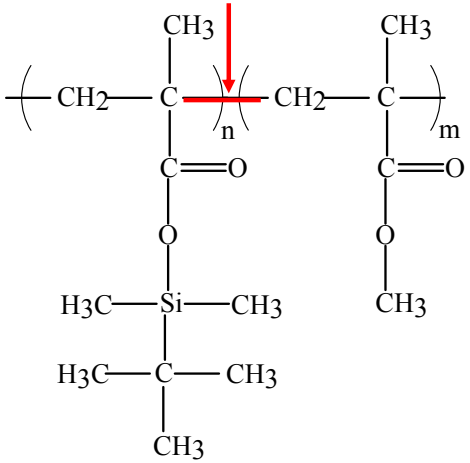
[1] Durand P., Cambon C., Yvelin F., Camail M., Margaillan A., Loiseau B., 8th ICMCF, Tarento, Italy (**1992**).
[2] Durand P., Margaillan A., Camail M., Vernet J.L., *Polymer* **1994**,35(20), 4392-4396.

I - Aim of the study

Effect of the architecture of macromolecules on polishing

Synthesis of well-defined random and diblock copolymers using the Reversible Addition-Fragmentation chain Transfer process (RAFT)

Covalent C-C bond



Poly(MASi-co-MMA)

1- Diblock copolymers

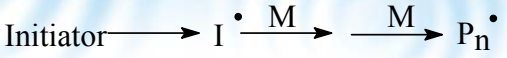
10,000 g.mol^{-1} < Mw < 30,000 g.mol^{-1}

PDI close to 1.0

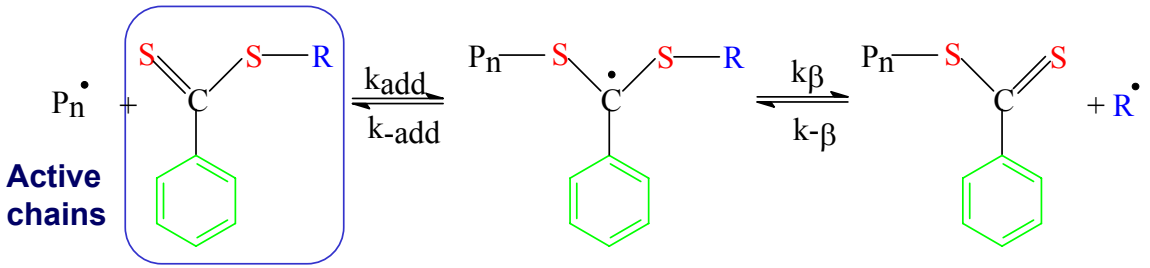
2- Random copolymers

II - Synthesis of copolymers

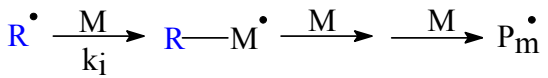
Initiation



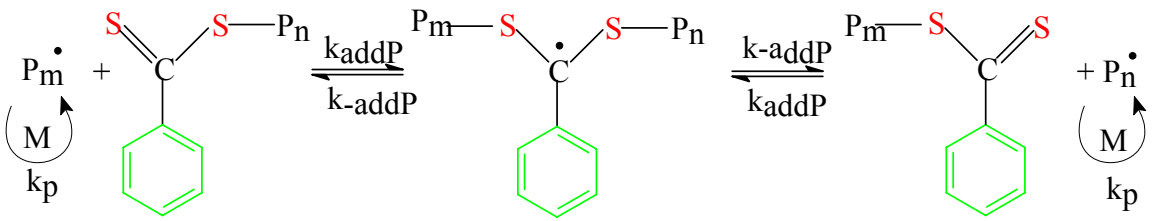
Reversible chain transfer



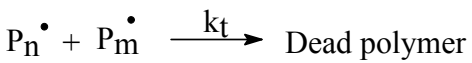
Re-initiation



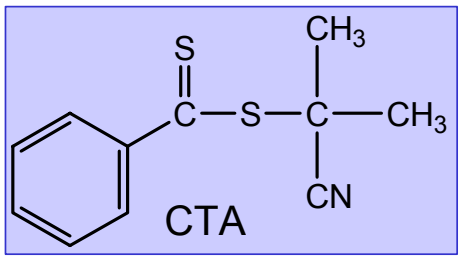
Chain equilibration



Termination



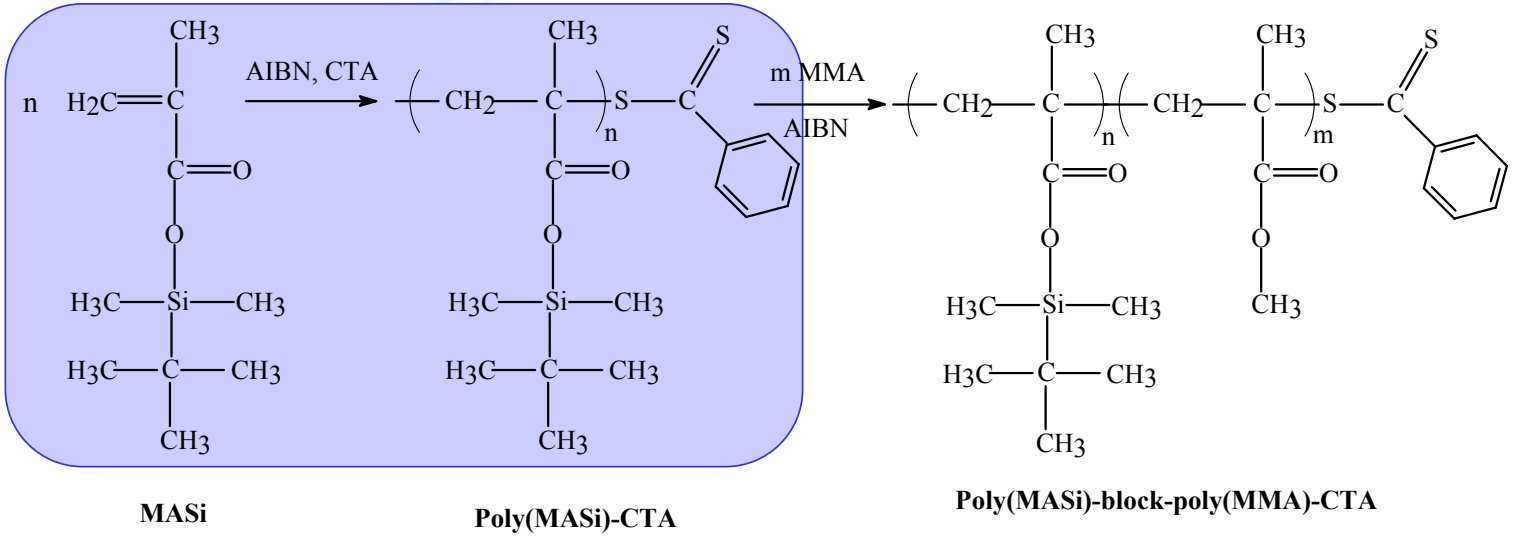
RAFT process
Controlled Radical Polymerization



2-cyanoprop-2-yl dithiobenzoate (CPDB)

II - Synthesis of copolymers

➢ Diblock copolymers synthesis by one-pot method



MASi | **Poly(MASi)-CTA** | **Poly(MASi)-block-poly(MMA)-CTA**

1st step: synthesis of the first block

Toluene solution at 70°C
Monomer concentration = 1.5M
[CTA]/[AIBN] = 5/1

Nguyen, M. N.; Bressy, C.; Margaillan, A. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5680-5689.

II - Synthesis of copolymers

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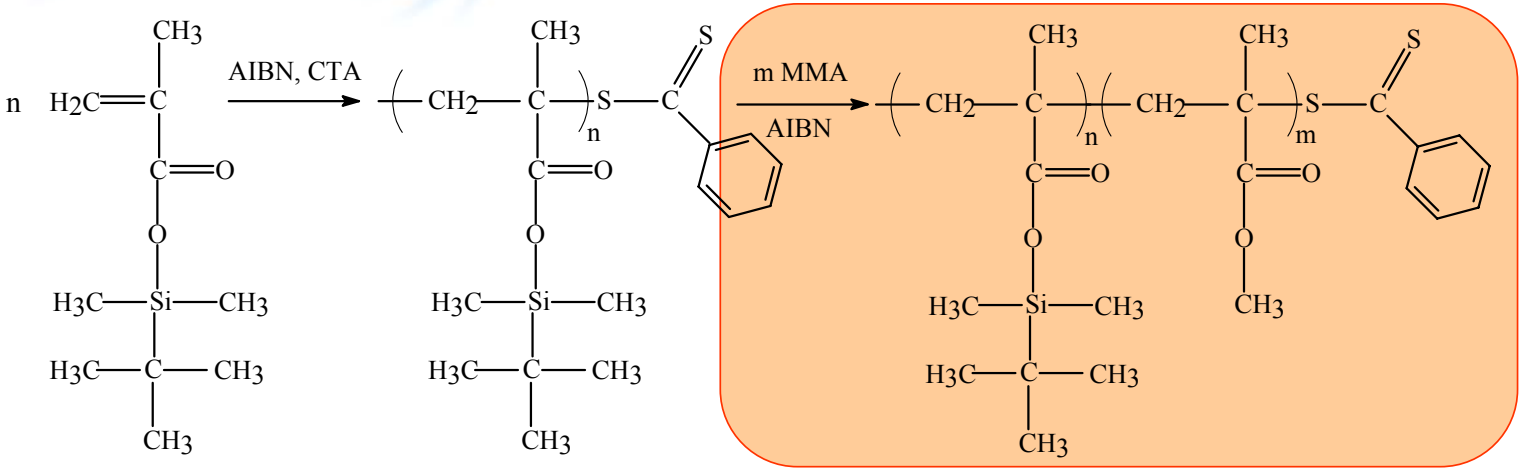

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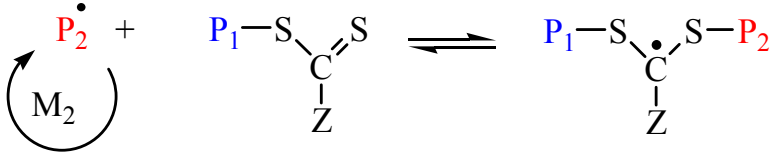
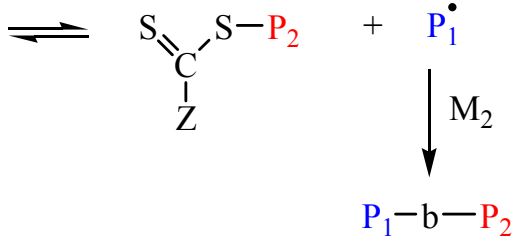
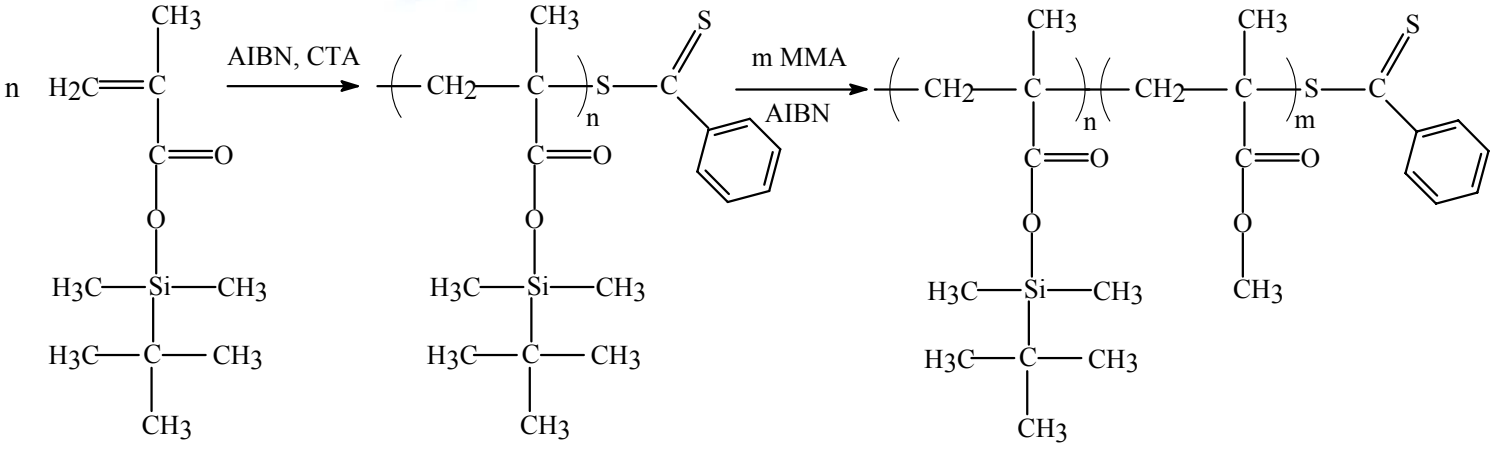


2nd step: chain extension



II - Synthesis of copolymers

➢ Diblock copolymers synthesis by one-pot method



➢ Random copolymers synthesis by one-pot method

Polymerization of the two monomers in a one-step reaction

1- Diblock copolymers

	First block Poly(MASi)-CTA				Diblock copolymers Poly(MASi)-block-Poly(MMA)					
Entry	M_n^{th}	M_n^{exp}	PDI	MASi Conv. (%)	$M_{n,Copo}^{th}$	$M_{n,Copo}^{exp}$	PDI	MMA Conv. (%)	[MASi] / [MMA] molar ratio initial	[MASi] / [MMA] molar ratio exp.
1	3,580	6,300	1.13	>99	18,500	14,000	1.07	98	20 / 80	21 / 79
2	6,670	9,200	1.14	97	21,480	18,500	1.10	89	25 / 75	27 / 73
3	6,040	8,800	1.14	98	14,770	14,900	1.07	92	40 / 60	42 / 58
4	7,640	9,950	1.15	98	12,870	15,800	1.08	88	60 / 40	63 / 37
5	8,430	11,000	1.16	>99	13,030	15,200	1.10	87	70 / 30	73 / 27

M_n^{exp} measured by SEC (universal calibration) $M_{n,copo}^{exp}$ SEC (LS)

High monomer conversion values

1- Diblock copolymers

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M_n^{exp} measured by SEC (universal calibration) $M_{n,copo}^{exp}$ SEC (LS)

Good control of the CTA-mediated polymerization
Narrow molecular weight distribution (PDI< 1.2)

1- Diblock copolymers

Entry	First block Poly(MASi)-CTA				Diblock copolymers Poly(MASi)-block-Poly(MMA)					
	M_n^{th} g.mol^{-1}	M_n^{exp} g.mol^{-1}	PDI	MASi Conv. (%)	$M_{n,Copo}^{th}$ g.mol^{-1}	$M_{n,Copo}^{exp}$ g.mol^{-1}	PDI	MMA Conv. (%)	[MASi] / [MMA] molar ratio	
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M_n^{exp} measured by SEC (universal calibration) $M_{n,copo}^{exp}$ SEC (LS)

Expected molar composition of diblock copolymers

2- Random copolymers

[MMA]/[MASi] = 75/25 $M_{n,Copo}^{th}$ = 10,000 g.mol^{-1}

CTA	MMA conv. (%)	MASi conv. (%)	M_n^* (g.mol^{-1})	PDI	[MMA]/[MASi] molar ratio
CPDB	88.6	92.6	11,000	1.16	73 / 27

* measured by SEC (LS)

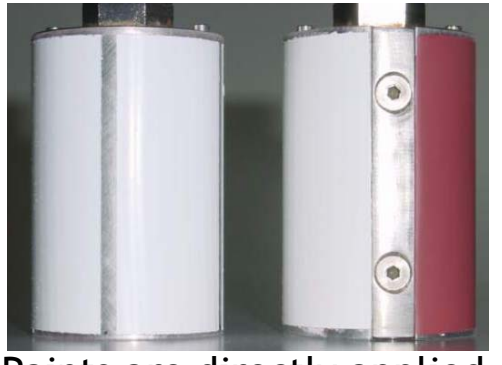
Good control of molecular weights and low PDI values (<1.2) for random copolymers

III - Polishing properties

Dynamic test on rotor Turbo- Eroder (FR 2 716 971, French Navy,1994)

Turbine

Rotor sand-blasted + application of an anticorrosive coating



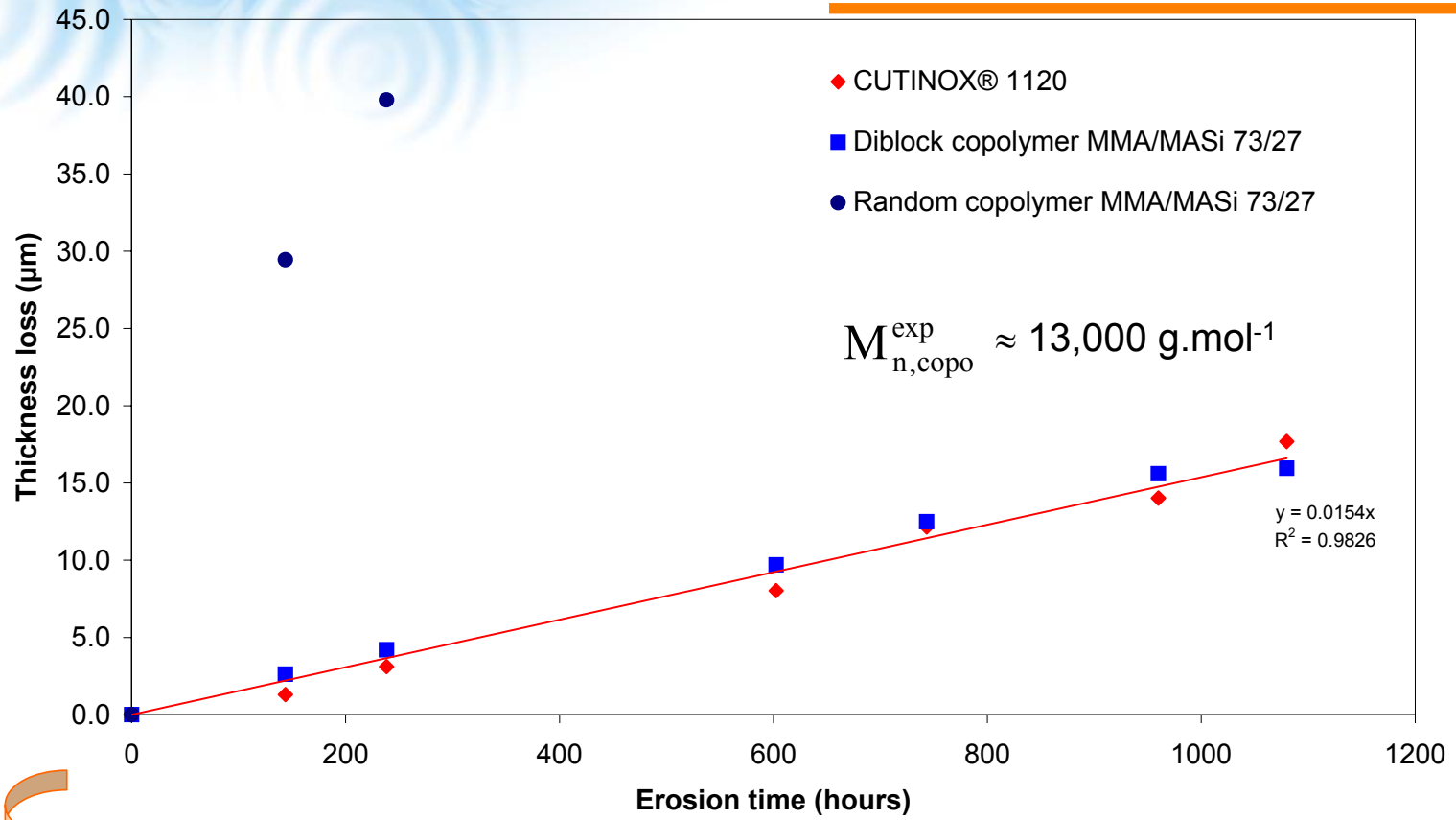
Paints are directly applied on a folio

Dimensions: Diameter : 45mm, Height : 70mm
Antifouling coatings: 2 or 3 by rotor
Rotation: 650 rpm (Turbine with 8 blades)
ASTM 1141.90 artificial sea water at 40° C
Reference system: TBT-based binder

150µm-thickness coatings

Control of the thickness decrease of the coating versus time of erosion

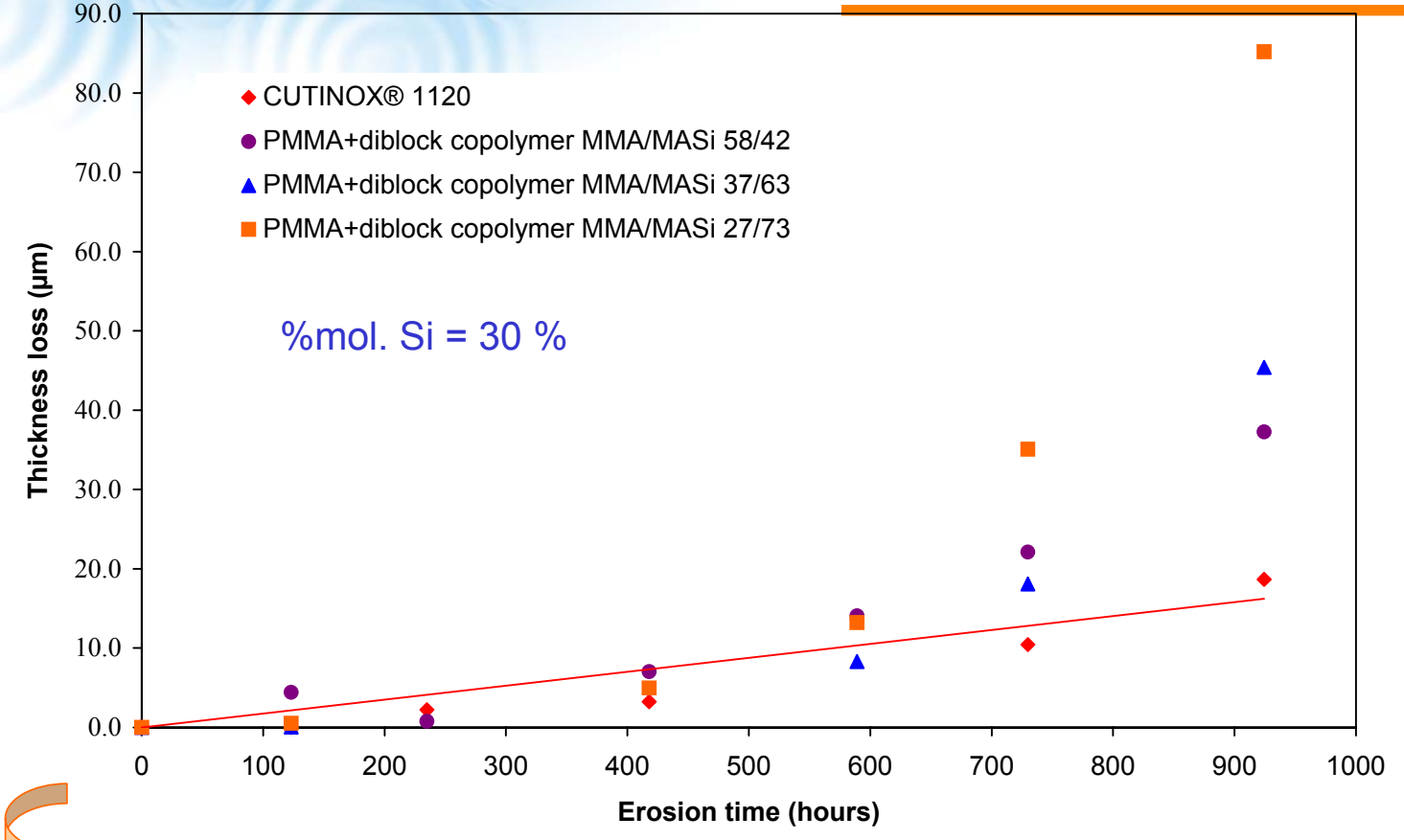
III - Polishing properties



Higher polishing rate for random copolymers with a complete dissolution after 250 h

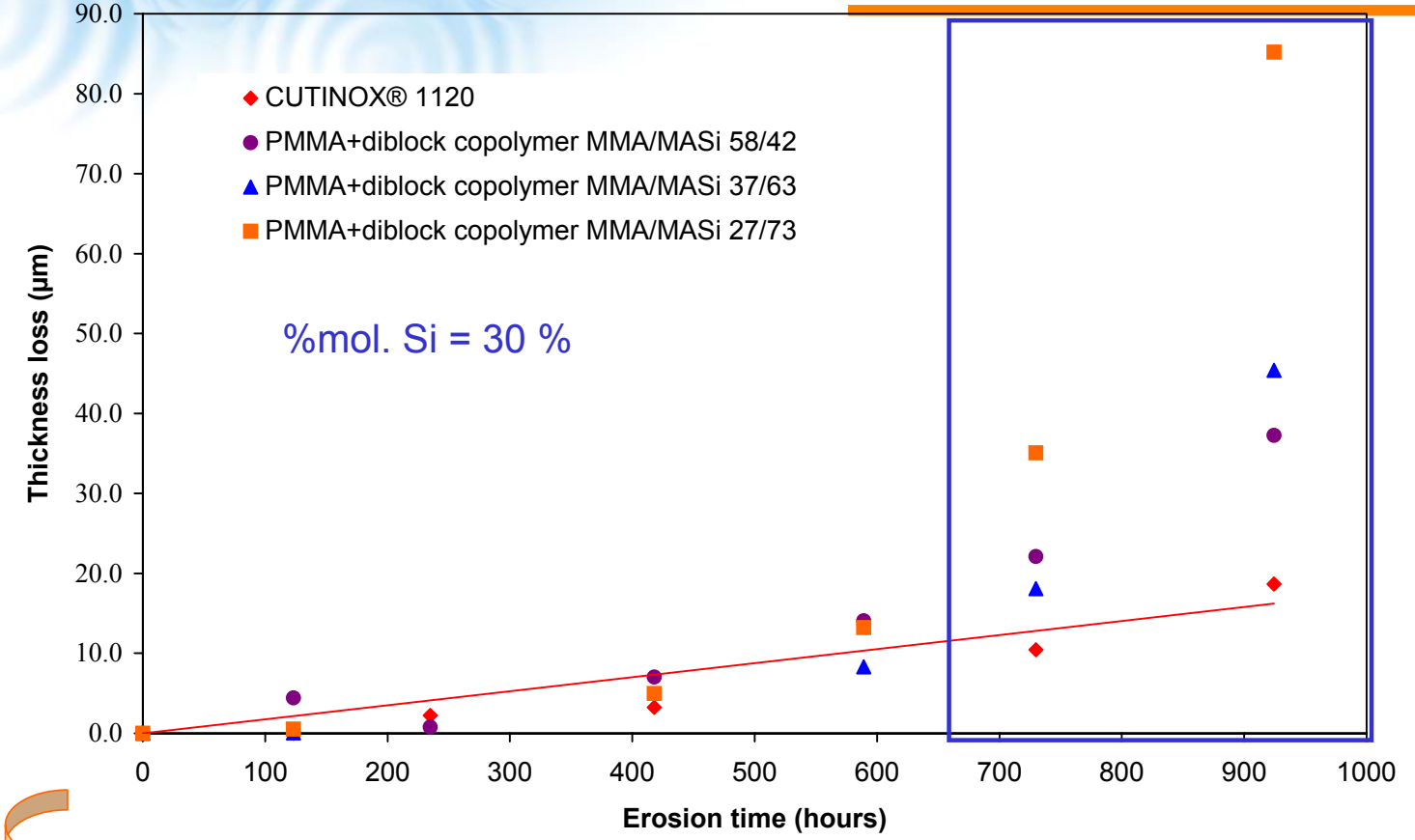
Linear polishing vs time for diblock copolymer - Effect of the microstructure

III - Polishing properties



Blends with PMMA (Mn = 6,300 g.mol^{-1}, PDI = 1.14) 30 % mol. Si enhance the film formation of coatings and adjust the hydrophobic/hydrophilic balance

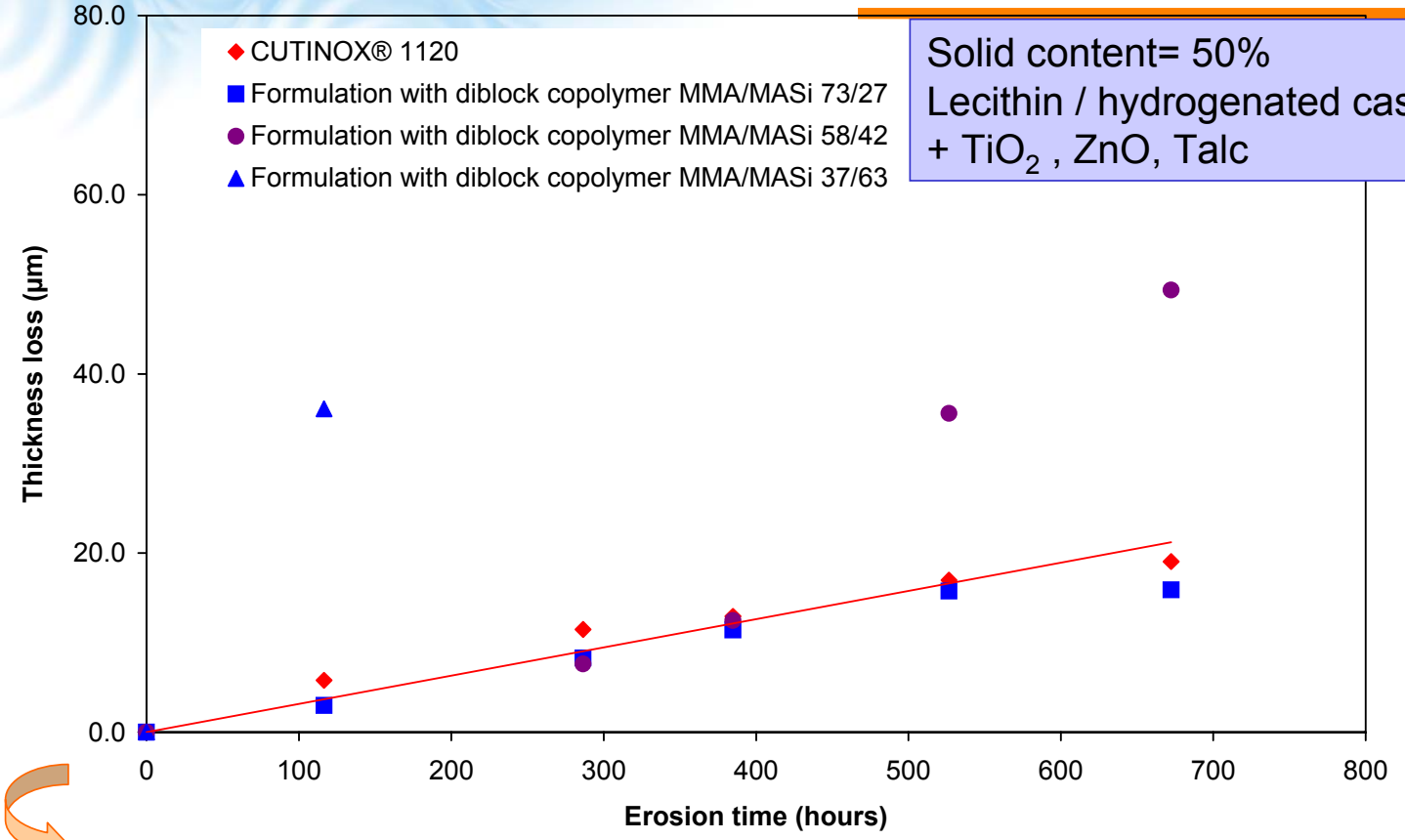
III - Polishing properties



Higher polishing rate for blends with higher amount of MASi monomer units onto macromolecular chains – Loss of linearity after 700h of erosion

Effect of the molar composition of hydrolyzable monomer units

III - Polishing properties



Solid content= 50%
Lecithin / hydrogenated castor oil
+ TiO_2 , ZnO, Talc

Higher mechanical properties of diblock copolymer-based paint than the corresponding binder

Higher polishing rate for paints with higher %mol. of MASi

III - Polishing properties

Polymer matrix	Average polishing rate (µm/d)
CUTINOX®1120	0.4 ± 0.2
Diblock copolymer MMA/MASi	
Diblock copo 79/21	0.4 ± 0.1
Diblock copo 73/27	0.4 ± 0.1
PMMA + diblock copolymer	
PMMA+ Diblock copo 58/42 (30 %mol. Si)	0.8 ± 0.1
Complete paint	
Diblock copo 73/27	0.5 ± 0.1
Diblock copo 58/42	1.4 ± 0.2

Conclusions

➢ RAFT process: This method, which uses thiocarbonyl-thio compounds as chain transfer agents (CTA), leads to the synthesis of (meth)acrylic-based copolymers with controlled molecular weight and narrow molecular weight distribution (PDI<1.2).

➢ Polymer blends with PMMA: improvement of film formation and mechanical properties and adjustment of polishing profiles of the resulting coatings.

➢ Effect of the microstructure of copolymers on controlled polishing of polymer matrix

Better control of the polishing rate over a long-time service in sea water for diblock copolymers poly(methyl methacrylate-b-*tert*-butyldimethylsilyl methacrylate) with Mn value around 13,000 $g.mol^{-1}$

Conclusions

➢ RAFT process: This method, which uses thiocarbonyl-thio compounds as chain transfer agents (CTA), leads to the synthesis of (meth)acrylic-based copolymers with controlled molecular weight and narrow molecular weight distribution (PDI<1.2).

➢ Polymer blends with PMMA: improvement of film formation and mechanical properties and adjustment of polishing profiles of the resulting coatings.

➢ Effect of the microstructure of copolymers on controlled polishing of polymer matrix

Phase separation (micro- or nano-scale) of two incompatible blocks

linked by a covalent bond

(hydrophobic matrix with hydrolyzable domains)

➢ The polishing rate could be modulated by varying the molar proportion of hydrolyzable side groups onto the copolymer and the weight amount of copolymers mixed with PMMA in toluene solution.

Thanks to:

Pr. André Margaillan (Ph.D. supervisor)

Dr. Minh Ngoc Nguyen (Ph.D. student)

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POSTER 28P21

Antifouling activity of novel trialkylsilyl methacrylate-based paints through bioassays and field tests

Christine BRESSY, Claire HELLIO, Minh Ngoc NGUYEN and André MARGAILLAN.