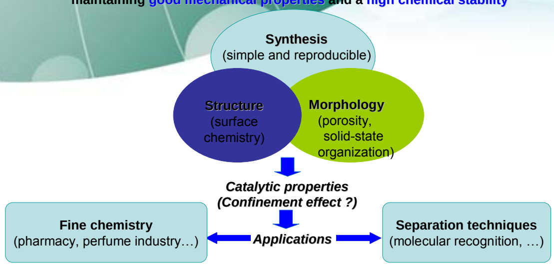
Journées J3N Réseau National en Nanosciences et en Nanotechnologies
6 au 8 novembre 2006

NANOPOROUS POLYMERIC MATERIALS:
APPLICATION TO MEMBRANE CATALYSIS

Objectives

Simultaneous control over the porosity and the functionality of polymeric membranes, maintaining good mechanical properties and a high chemical stability



Methodology

1) *Synthesis of nanostructured precursors*

diblock copolymer (PS-G-PLA) — G - functional group

Interpenetrating Polymer Networks (semi-IPNs and IPNs) (PMMA or PS/PLA)

2) *Alignment of nanodomains in precursors*

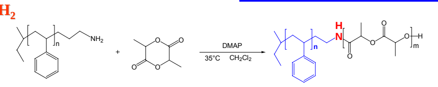
3) *Preparation of the functionalized porous matrix by hydrolysis of the polyester domains*

4) *Physico-chemical characterization of the porous membranes*
- *spectroscopy (solid state NMR ,…)*
- *microscopy (SEM, TEM, AFM)*
- *X-ray scattering*
- *calorimetric techniques (DSC,…)*
- *pycnometry*
- *adsorption and desorption of gas (BET, BJH)*

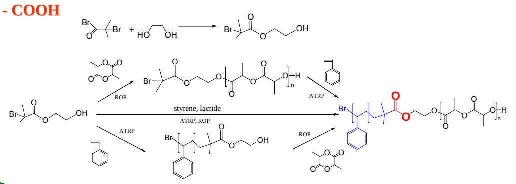
5) *Catalytic experiments*
catalytic sites: acidic (COOH, SO_3H) or basic (NH_2, Py) groups
model reactions: (trans) esterification, hydrolysis, isomerization, ...

Synthesis of Polystyrene-b-Poly(D,L-lactide) with Different Functions at the Junction Between both Blocks

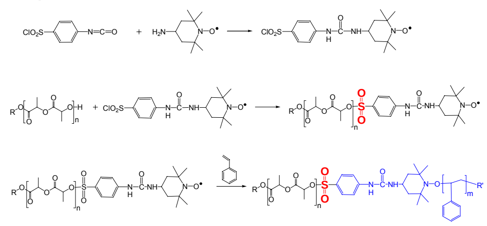
$-NH_2$



- COOH



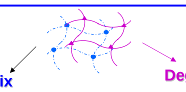
$-SO_3H$



Copolymer [a]	M_n[kg/mol] [b]	M_w/M_n [b]	f(PLA) [c]
PS-NH-PLA 12	44.6	1.1	0.18
PS-NH-PLA 13	49.5	1.1	0.26
PS-NH-PLA 15	48.2	1.1	0.24

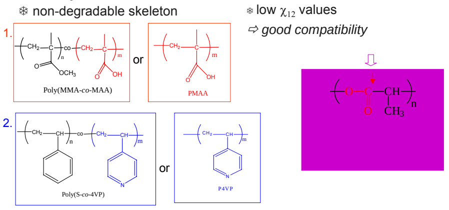
[a] PS macroinitiator: M_n = 36.6 kg/mol, M_w/M_n = 1.1
[b] copolymer data obtained from SEC using polystyrene standards
[c] PLA molar fraction: f(PLA) = $N_{PLA}/(N_{PLA} + N_{PS})$ as determined by H^1 NMR

Our Approach Towards Nanoporous Supported Catalysts from Functional IPNs



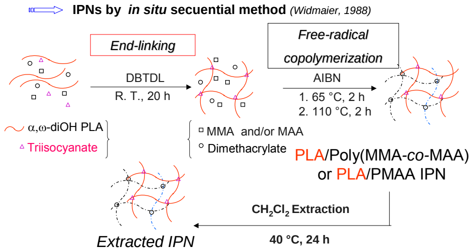
Rigid matrix
- high T_g polymer
- non-degradable skeleton

Degradable partner
- « soft » hydrolyzable polyester
- low χ_{12} values
- ⇨ *good compatibility*

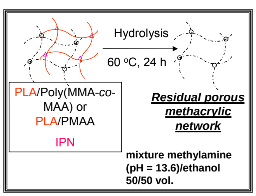


Approach to Functional Nanoporous Materials from IPNs

⇨ **IPNs by *in situ* secuential method** *(Widmaier, 1988)*



➡ **Quantitative hydrolysis of PLA sub-network**

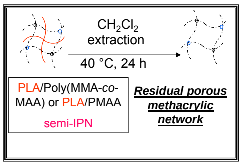


« methacrylic » IPNs	Δm (wt %)
PLA/Poly(MMA-*co*-MAA) **25**/75 1 % mol DUDMA MMA/MAA: 50/50 % mol	29
PLA/Poly(MMA-*co*-MAA) **50**/50 **1% mol DUDMA** MMA/MAA: 50/50 % mol	51
PLA/Poly(MMA-*co*-MAA) **50**/50 **10 % mol DUDMA** MMA/MAA: 50/50 % mol	52
PLA/**PMAA 50**/50 1 % mol DUDMA	54

⇩
Mass loss ≥ PLA composition

Approach to Functional Porous Materials from Semi-IPNs

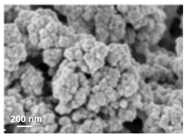
➡ **Quantitative extraction of PLA oligomers**



« methacrylic » semi-IPNs	Extractable content (wt %)
PLA/Poly(MMA-*co*-MAA) **25**/75 1% mol DUDMA MMA/MAA : 50/50 % mol	27
PLA/Poly(MMA-*co*-MAA) **50/50 1% mol DUDMA** MMA/MAA : 50/50 % mol	57
PLA/Poly(MMA-*co*-MAA) **50/50 10 %mol DUDMA** MMA/MAA : 50/50 % mol	62
PLA/**PMAA 50**/50 1 % mol DUDMA	56

⇩
Extractable content ≥ PLA composition

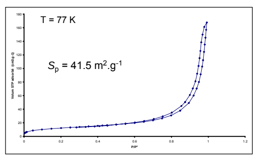
Morphological Analysis by SEM



PLA/PMAA 50/50 1 % mol DUDMA semi-IPN *after extraction*

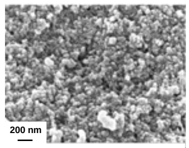
« methacrylic » semi-IPNs	Pore diameter (nm)
PLA/Poly(MMA-*co*-MAA) 25/75 1 % mol DUDMA MMA/MAA : 50/50 % mol	50 - 450
PLA/Poly(MMA-*co*-MAA) 50/50 1 % mol DUDMA MMA/MAA : 50/50 % mol	70 - 475
PLA/Poly(MMA-*co*-MAA) 50/50 10 % mol DUDMA MMA/MAA : 50/50 % mol	150 - 600
PLA/ **PMAA** 50/50 1 % mol DUDMA	50 - 400

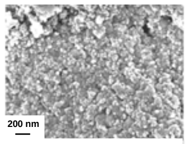
N_2 Adsorption-Desorption



PLA/PMAA 50/50 1 % mol DUDMA semi-IPN *after extraction*

Morphological Analysis by SEM





PLA/Poly(MMA-*co*-MAA) 50/50 10 % mol DUDMA IPN *after hydrolysis* — PLA/PMAA 50/50 1 % mol DUDMA IPN *after hydrolysis*

Porosity Analysis by thermoporometry (DSC)

« methacrylic » IPNs	Pore diameter (nm)
PLA/Poly(MMA-*co*-MAA) 25/75 1 % mol DUDMA MMA/MAA : 50/50 % mol	10 - 200
PLA/Poly(MMA-*co*-MAA) 50/50 1 % mol DUDMA MMA/MAA : 50/50 % mol	20 - 150
PLA/Poly(MMA-*co*-MAA) 50/50 10 % mol DUDMA MMA/MAA : 50/50 % mol	**10 - 200**
PLA/**PMAA** 50/50 1 % mol DUDMA	20 - 200

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