Bio-based copolymers for membrane end products for gas separations

BioCoMem

PEBA polymer synthesis pathways to membrane processing

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WEBINAR: Pathways to demonstrate the BIOCOMEM technology for future bio-based membranes deployment in industry

November 24th – 10:00 – 12:30

BBI JU

Bio-based Industries Consortium

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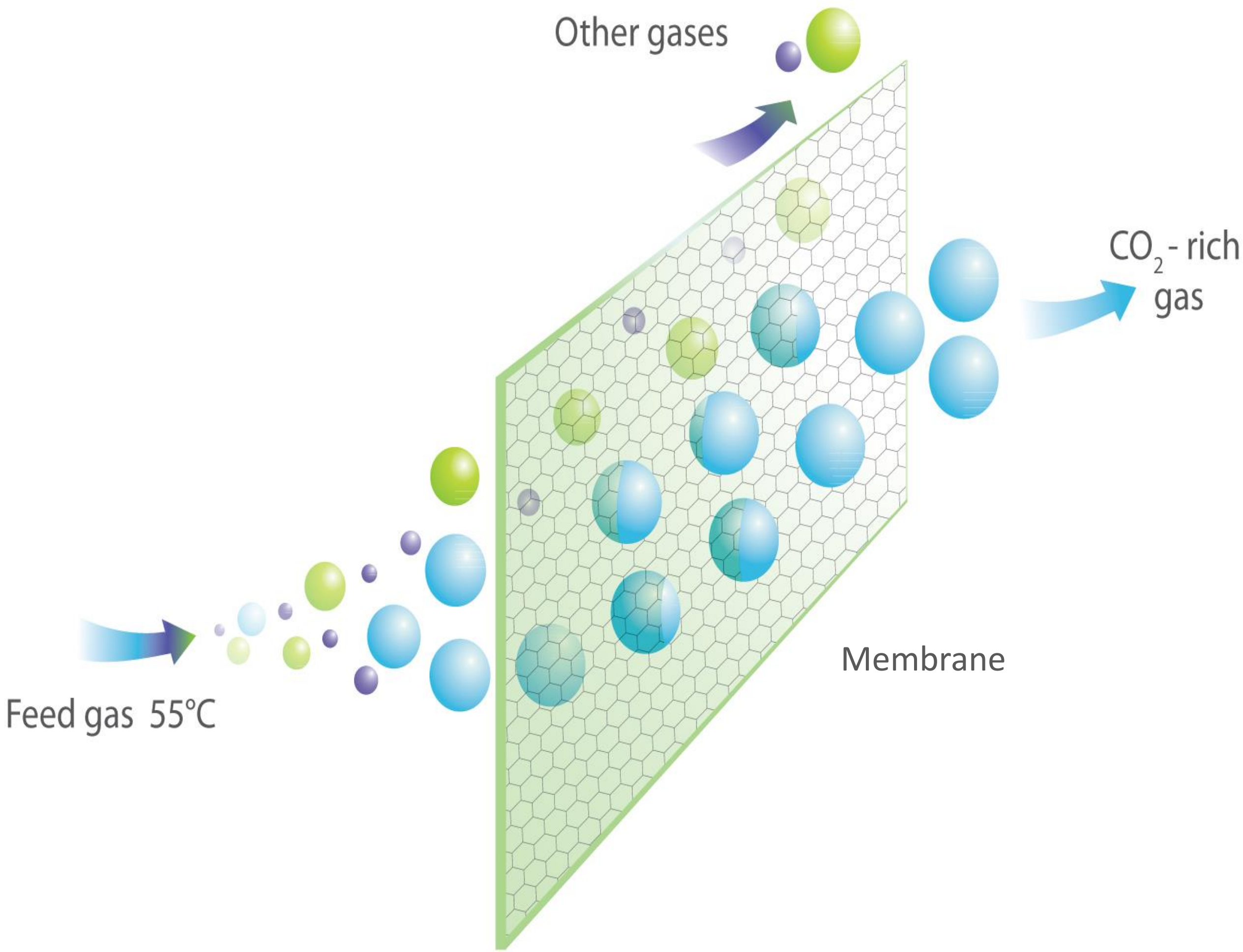
Introduction

Gas separation membranes



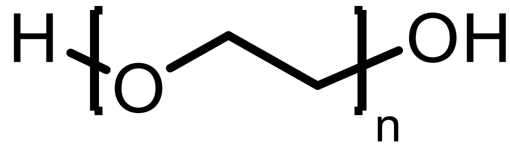
- Permeability is the rate at which gaseous molecules permeate through membrane
- Selectivity is the ability of membrane to separate the gas molecule from their mixture

Membrane materials for gas separation

Membrane

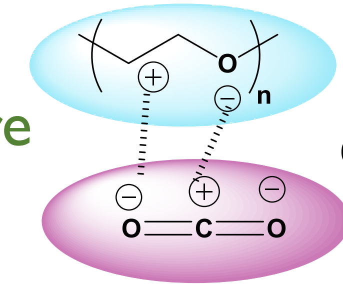
Inorganic (e.g. Silica, zeolites)	Metallic	Polymeric
✓ Can withstand aggressive conditions as well as high temperatures ○ High cost, modest reproducibility, brittleness and low permeability	✓ Mostly used for hydrogen separation ○ Associated with high cost and scalability issues	✓ Easy processability ✓ easy tunability

Polymeric gas separation membranes



Advantages

- Especially for CO_2 capture



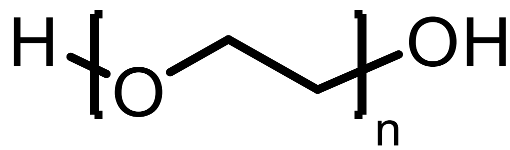
quadrupole-quadrupole interaction

- PEG-based polymers show a considerable CO_2 solubility, and the CO_2 selectivity mainly stems from the solubility selectivity.

Disadvantages

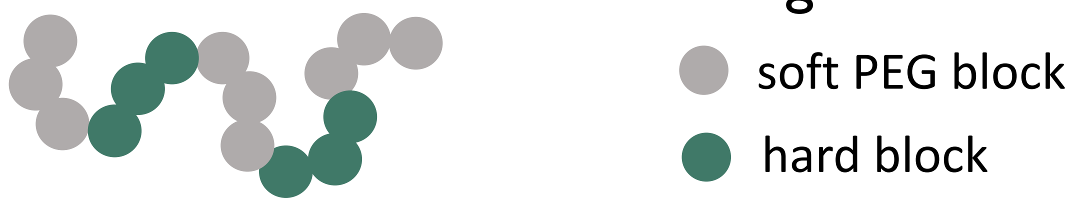
- Permeability Selectivity Trade-off
- Swelling and Plasticization
- Membrane Aging
- Limited Resistance to Fouling
- Mechanical Strength

Polymeric gas separation membranes

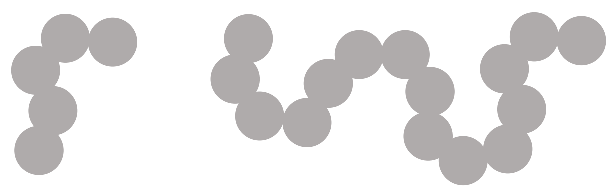


Various approaches to overcome these limitations

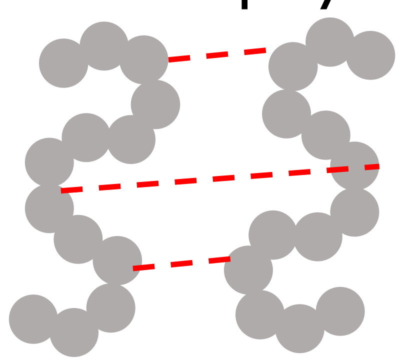
- Block copolymerization with other hard segments



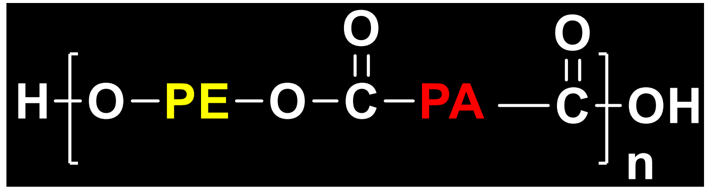
- Blending with low molecular weight PEG and PEG-derivatives



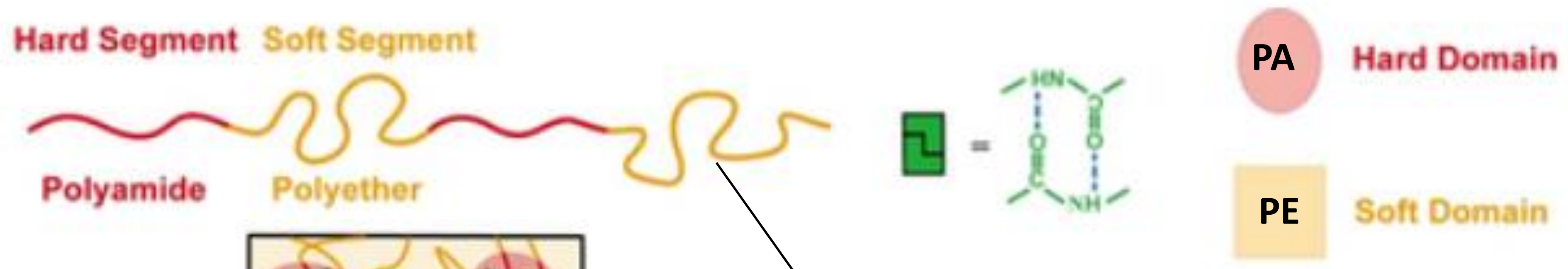
- Crosslinking to form PEG polymer network.

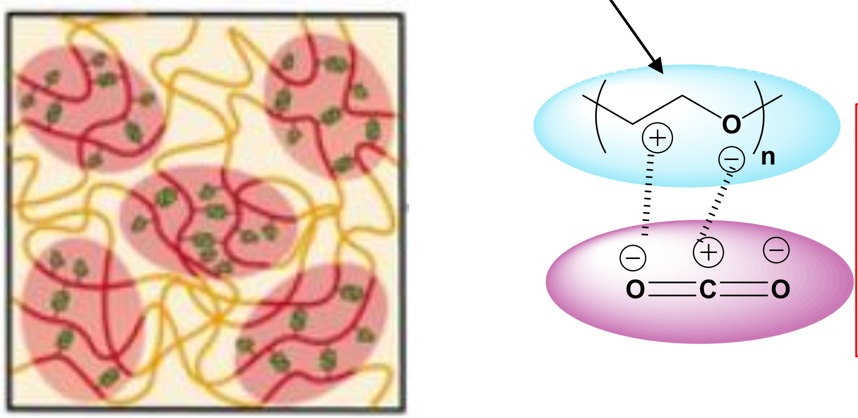


Block copolymers



poly(ether-*b*-amide) PEBA
thermoplastic elastomer





BUT: solubility issues upon processing into monolitic hollow fiber membrane

- Polyamide (PA)
- Semi-crystalline segments
- Hard PA segments provide mechanical stability

- Polyether (PE)
- Soft PE blocks,
- Owing to dipole interactions and high chain mobility, gas permeable

Process steps from monomer to membrane

Lab scale PEBA synthesis → PEBA screening → Upscaling most promising PEBA → Membrane fabrication

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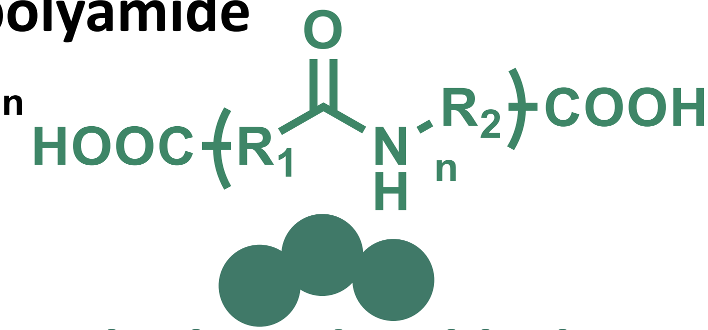
PEBA synthesis

Step 1: synthesis of COOH functionalized polyamide

$COOH\text{-}R_1\text{-}COOH + NH_2\text{-}R_2\text{-}NH_2 \xrightarrow{\text{polycondensation}}$



biobased PA block

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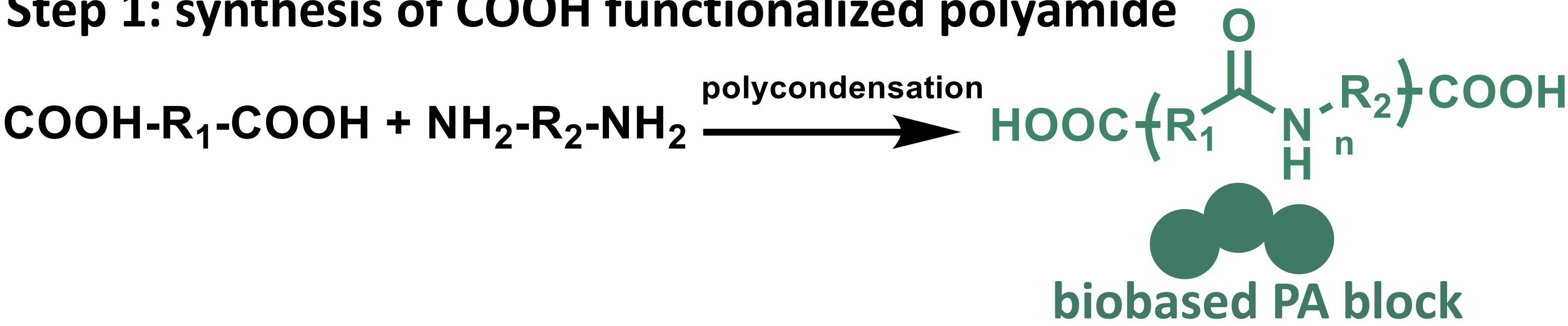
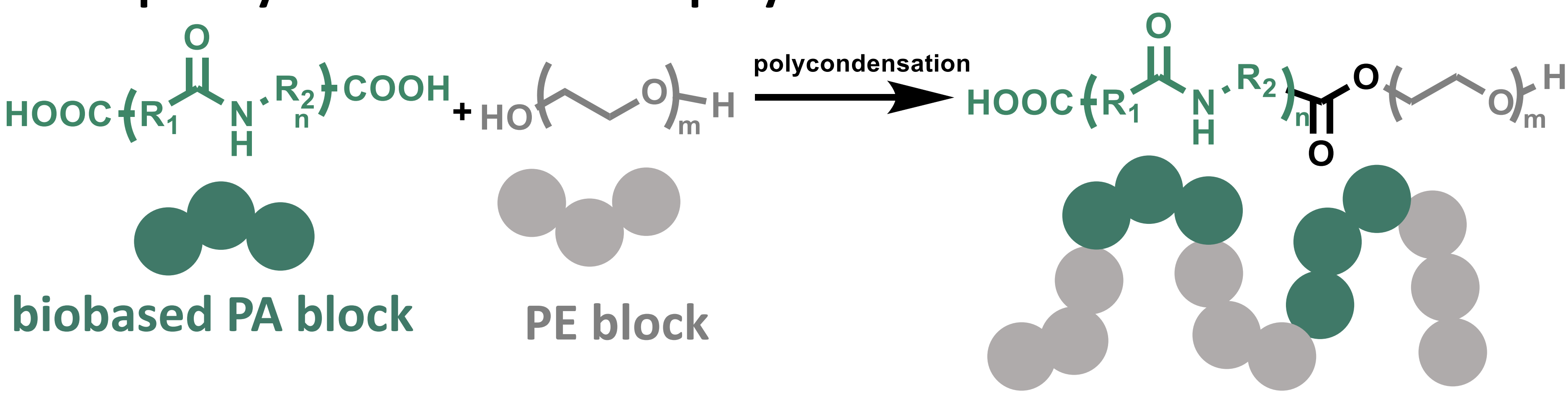
PEBA synthesis

Step 1: synthesis of COOH functionalized polyamide



Step 2: synthesis of block copolymer



(PA-*b*-polyether)$_n$

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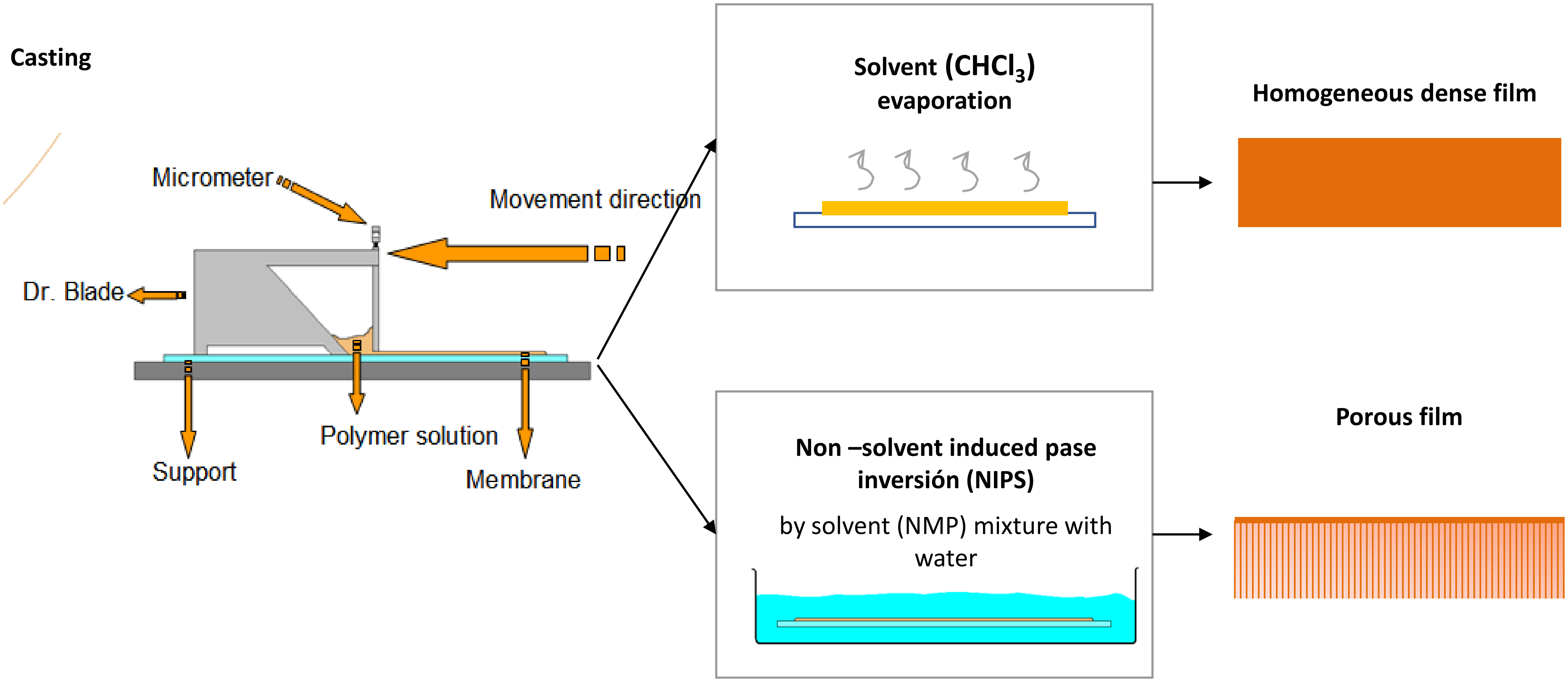
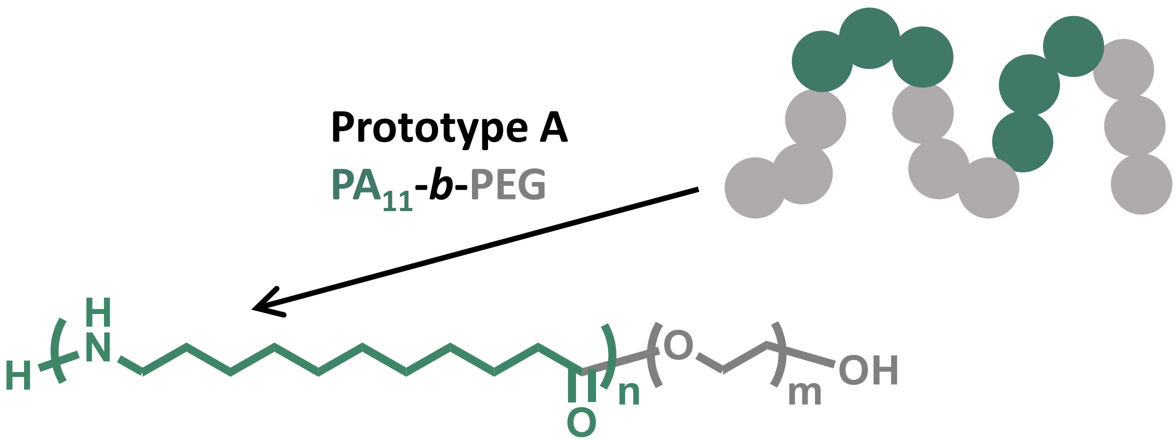
PEBA screening



BIOCOMEM results

PEBA with improved processability/solubility



PEBA reference with solubility issues

PEG: T_m = 13 °C; ΔH_m=40 J/g
PA: T_m=149 °C; ΔH_m=29 J/g

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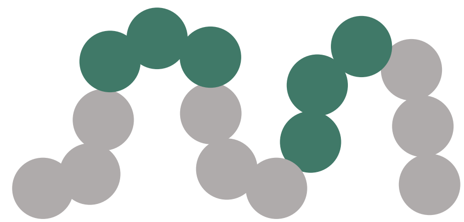
PEBA with improved processability/solubility

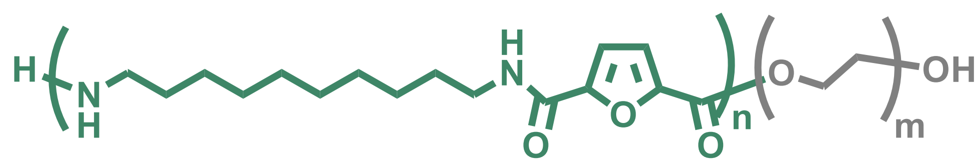


Prototype A

PA$_{11}$-*b*-PEG

Prototype B

PA10.F-*b*-PEG



PEBA reference with solubility issues

PEG: T_m = 13 °C; ΔH_m=40 J/g

PA: T_m=149 °C; ΔH_m=29 J/g

Goals:

- better solubility then prototype A
- less crystalline PA,
  compensate for mechanics via aromatic
- biobased PA

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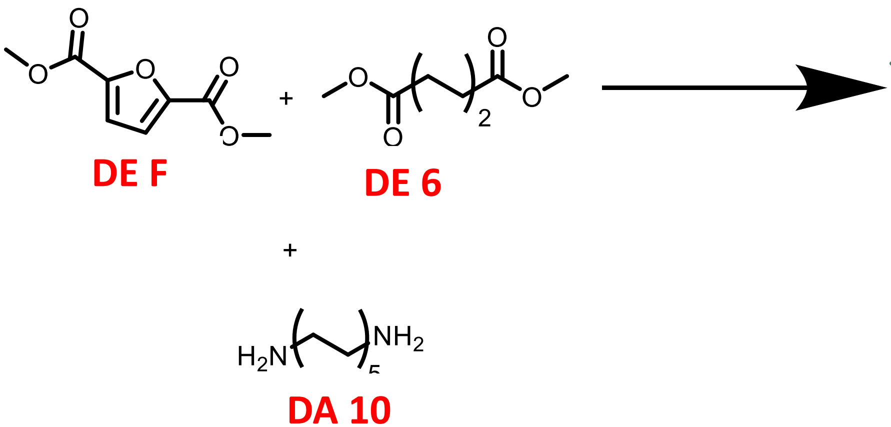
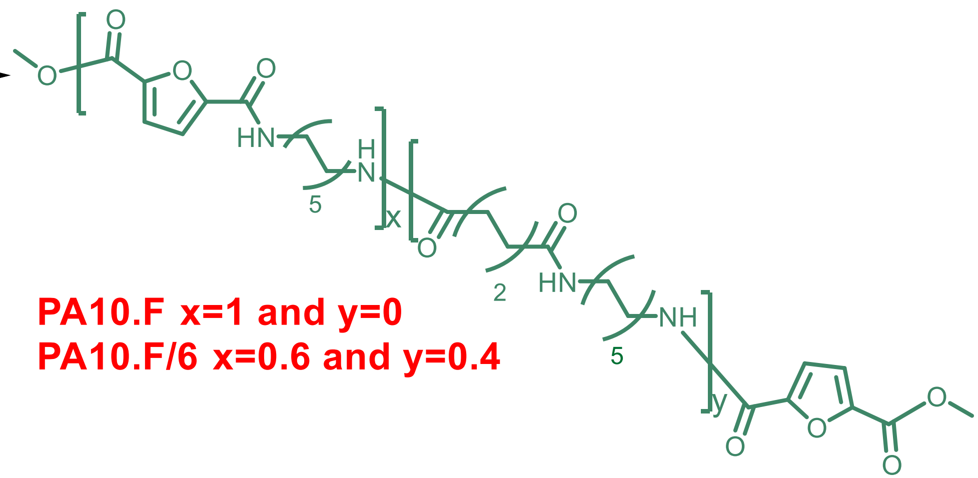
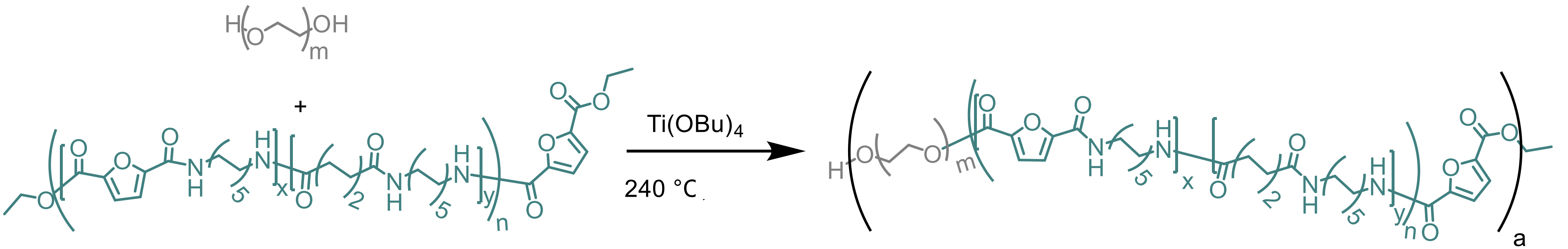
Prototype B synthesis

Step 1: polyamide synthesis

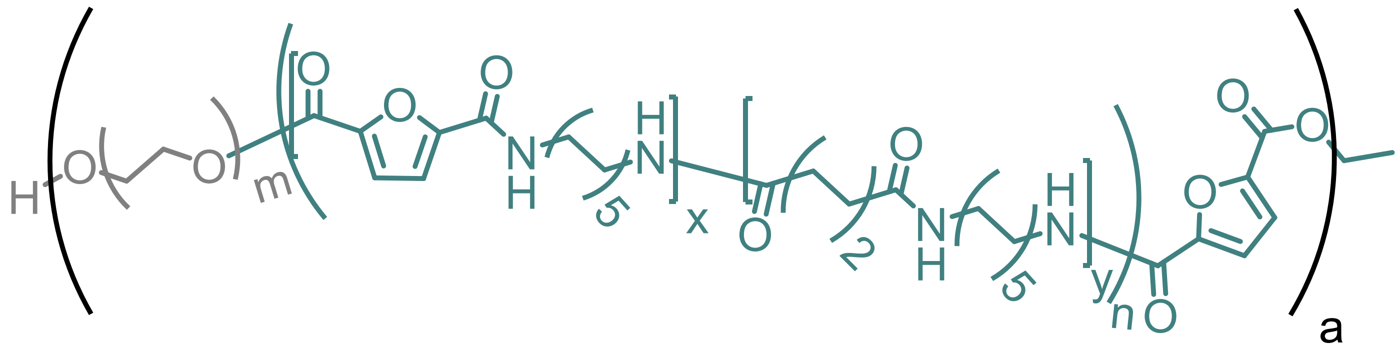




Step 2: PEBA synthesis



Prototype B synthesis



PA (DA.DE)	$M_{n,PA}$ [g/mol]	$M_{n,PEG}$ [g/mol]	$M_{n,PEBA}$ [g/mol]	Đ	wt% PA/PEG	T_g[°C]	$T_{m,PEG}$ [°C]	$T_{m,PA}$ [°C]	$\Delta H_{m,PEG}$ [J/g]	$\Delta H_{m,PA}$ [J/g]
PA10.F	900	1500	22 000	1.60	40/60	-45	30	-	143	-.
PA10.F	1500	1500	7 000	1.35	48/52	-45	37	-	140	-
PA10.F/6 x=0.6, y=0.4	1500	1500	8 500	1.51	41/59	-60	48	-	148	-

Polymer is too low M_n and shows poor mechanical properties at temperatures above melting of PEG block.

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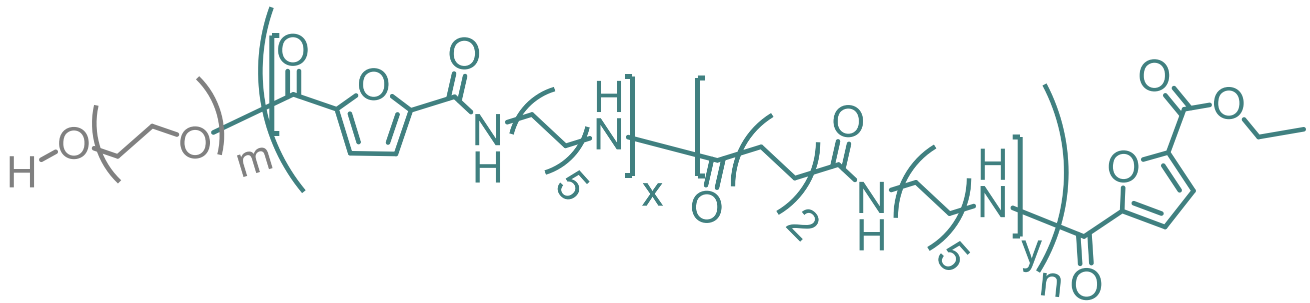
Prototype B screening



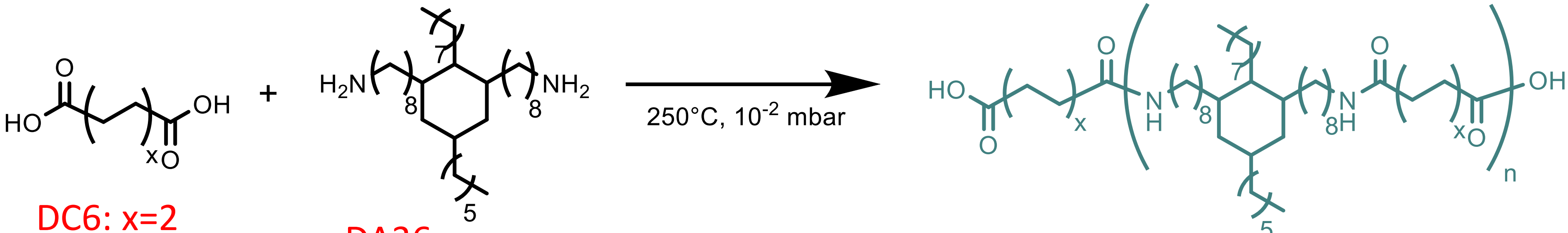
PA (DA.DE)	$M_{n,PA}$ [g/mol]	$M_{n,PEG}$ [g/mol]	$M_{n,PEBA}$ [g/mol]	$T_{m,PEG}$ [°C]	$T_{m,PA}$ [°C]	CO_2 permeability (Barrer)	CO_2/N_2 selectivity	CO_2/CH_4 selectivity	NIPS membrane formation?
10.F	900	1500	22 000	30	-	20,87	22,5	n.d	no
10.F	1500	1500	7 000	37	-	150	12,6	n.d	no
10.F/6 x=0.6, y=0.4	1500	1500	8 500	48	-	Could not form a dense film			no

Issues membrane evaluation:

- Polymer properties obstacle protocols with temperatures above 50 ℃ are used to prepare membranes.
- high degree of crystallinity of PEG block is detrimental for CO_2 absorption properties

Modified Prototype B – synthesis route A

Step 1: polyamide synthesis

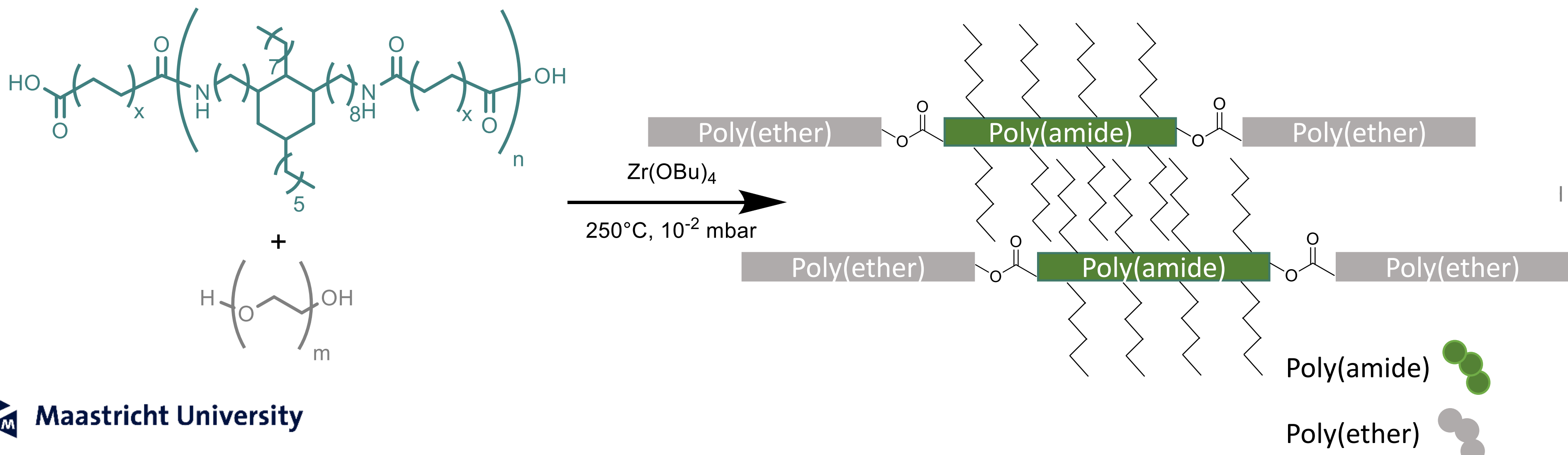


DC6: x=2
DC10: x=4

DA36

PA36.6 or PA36.10

Step 2: PEBA synthesis



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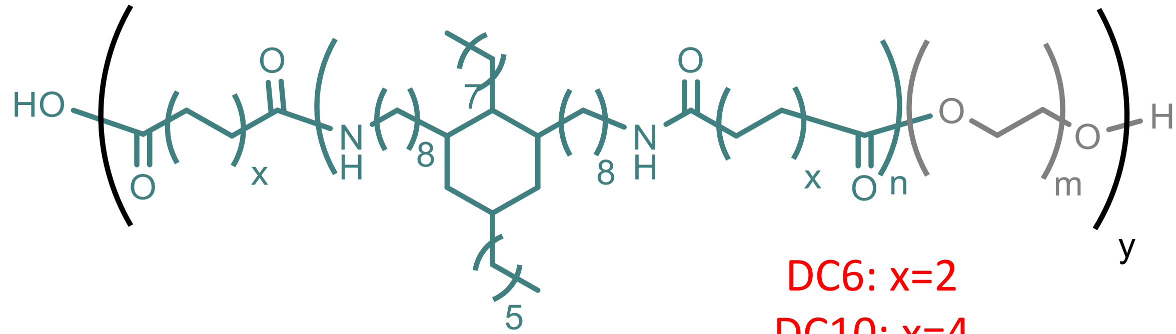
Modified Prototype B – synthesis route A

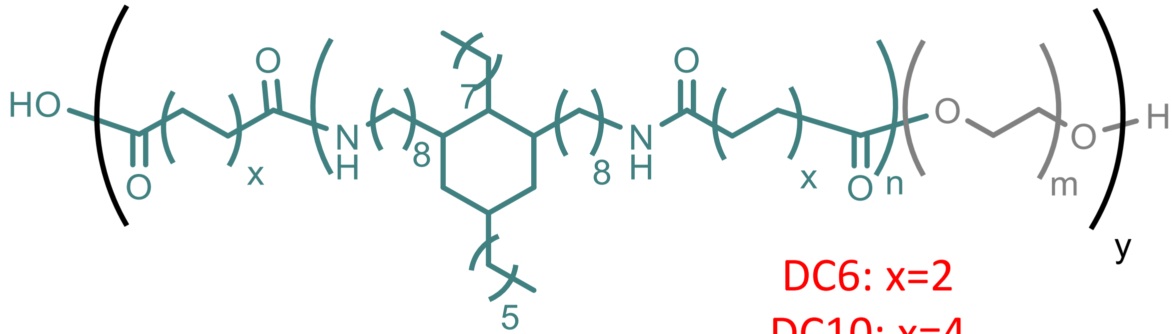


DC6: x=2
DC10: x=4

PA (DA.DC)	$M_{n,PA}$ [g/mol]	$M_{n,PEG}$ [g/mol]	$M_{n,PEBA}$ [g/mol]	Đ	wt% PA/PEG	T_g[°C]	$T_{m,PEG}$ [°C]	$T_{m,PA}$ [°C]	$\Delta H_{m,PEG}$ [J/g_P	$\Delta H_{m,PA}$ [J/g]
36.6	**3200**	1500	33 000	1.49	**67/33**	<-40	31	102	89	13
36.6	**2100**	1500	27 500	1.61	**59/41**	<-40	34	100	93	11
36.6	**1200**	1500	28 000	1.56	**48/52**	<-40	40	98	86	5
36.10	2600	1500	24 000	1.45	62/38	<-40	41	92	92	14

$M_{n,PEBA}$ lower then expected due to sublimation

Modified Prototype B – screening route A



DC6: x=2
DC10: x=4

PA (DA.DC)	wt% PA/PEG	$M_{n,PEBA}$ [g/mol]	$T_{m,PEG}$ [°C]	$T_{m,PA}$ [°C]	CO_2 permeability (Barrer)	CO_2/N_2 selectivity	CO_2/CH_4 selectivity	NIPS membrane formation?
36.6	**67/33**	33 000	31	102	139,4	24,3	8,0	no
36.6	**59/41**	27 500	34	100	234,4	29,0		no
36.6	**48/52**	28 000	40	98	45,1	23,9	8,4	no
36.10	62/38	24 000	41	92	70,9	22,6	7,6	no

- Screening experiments at 35 °C. If $T_{m,PEG}$ > 35 °C, bad gas separation performance because of lack of mobility in the PEG phase
- NIPS membrane formation not succesfull

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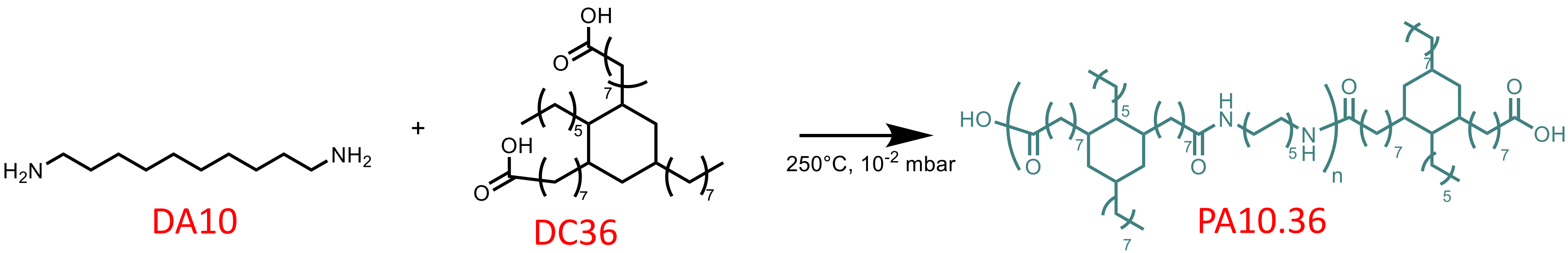
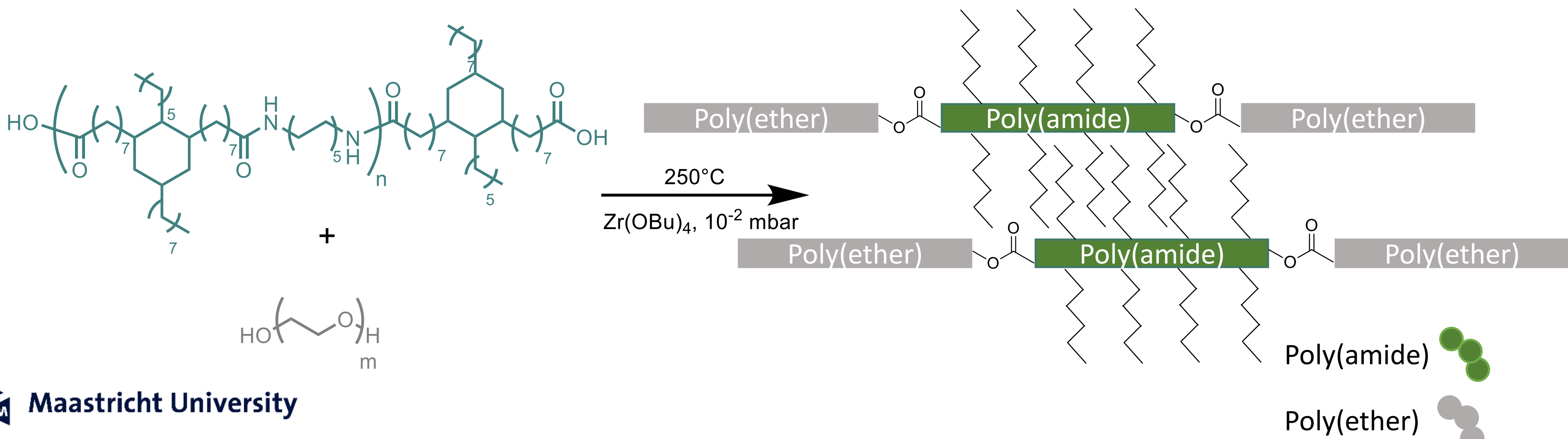
Modified Prototype B – synthesis route B

Step 1: polyamide synthesis



Step 2: PEBA synthesis



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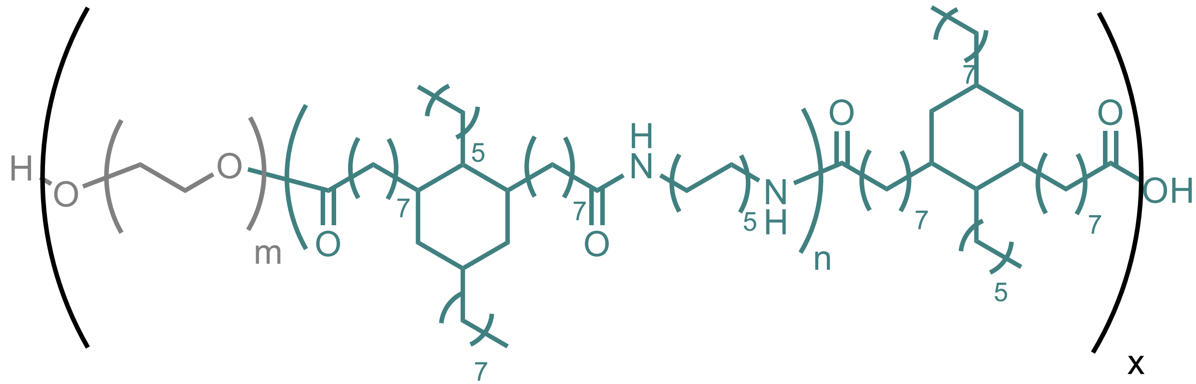
Modified Prototype B – synthesis route B



PA (DA.DC)	$M_{n,PA}$ [g/mol]	$M_{n,PEG}$ [g/mol]	$M_{n,PEBA}$ (g/mol)	Đ	wt% PA/PEG	T_g [°C]	$T_{m,PEG}$ [°C]	$T_{m,PA}$ [°C]	$\Delta H_{m,PEG}$ [J/g]	$\Delta H_{m,PA}$ [J/g]
10.36	2000	1500	48 000	2.23	60/40	n/d	16	80	57	20
10.36	2300	1500	43 000	1.77	64/36	-60	14	79	64	19
10.36	2600	**3350**	34 300	2.07	36/64	n/d	54	78	113	12

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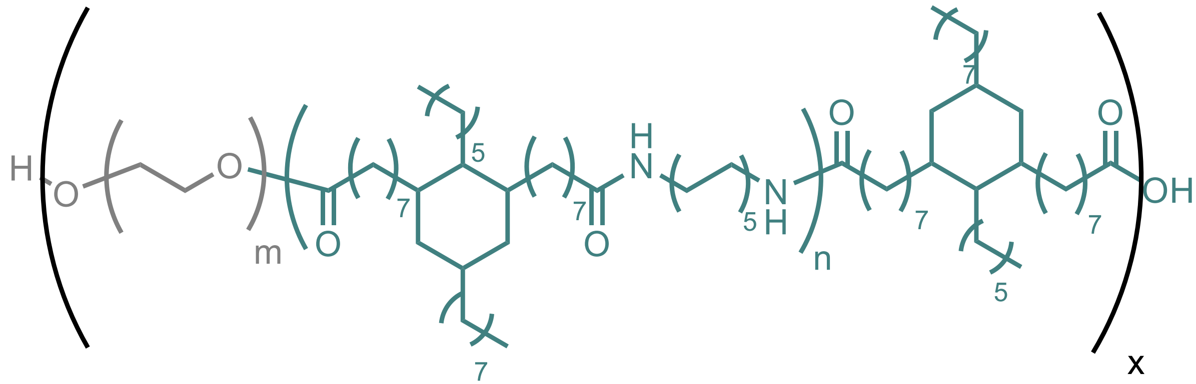
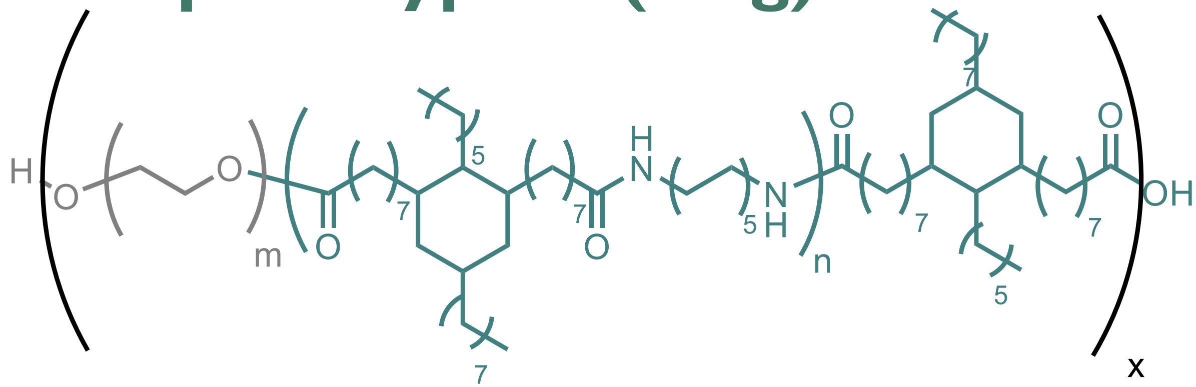
Modified Prototype B – screening route B



PA (DA.DC)	wt% PA/PEG	$M_{n,PEBA}$ [g/mol]	$T_{m,PEG}$ [°C]	$T_{m,PA}$ [°C]	CO_2 permeability (Barrer)	CO_2/N_2 selectivity	CO_2/CH_4 selectivity	NIPS membrane formation?
10.36	60/40	48 000	16	80	228,8 ±8,2	27,5 ±1,64	9,2 ±0,7	yes
10.36	64/36	43 000	14	79	219,0 ±0,2	26,9 ±0,14	8,7 ±0,02	yes
10.36	36/64	34 300	54	78	40,1	27,3	8,8	no

Good gas separation properties and NIPS membrane formation succesfull with short PEG (low crystallinity)

Synthesis of upscaled PEBA modified prototype B (3 kg)



PA (DA.DC)	$M_{n,PA}$ [g/mol]	$M_{n,PEG}$ [g/mol]	$M_{n,PEBA}$ [g/mol]	Đ	wt% PA/PEG	$T_{m,PEG}$ [°C]	$T_{m,PA}$ [°C]	$\Delta H_{m,PEG}$ [J/g]	$\Delta H_{m,PA}$ [J/g]
10.36*	2300	1500	43 000	1.77	**64/36**	14	79	64	19
10.36	2300	1500	52 900	2.19	**55/45**	13	77	28	14
11 endcapped with DC36	1000	1500	82 900	2.57	42/58	24	122	49	5
11/10.36	2100	1500	44 700	2.04	**56/44**	20	94	30	13
11/10.36	6000	1500	50 200	2.38	**78/22**	15	105	20	20

* Only upscaled to 100 g

Membrane properties upscaled PEBA Modified prototype B

Sample	PA (DA.DC)	wt% PA/PEG	$T_{m,PEG}$ [°C]	$T_{m,PA}$ [°C]	CO_2 permeability (Barrer)	CO_2/N_2 selectivity	CO_2/CH_4 selectivity	CO_2/H_2 selectivity
Polyactive	$PEG1500_{77}PBT_{23}$		27	110	115	45.6	n.d.	n.d.
Prot A	11	40/60	25	160	311	45	14.07	9.35
Prot B1	10.36	64/36	14	79	219	26.9	8.7	n.d.
Prot B2	10.36	55/45	13	77	354	28.83	8.99	5.48
Prot B3	11 endcapped with DC36	42/58	24	122	360	36.13	10.9	7.46
Prot B4	11/10.36	56/44	20	94	343	30.13	9.25	5.37
Prot B5	11/10.36	78/22	15	105	106	21.02	7.16	2.81

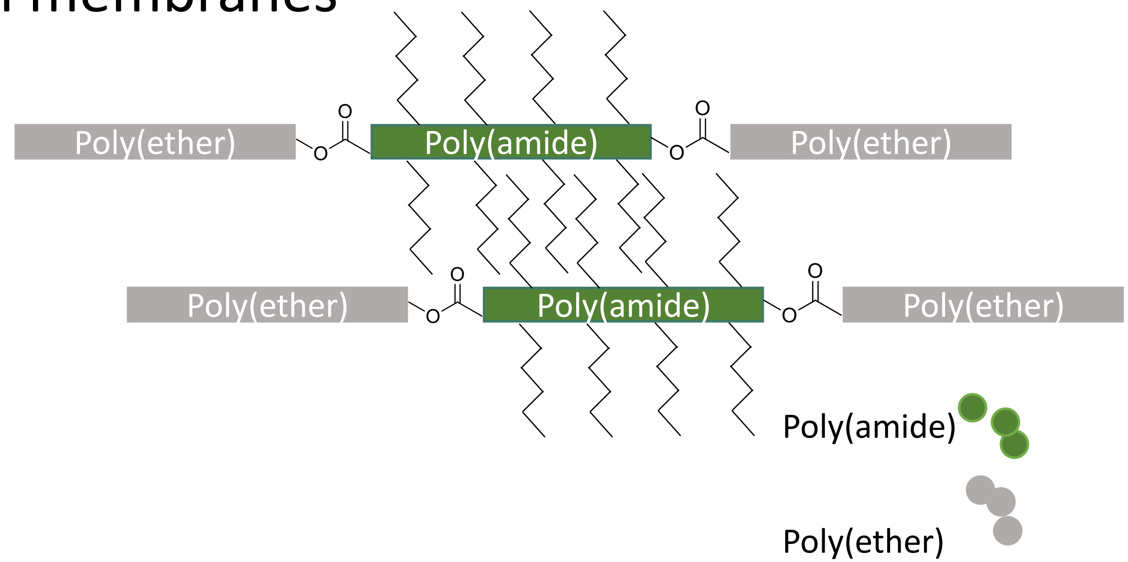
Test conditions: 35 °C and 3 bar Δp for all samples, except Polyactive 30 ºC, 300 mbar

Conclusion:

- Higher PEG content better for gas separation properties
- Prot B3 best tradeoff between processability and gas separation

Conclusions

- Succesfull synthesis of a new class of PEBA for gas separation membranes



- Dimer fatty acid in the polyamide block increases solubility/processability into membranes
- Gas separation properties of screening results very promising