INFLUENCE OF SEMI-CRYSTALLINE MICROSTRUCTURE ON HYDROGEN PERMEABILITY OF POLY(ETHER-KETONE-KETONE)

HYPOCCRYT Project

HYdrogen **P**ermeability of **O**rganic **C**omposites at **CRY**ogenic **T**emperature

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[1] Clément Ader Institute. IMT Mines Albi. Albi. France

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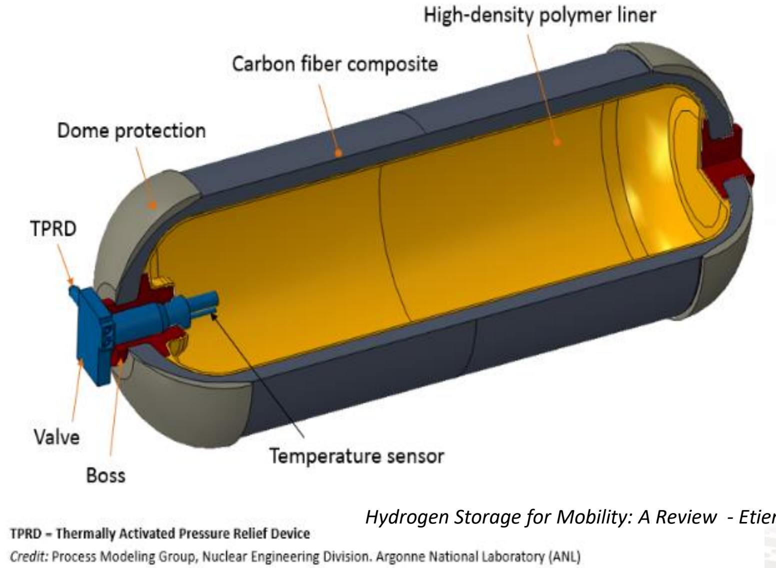
LH2 storage for aerospace applications

H_2 gas storage (P = 350 → 700 bar)

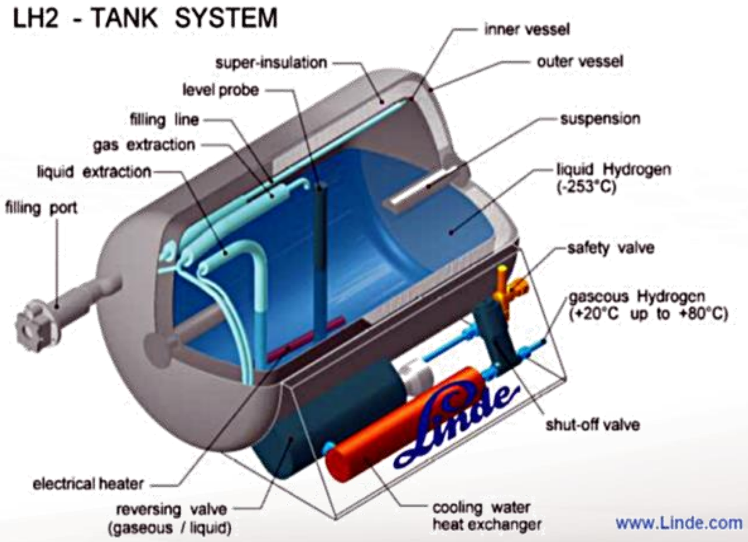
ρ = 25-35 kg.m^{-3}



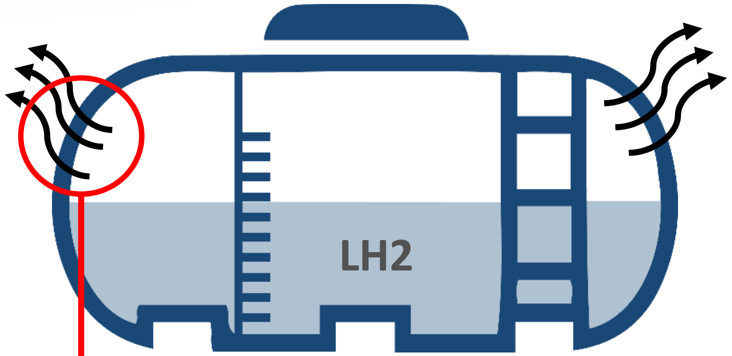
Hydrogen Storage for Mobility: A Review - Etienne Rivard

Liquid H_2 storage (T = 20 K)

ρ = 65-70 kg.m^{-3}

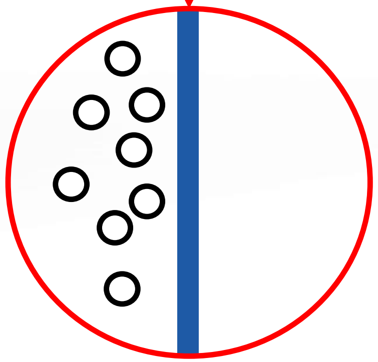


LH2 storage : leakage control



P = 1-4 bar
T = -253 °C

Permeability **P**
(mol.m.m^{-2}MPa^{-1}s^{-1})



Diffusion **D**
(m^2.s^{-1})

Solubility **S**
(mol.MPa^{-1}m^{-3})

Diffusion [1] **Solubility**

Fick's law — *Henry's law*

$$J = -D\,\frac{\partial C}{\partial x}$$

$$C = S \times p$$

$$J = -D \times S \times \frac{\partial p}{\partial x}$$

$$P = D \times S$$

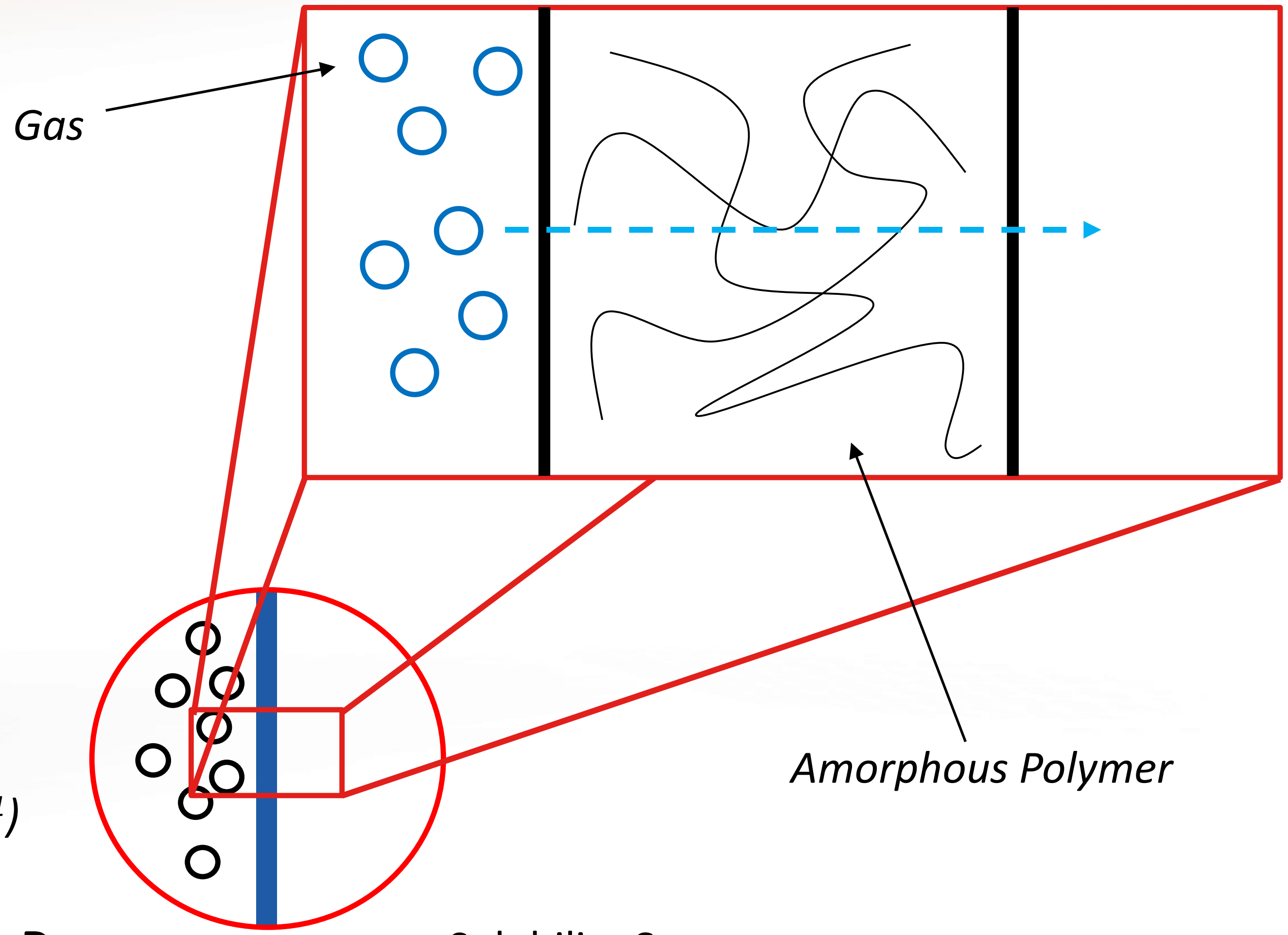
[1] : Klopffer et al. – Rev. IFP, Vol. 56 - 2001

Permeability theory

Influencing parameters

Density

Polymer State



Permeability **P**
(mol.m.m^{-2}MPa^{-1}s^{-1})

Diffusion **D**
(m^{2}.s^{-1})

Solubility **S**
(mol.MPa^{-1}m^{-3})

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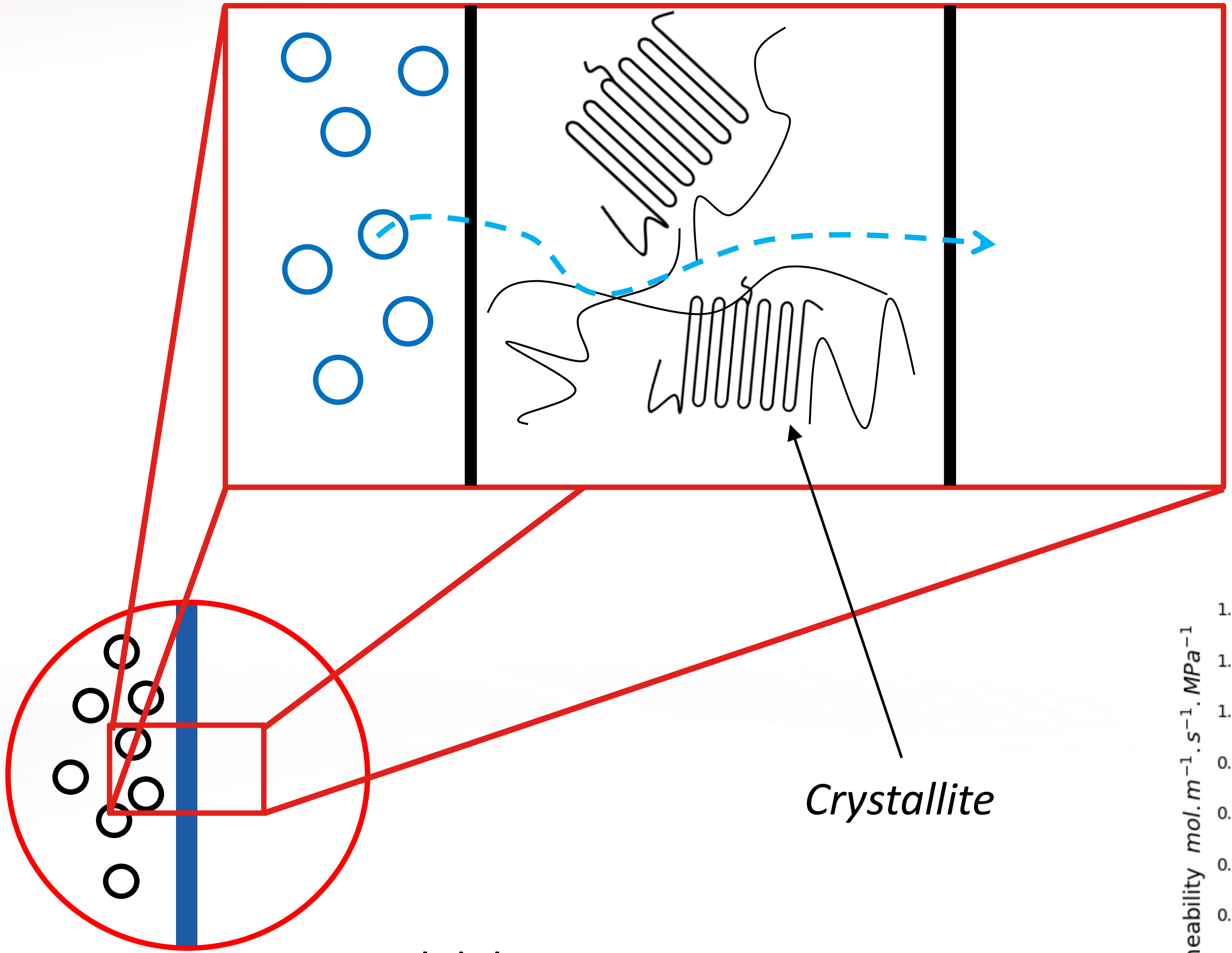
Permeability theory

Influencing parameters

Density

Polymer State

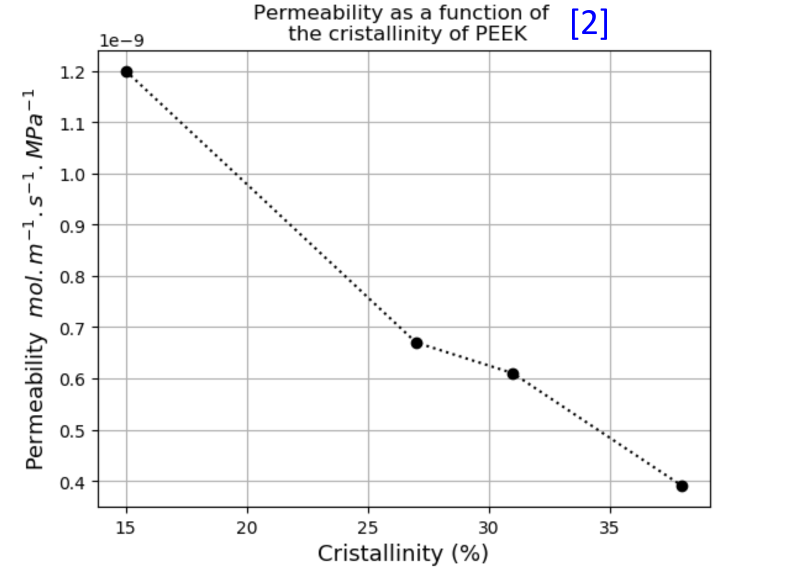
Crystallinity



Permeability **P**
(mol.m.m^{-2}MPa^{-1}s^{-1})

Diffusion **D**
(m^2.s^{-1})

Solubility **S**
(mol.MPa^{-1}m^{-3})

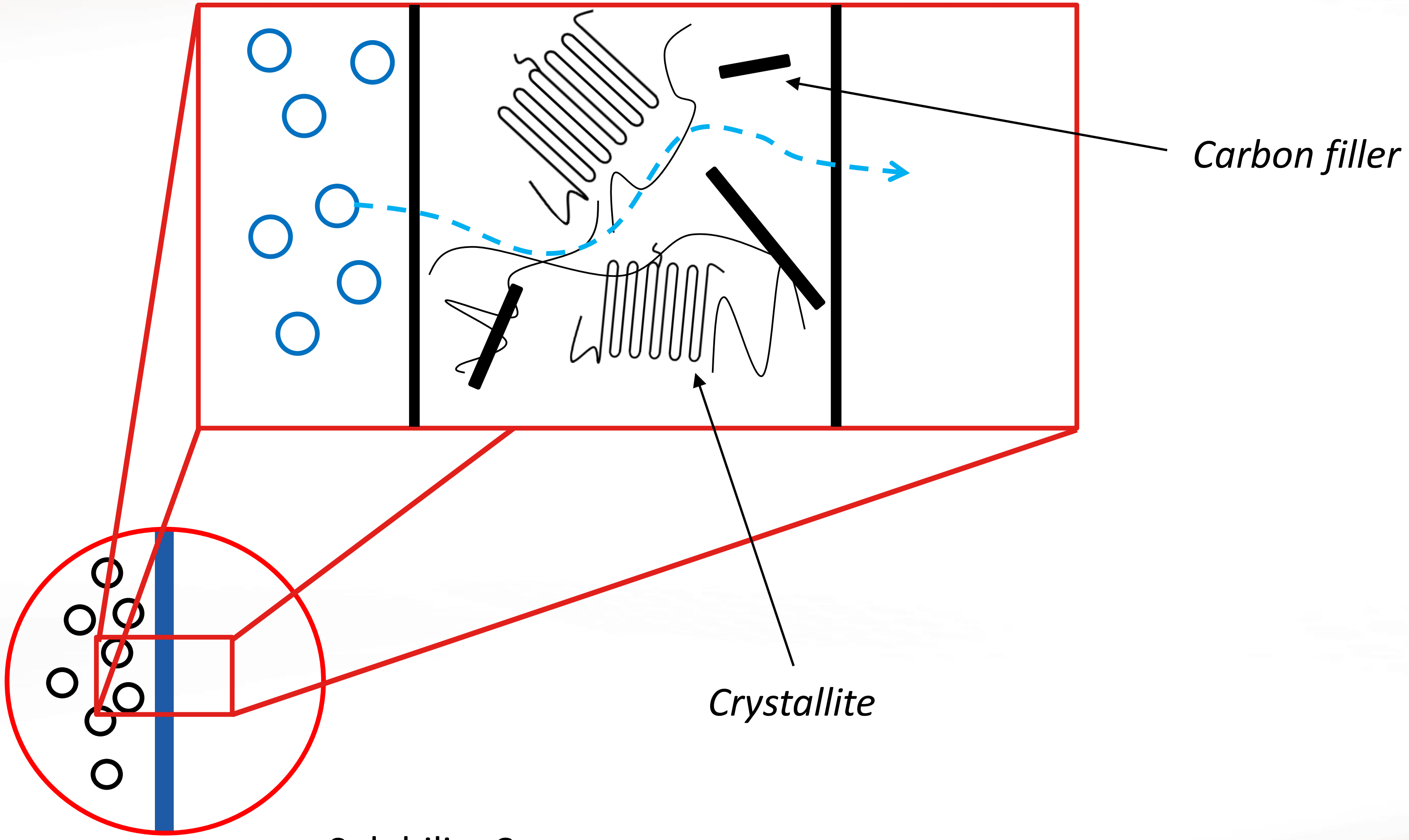


[2] : Monson et al. – J. APPL. POLYM. SCI. - 2013

Permeability theory

Influencing parameters

- **Density**
- **Polymer State**
- **Crystallinity**
- **Carbon Content**



Permeability **P**
(mol.m.m^{-2}MPa^{-1}s^{-1})

Diffusion **D**
(m^{2}.s^{-1})

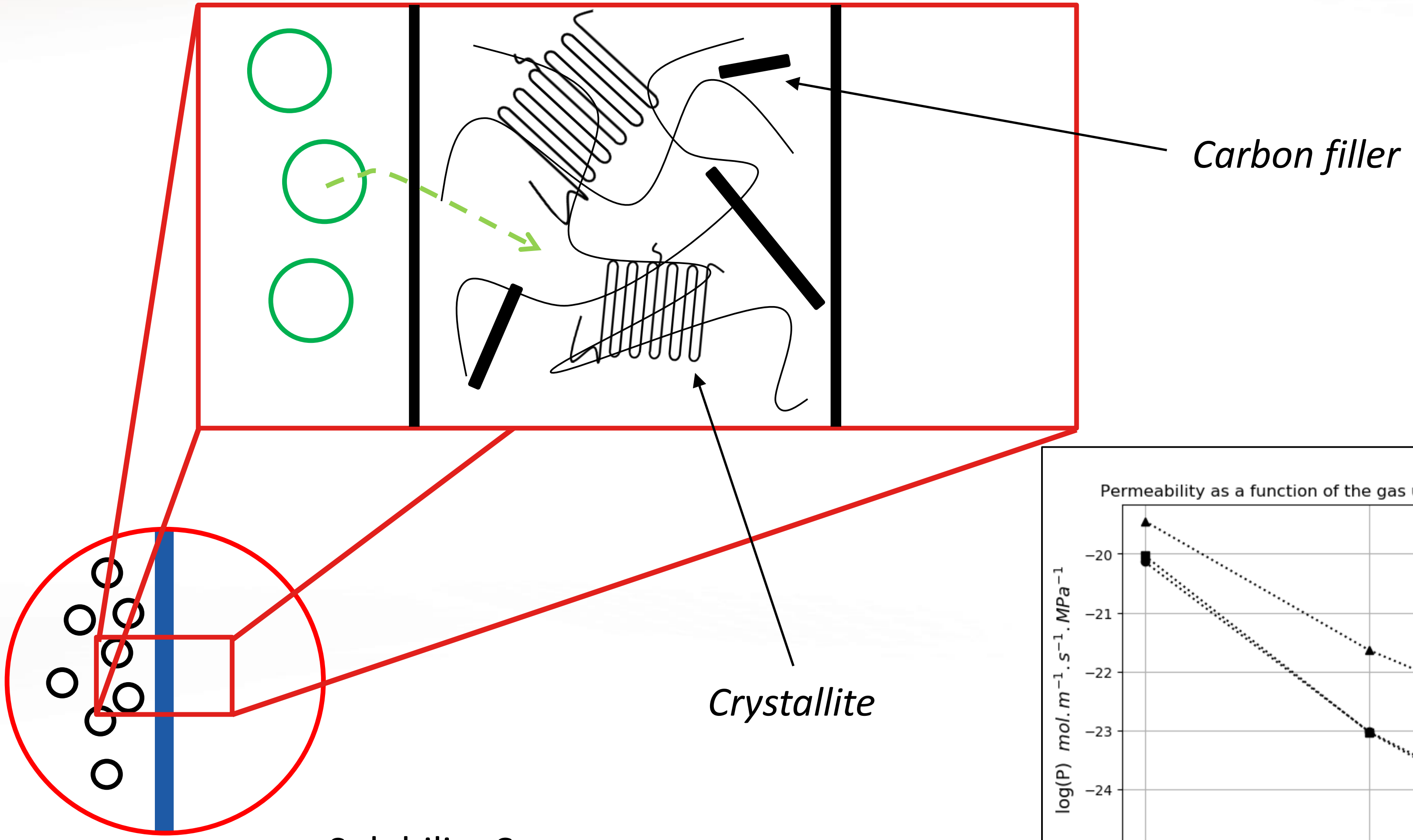
Solubility **S**
(mol.MPa^{-1}m^{-3})

Permeability theory

Influencing parameters

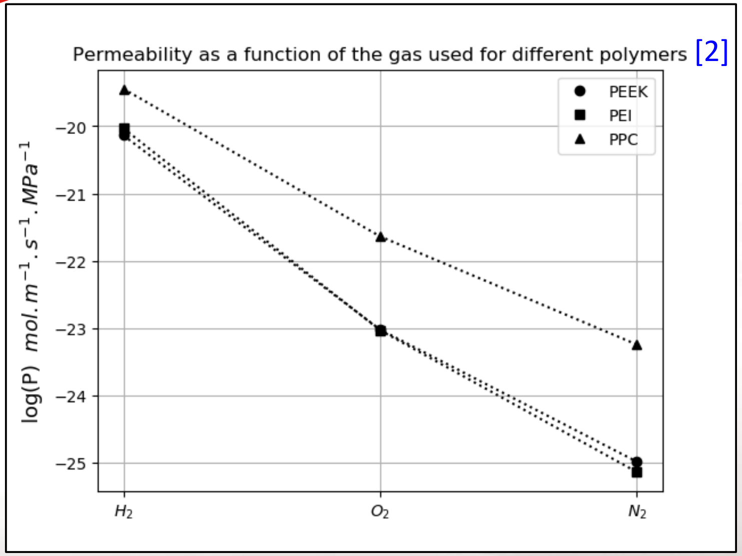
- **Density**
- **Polymer State**
- **Crystallinity**
- **Carbon Content**
- **Gas size**
- **And more**

Permeability **P**
($mol.m.m^{-2}MPa^{-1}s^{-1}$)



Diffusion **D**
($m^2.s^{-1}$)

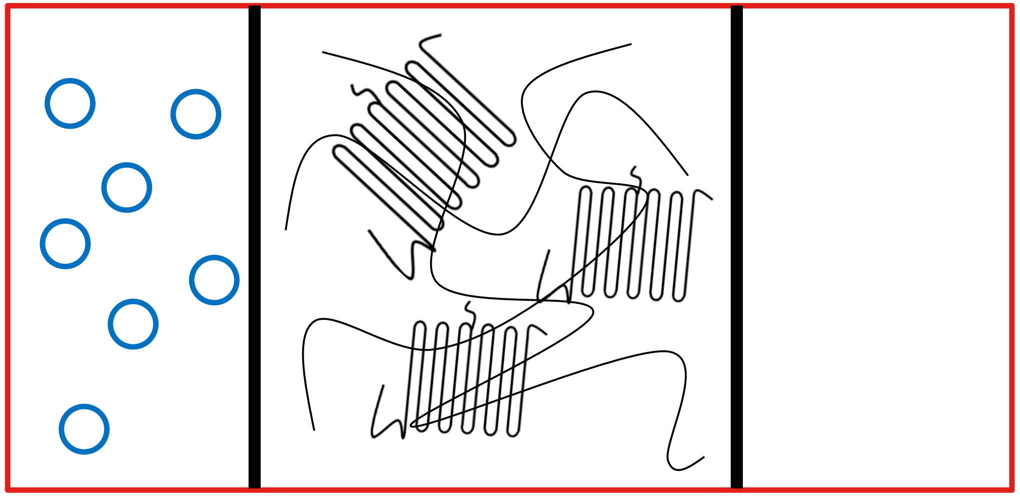
Solubility **S**
($mol.MPa^{-1}m^{-3}$)



[2] : Monson et al. – J. APPL. POLYM. SCI. - 2013

Permeability theory

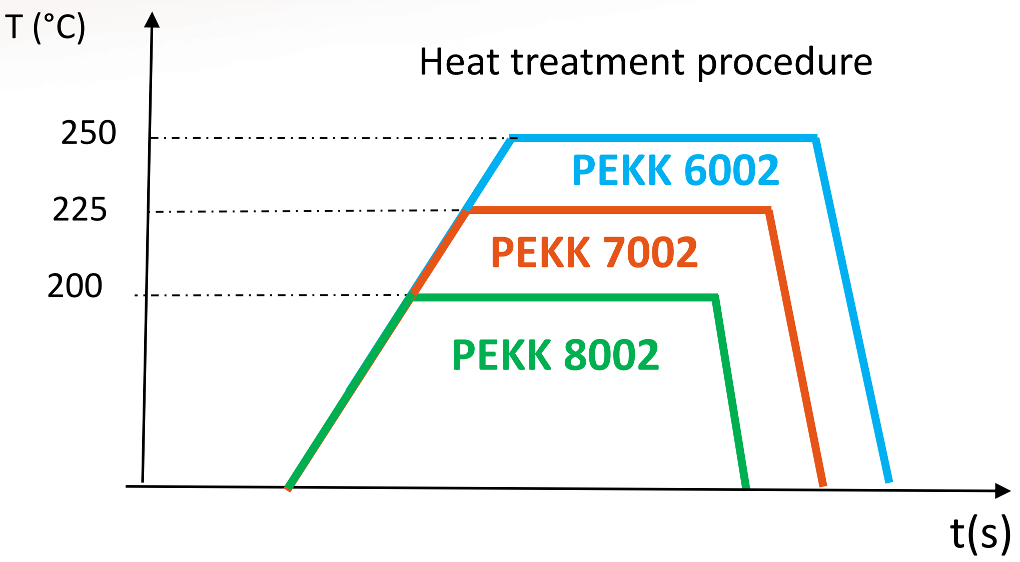
Influencing parameters



Carbon Content | Density | **Crystallinity** | Polymer State | Gas size

How the semi-crystalline microstructure of thermoplastic polymers influences its permeability ?

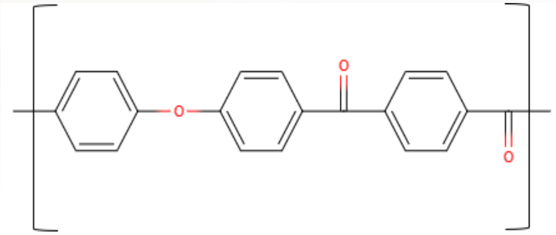
PEKK grades for investing the effect of crystallinity



PEKK	6002		7002		8002	
	AR	CC	AR	CC	AR	CC
Xc (%)	1.1	22	1.2	28	6.2	33

* AR = As Received ; CC = Cold Crystallized

Crystallinity of the as received (AR) PEKK 6002. 7002 and 8002 films and cold crystallized (CC) films determined from DSC results at 10°C/min

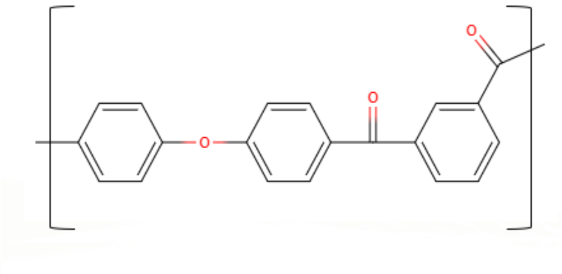


(T)

PEKK	6002	7002	8002
Monomer	--------------$C_{20}H_{12}O_3$--------------		
T_g (°C)	160	162	165
T_m (°C)	305	332	358
T/I Ratio	60/40	70/30	80/20

[3]

Monomers of the T and I forms



(I)

[3] : T. Choupin – PhD ParisTech - 2017

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Measurement of helium permeability, diffusion and solubility

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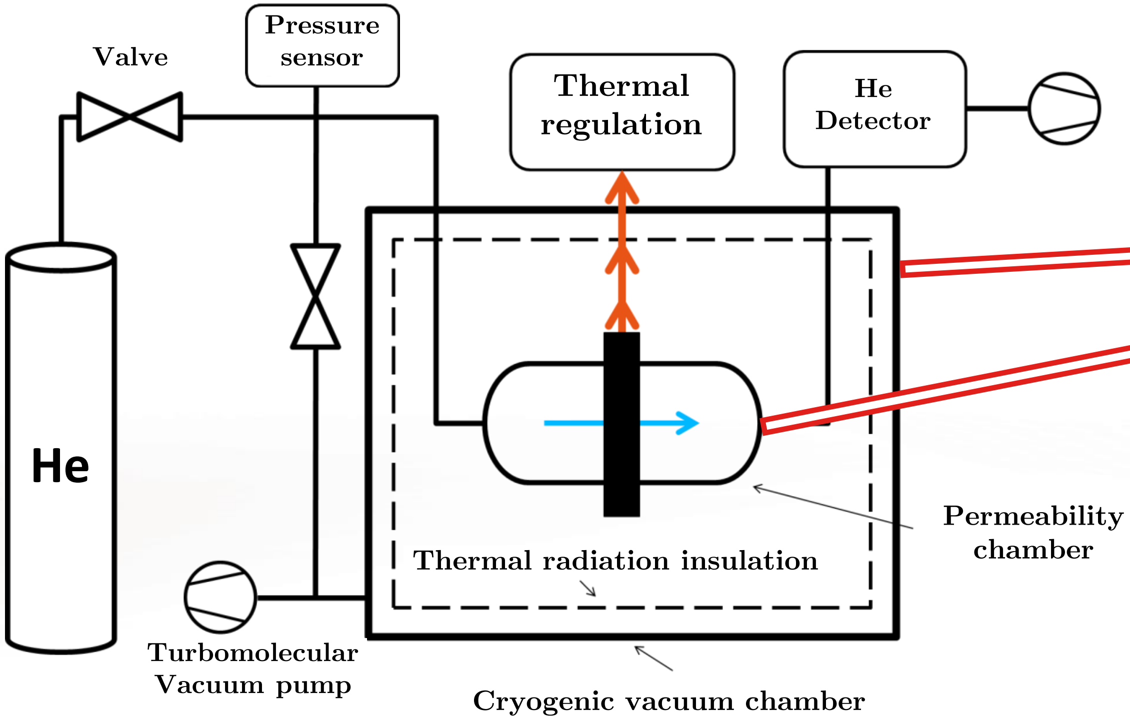
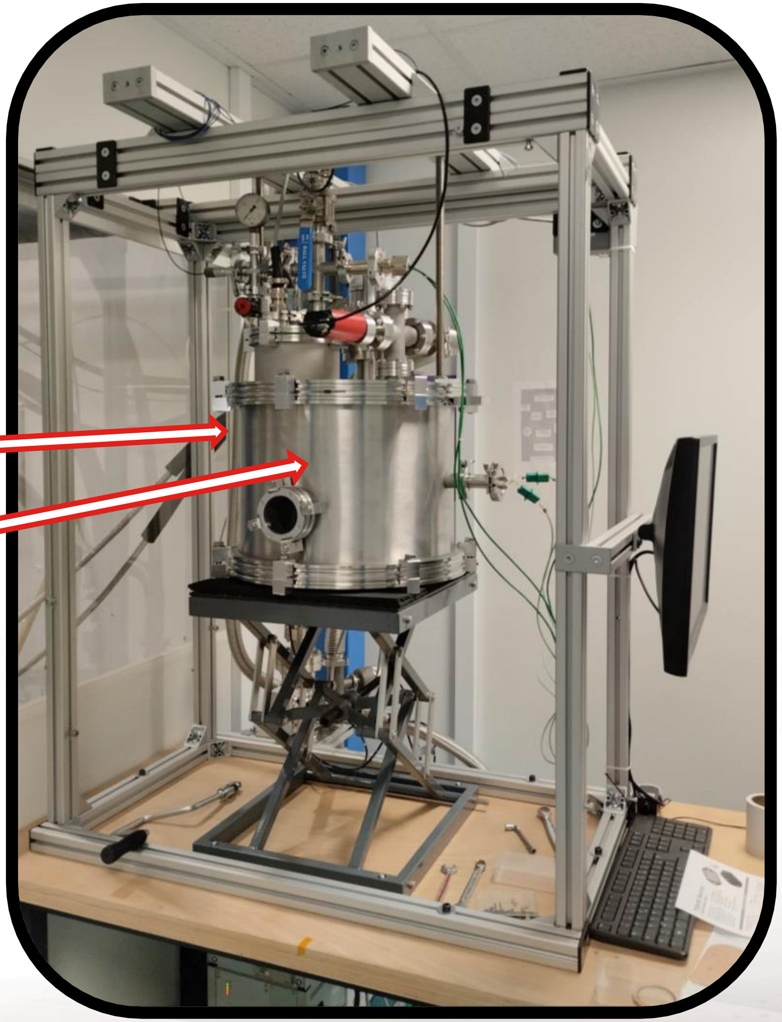
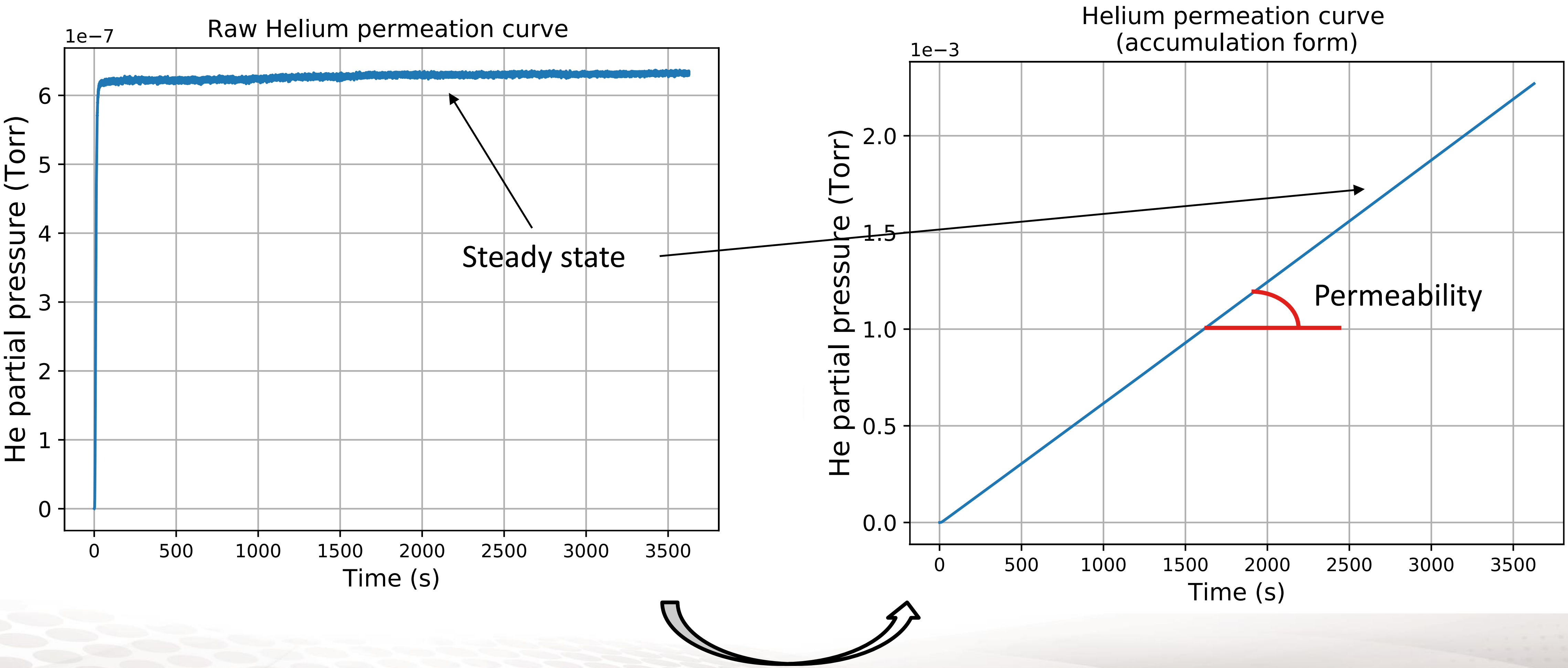
➢ Permeability Apparatus





Measurement of permeability, diffusion and solubility

Raw data



$$p_{He,acc}(i) = p_{He,acc}(i-1) + p_{He}(i)$$

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Experimental permeability, diffusion and solubility of PEKK grades

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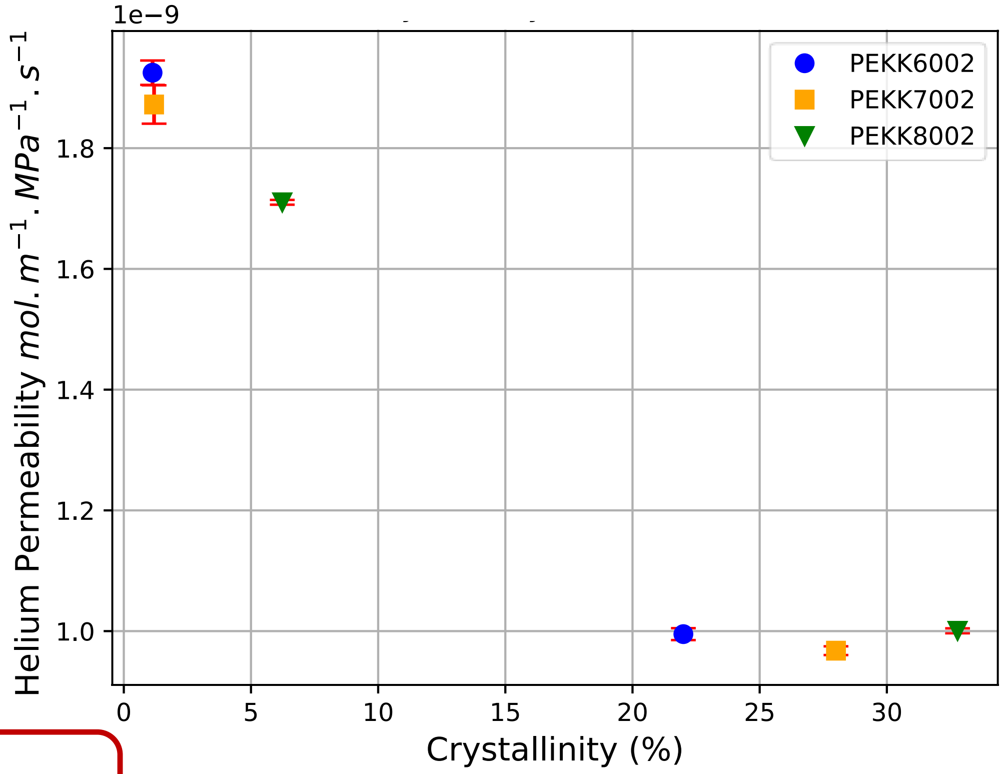
Helium permeability, diffusion and solubility results of PEKK for 0,5 bar of differential pressure at 293K

PEKK	6002 ●		7002 ■		8002 ▼	
	AR	CC	AR	CC	AR	CC
Permeability (mol/m/s/MPa) $\times 10^9$	1.93	0.995	1.87	0.968	1.71	1.00
Diffusion (m^2/s) $\times 10^{10}$	1.69	1.20	1.66	1.26	1.55	1.34
Solubility ($mol/m^3/MPa$)	11.4	8.28	11.3	7.67	11.0	7.46



Can we consider all materials identical in terms of permeability ?
→ Is there a crystallinity threshold above which permeability remains constant ?

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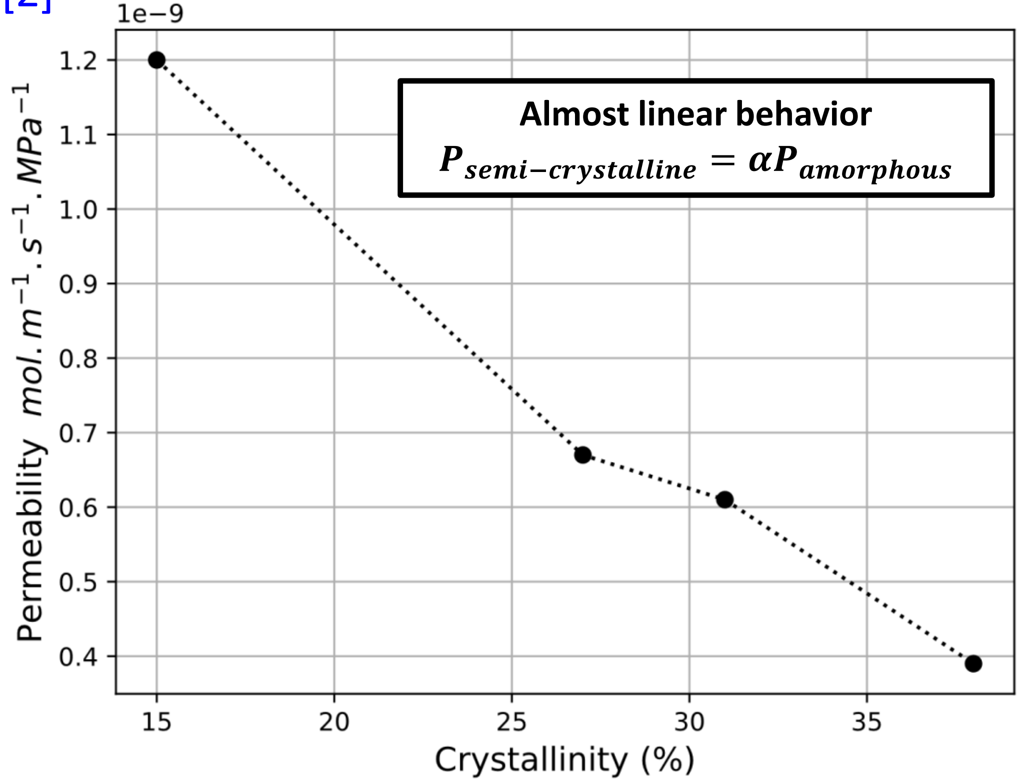
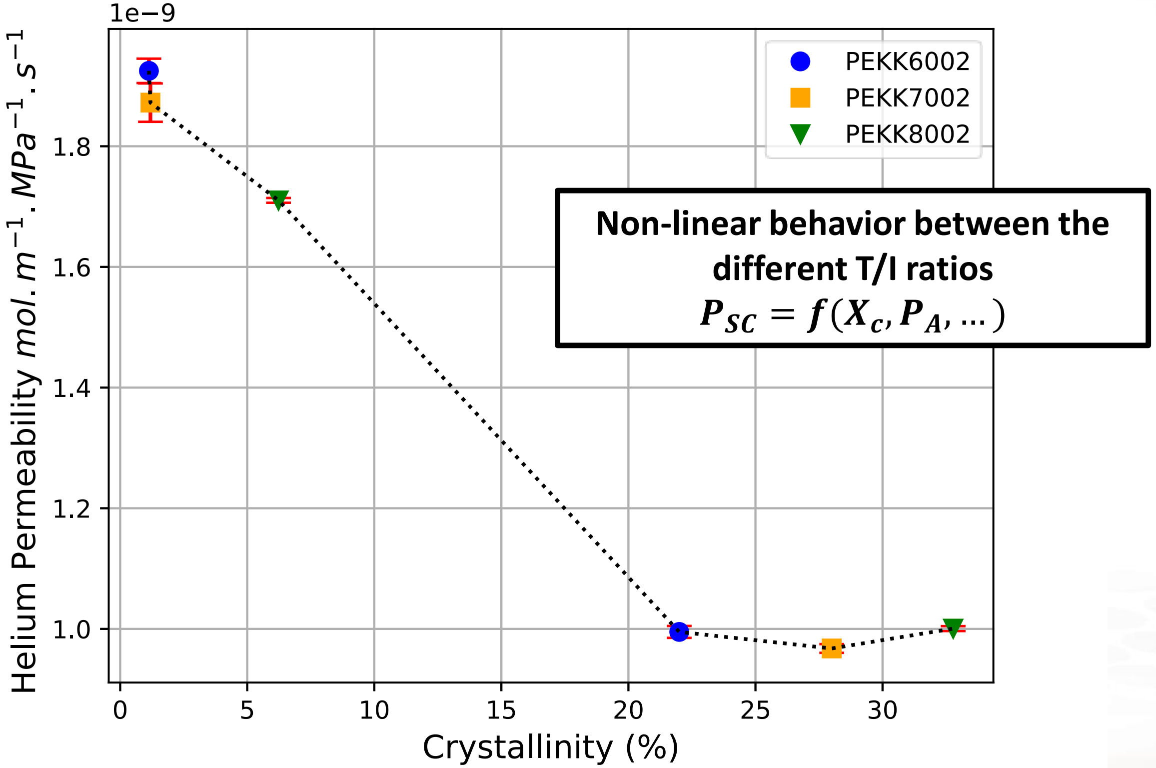
Experimental permeability, diffusion and solubility of PEKK grades

[2]





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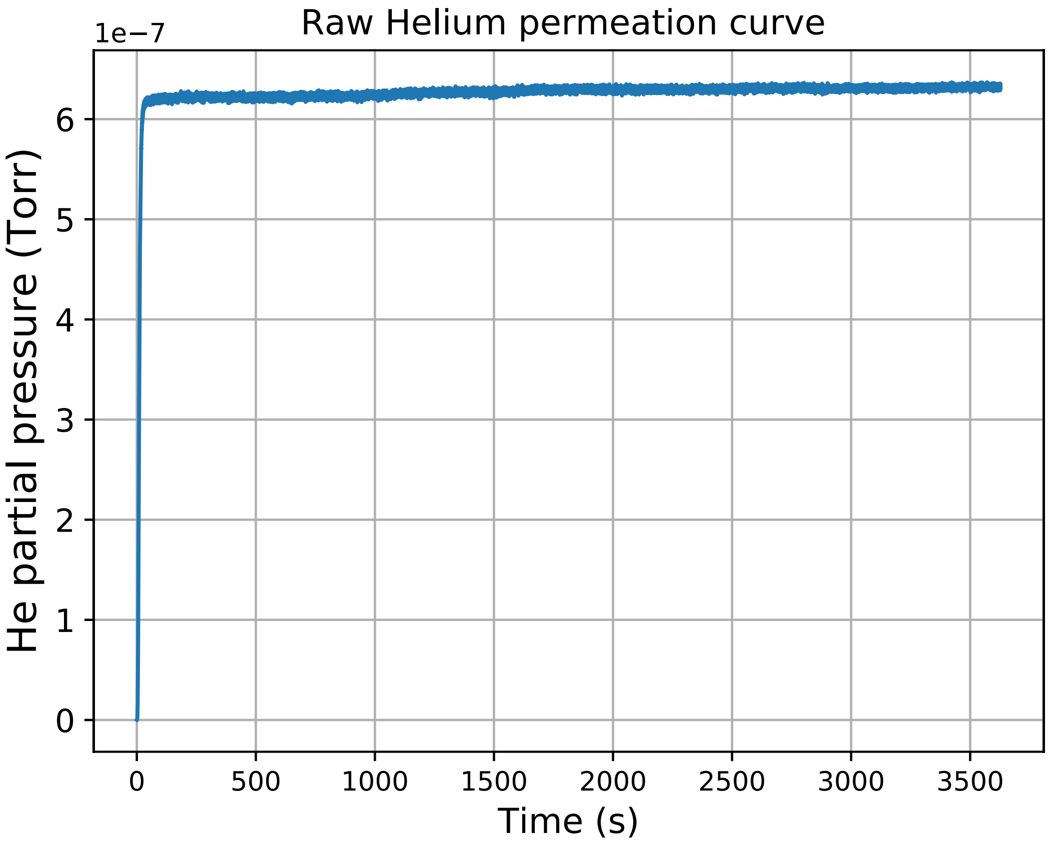
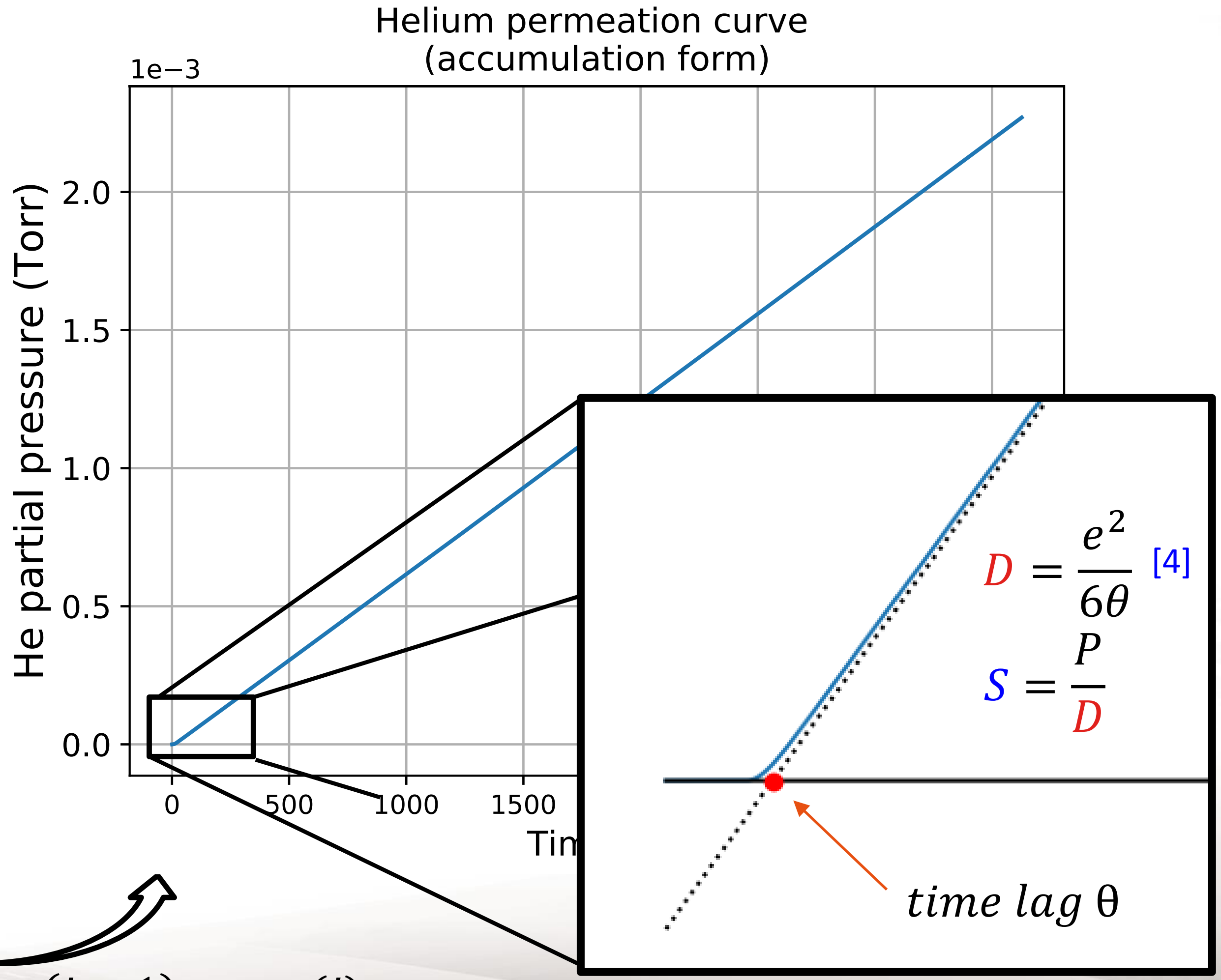
[2] : Monson et al. – J. APPL. POLYM. SCI. - 2013

Measurement of permeability, diffusion and solubility

Raw data





$$p_{He,acc}(i) = p_{He,acc}(i-1) + p_{He}(i)$$

[4] : J. Crank – "The mathematics of diffusion" - 1975

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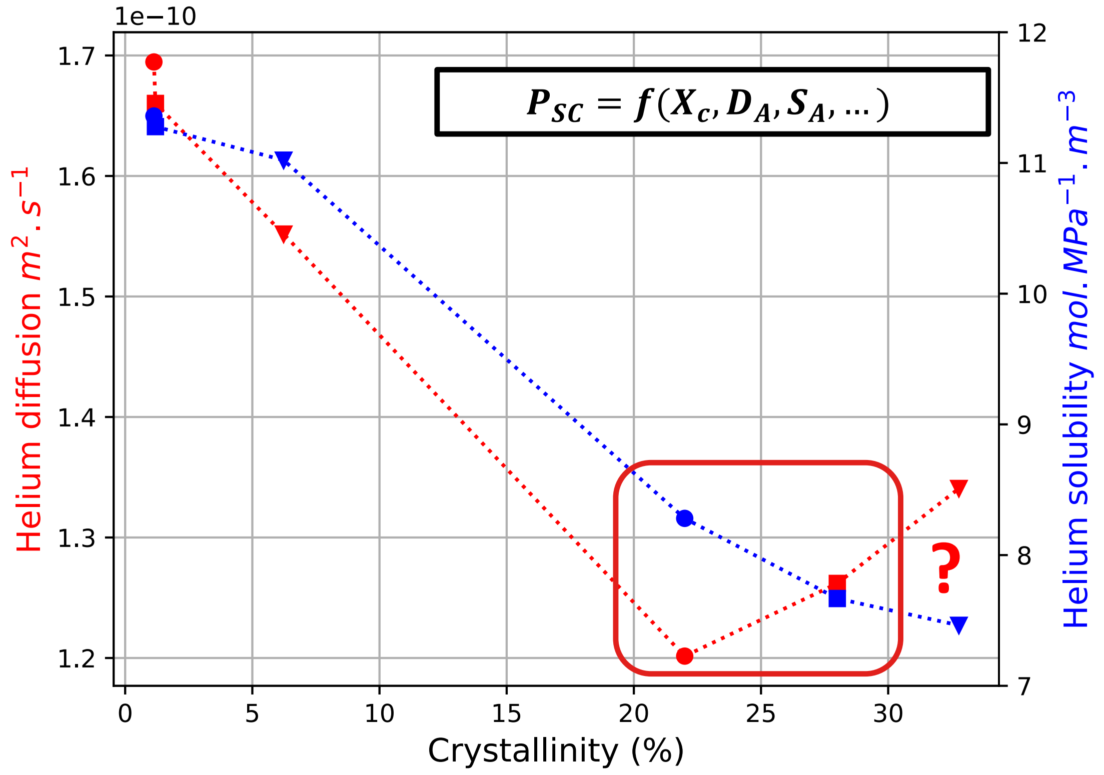
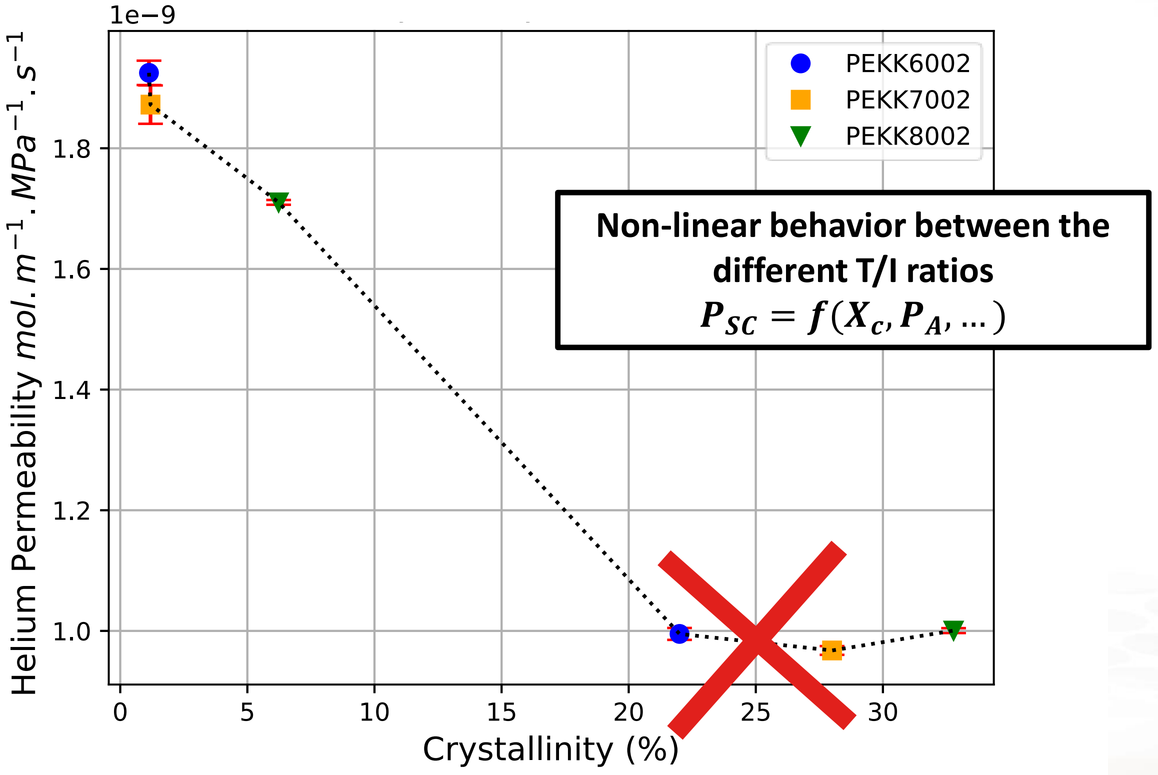
Experimental permeability, diffusion and solubility of PEKK grades





Can we consider all materials identical in terms of permeability ?
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Permeability as a function of T/I ratio

[2] : Monson et al. – J. APPL. POLYM. SCI. - 2013

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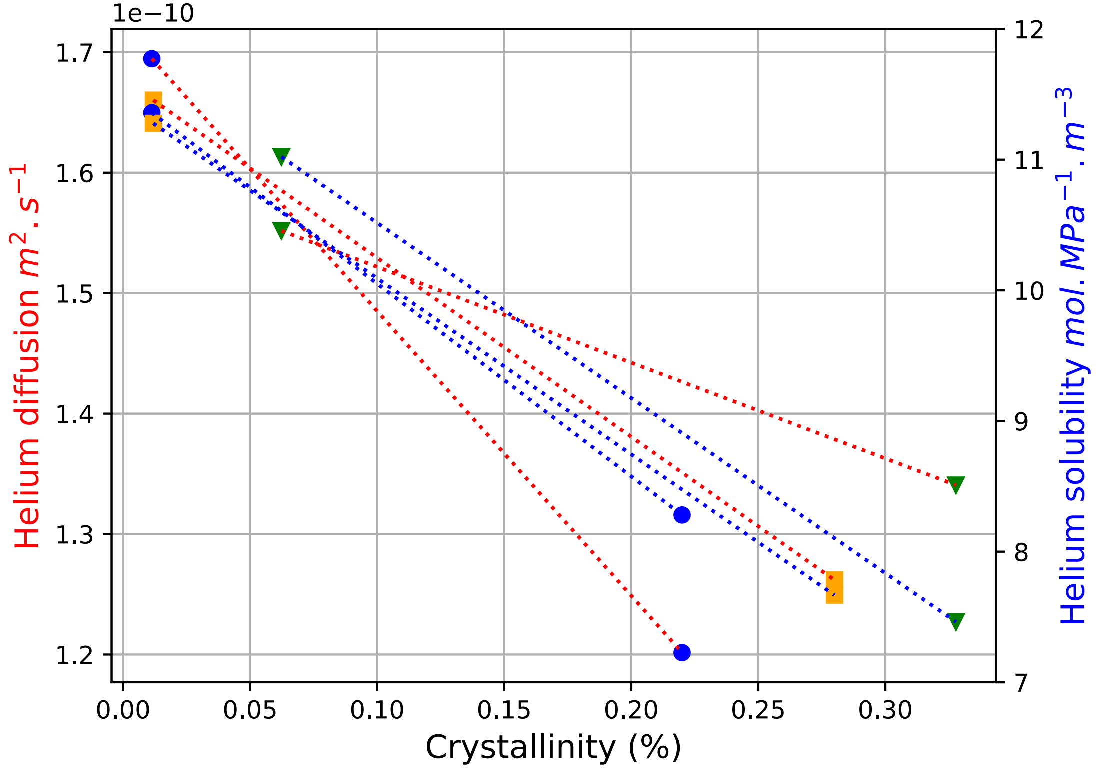
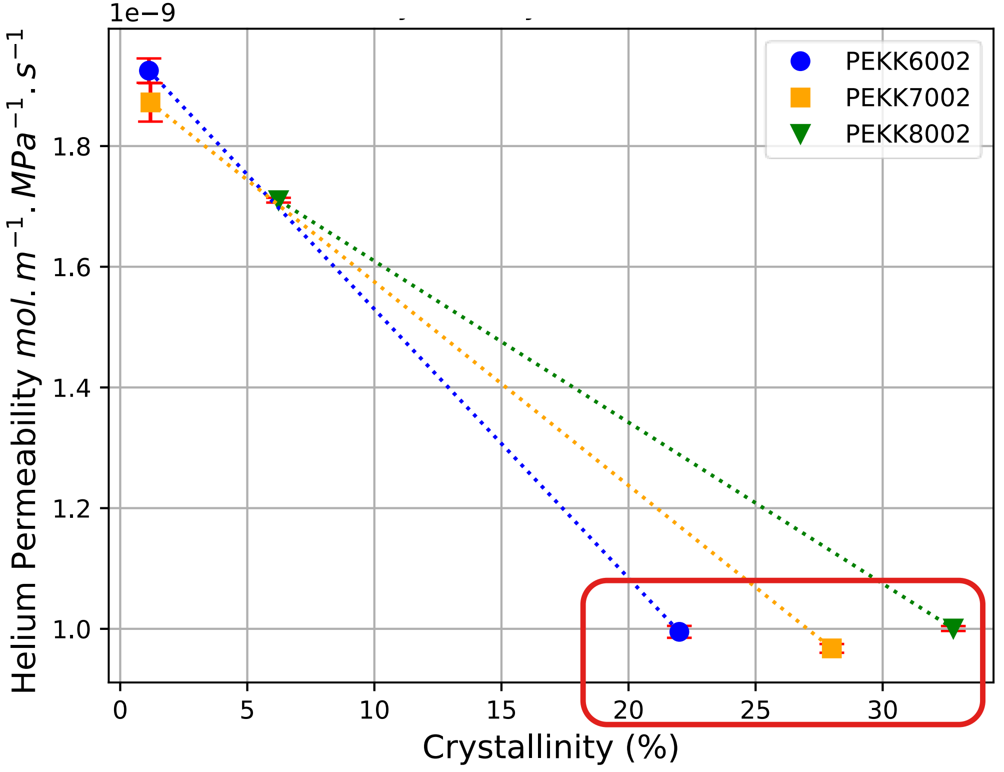
Experimental permeability, diffusion and solubility of PEKK grades





Which model can explain the influence of the T/I ratio on permeability ?

Permeability vs. Crystallinity

Two-Phase Model (2PM)

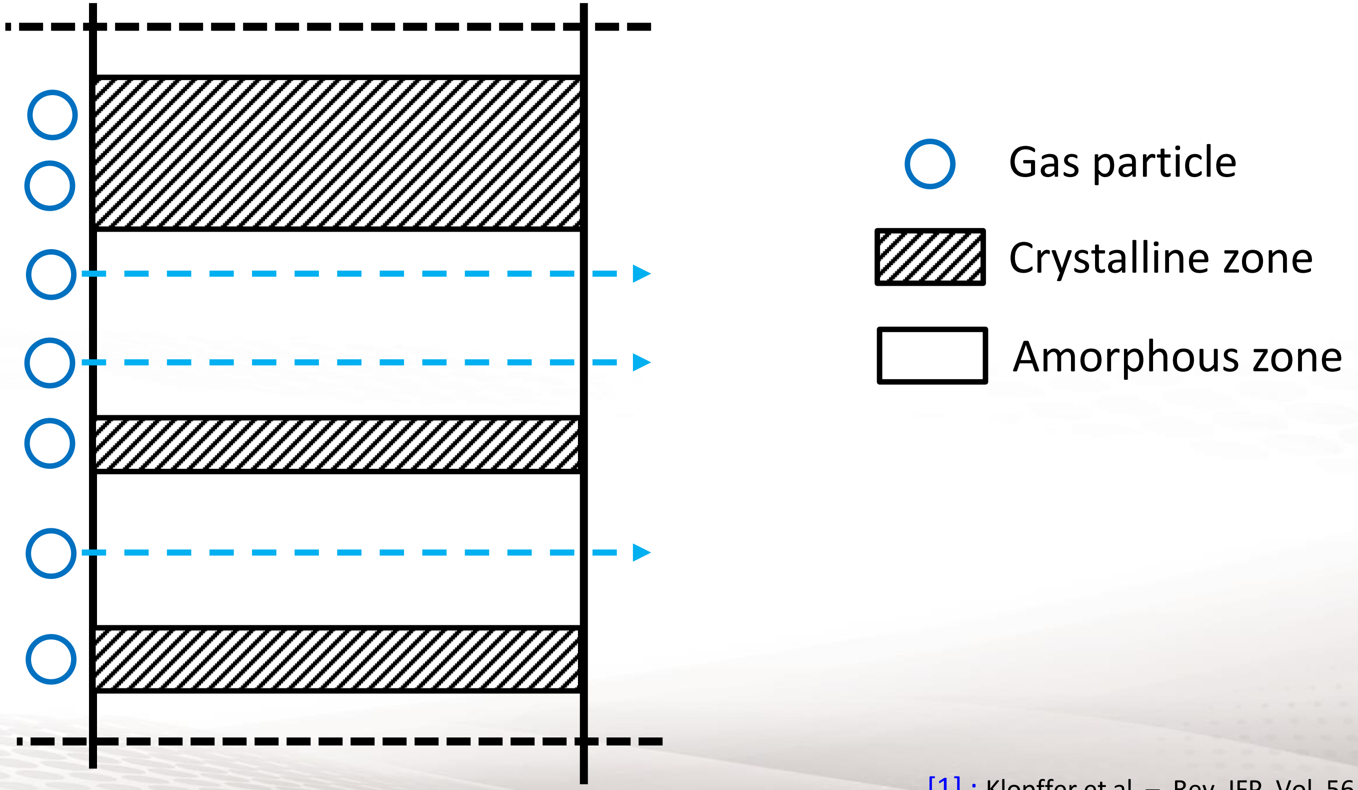
PEKK	6002		7002		8002	
	AR	CC	AR	CC	AR	CC
Xc (%)	1.10	22.0	1.20	28.0	6.20	33.0

* AR = As Received ; CC = Cold Crystallized

« Two-Phase Model (2PM) » [1]

$$P_{SC} = (1 - X_c)D_a \times (1 - X_c)S_a$$
$$P_{SC} = (1 - X_c)^2 P_a$$

SC = Semi-Crystalline
A = Amorphous



[1] : Klopffer et al. – Rev. IFP, Vol. 56 - 2001

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Permeability vs. Crystallinity

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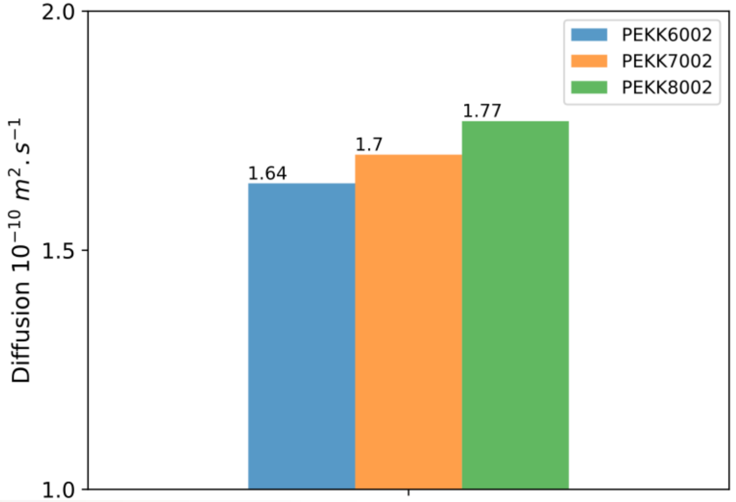

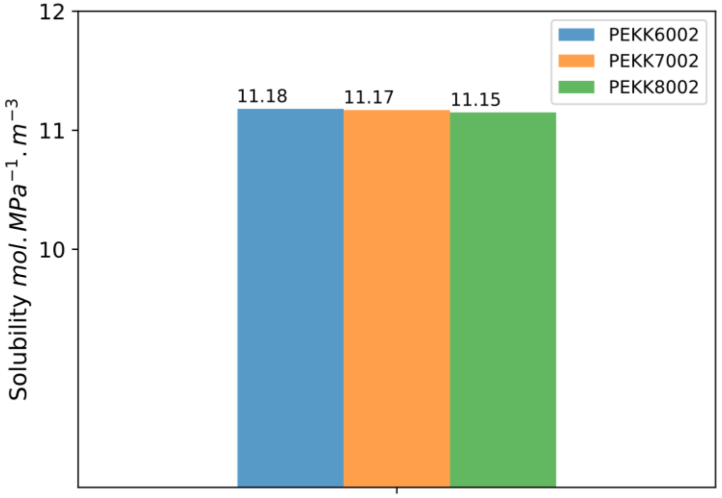

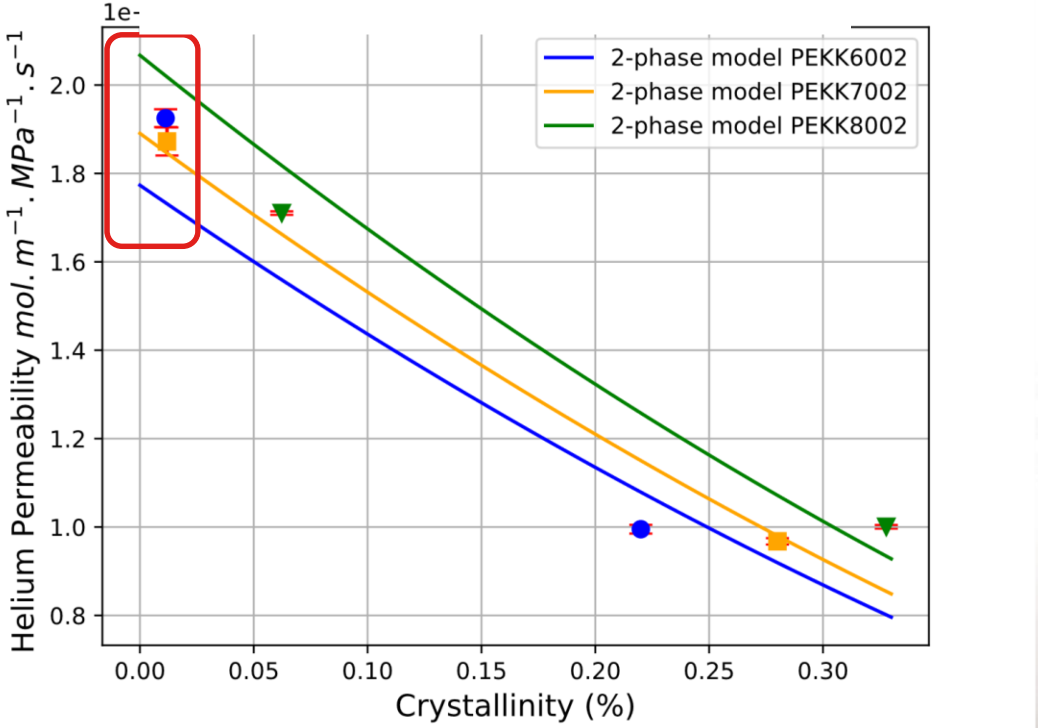

The 2-phase Model provides a rough prediction without describing the effect of the T/I ratio on the change in permeability.

[1] : Klopffer et al. – Rev. IFP, Vol. 56 - 2001

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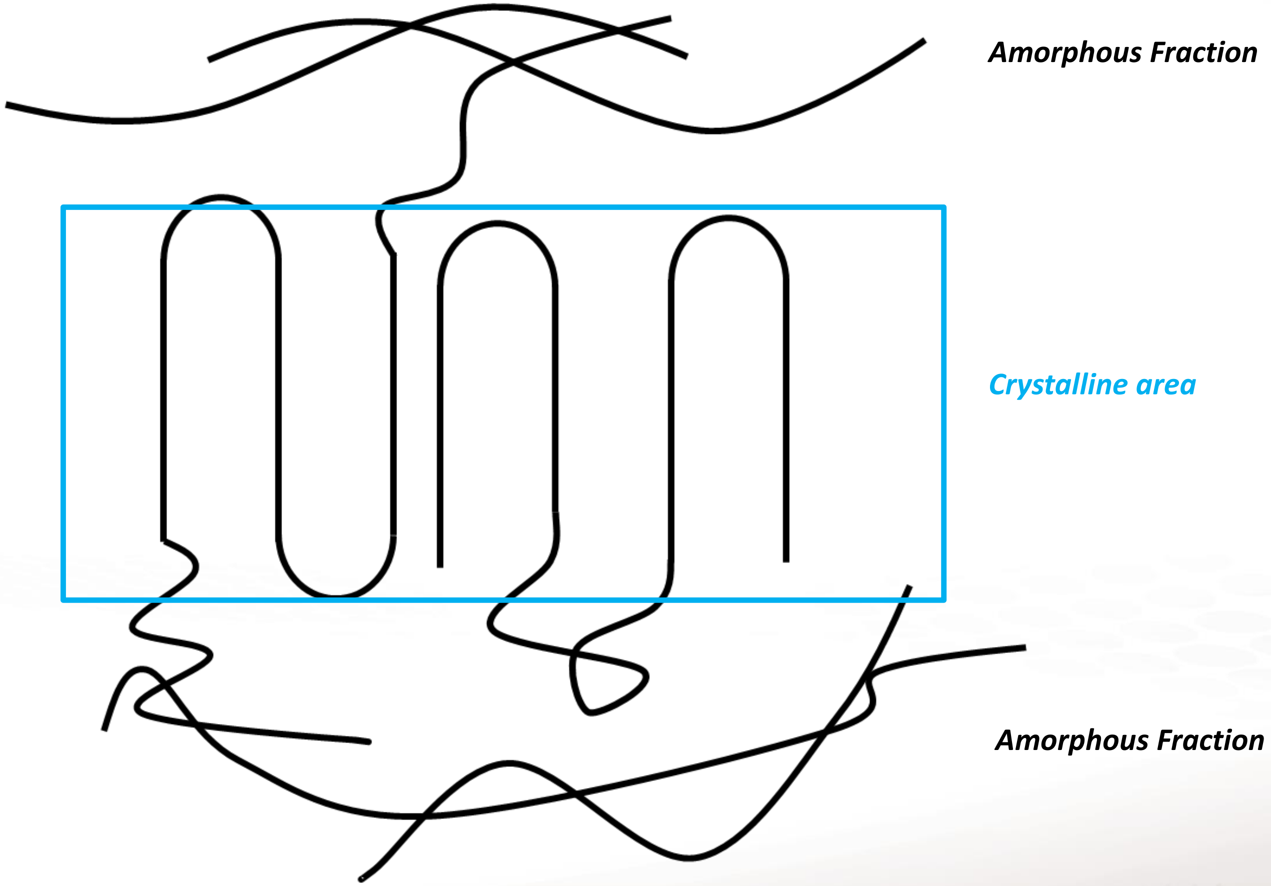
Permeability vs. Crystallinity

Refining the Two-Phase Model (2PM)

PEKK	6002 AR	6002 CC	7002 AR	7002 CC	8002 AR	8002 CC
Xc (%)	1.10	22.0	1.20	28.0	6.20	33.0

* AR = As Received ; CC = Cold Crystallized

$$\begin{cases} X_c = \dfrac{\Delta h_m - \Delta h_{cf}}{\Delta h_{100\%}} \\ X_A = \dfrac{\Delta C_p(T_g)}{\Delta C_{p.0\%}(T_g)} \\ X_A = 1 - X_c \end{cases}$$



[6] : Sonchaeng et al. - Prog. Polym. Sci. Vol. 86 - 2018

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[6]

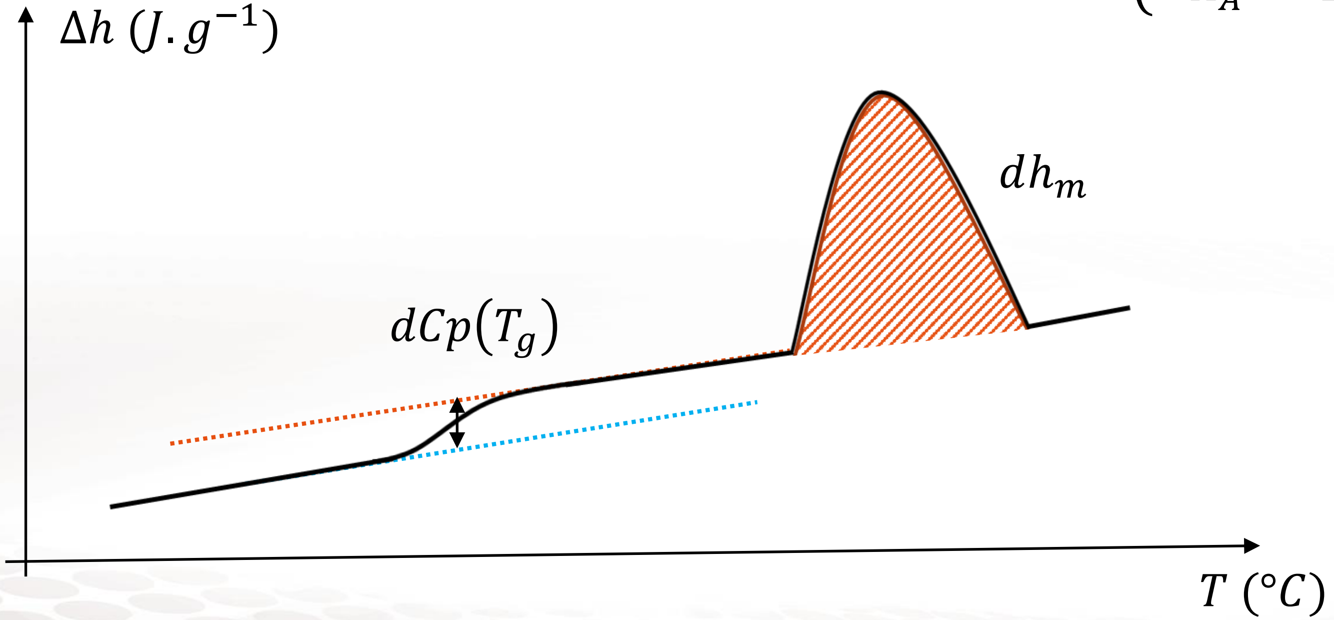
$$X_c = \frac{\Delta h_m - \Delta h_{cf}}{\Delta h_{100\%}}$$

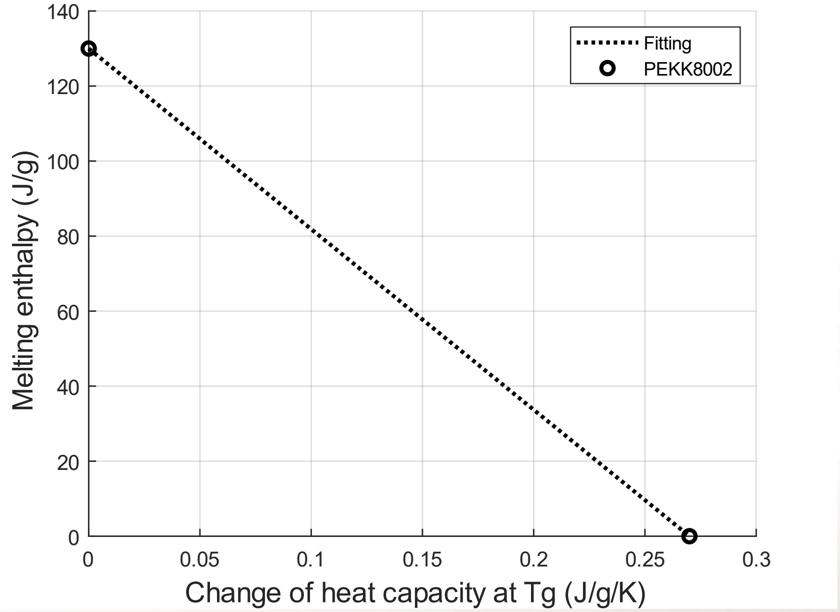
$\Delta h_{100\%}$ → 130 J.g^{-1} [5]

$$X_A = \frac{\Delta C_p(T_g)}{\Delta C_{p.0\%}(T_g)}$$

$\Delta C_{p.0\%}(T_g)$ → 0.27 J.K^{-1}.g^{-1} (PEEK [7])

$$X_A = 1 - X_c$$





Linearity considering a 2-phase model

[5] : Blundell et al. – Polymer, Vol. 24 - 1983
[6] : Sonchaeng et al. - Prog. Polym. Sci. Vol. 86 – 2018
[7] : B. Wunderlich - Pure Appl. Chem.. vol. 67 -1995

Permeability vs. Crystallinity

Three-Phase Model (3PM)

PEKK	6002 AR	6002 CC	7002 AR	7002 CC	8002 AR	8002 CC
Xc (%)	1.10	22.0	1.20	28.0	6.20	33.0

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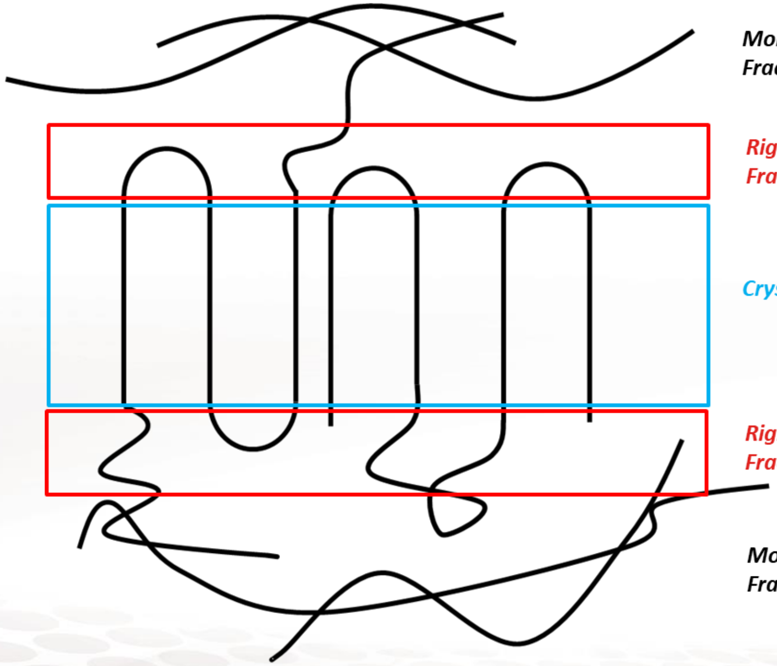

[6]

$$X_c = \frac{\Delta h_m - \Delta h_{cf}}{\Delta h_{100\%}}$$

$\Delta h_{100\%}$ → 130 J.g^{-1} [5]

$$X_{MAF} = \frac{\Delta C_p(T_g)}{\Delta C_{p.0\%}(T_g)}$$

$\Delta C_{p.0\%}(T_g)$ → 0.27 J.K^{-1}.g^{-1} (PEEK [7])

$$X_{RAF} = 1 - X_{MAF} - X_c$$

« Three-Phases Model (3PM) » [6]

$$D_{SC} = X_{MAF} D_{MAF} + X_{RAF} D_{RAF}$$
$$S_{SC} = X_{MAF} S_{MAF} + X_{RAF} S_{RAF}$$
$$P_{SC} = D_{SC} \times S_{SC}$$

[5] : Blundell et al. – Polymer, Vol. 24 - 1983
[6] : Sonchaeng et al. - Prog. Polym. Sci. Vol. 86 – 2018
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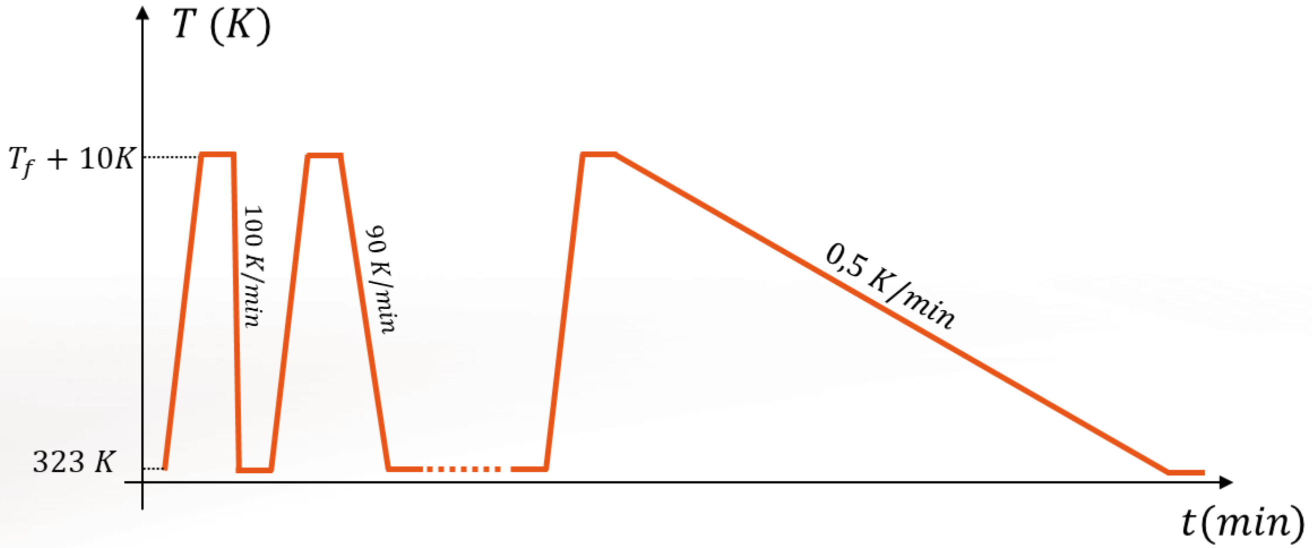


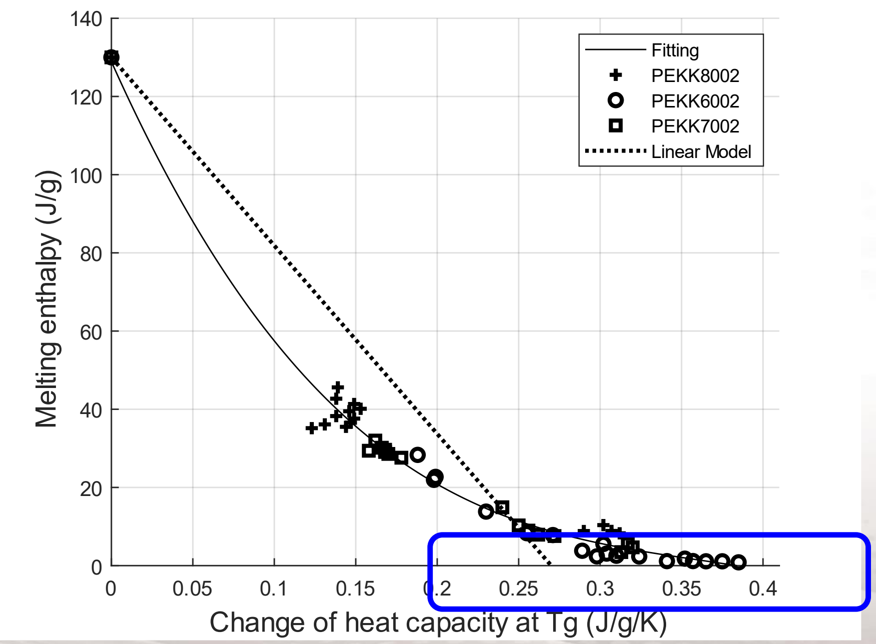
[6]

$$X_c = \frac{\Delta h_m - \Delta h_{cf}}{\Delta h_{100\%}}$$

$$X_{MAF} = \frac{\Delta C_p(T_g)}{\Delta C_{p.0\%}(T_g)}$$

$$X_{RAF} = 1 - X_{MAF} - X_c$$

$0.384\ J.K^{-1}.g^{-1}$ (≠PEEK [7])



dHm = f(dCp) identical for all 3 grades

Same thermal behavior but different permeation behavior

[6] : Sonchaeng et al. - Prog. Polym. Sci. Vol. 86 - 2018 [7] : B. Wunderlich - Pure Appl. Chem.. vol. 67 -1995

Permeability vs. Crystallinity

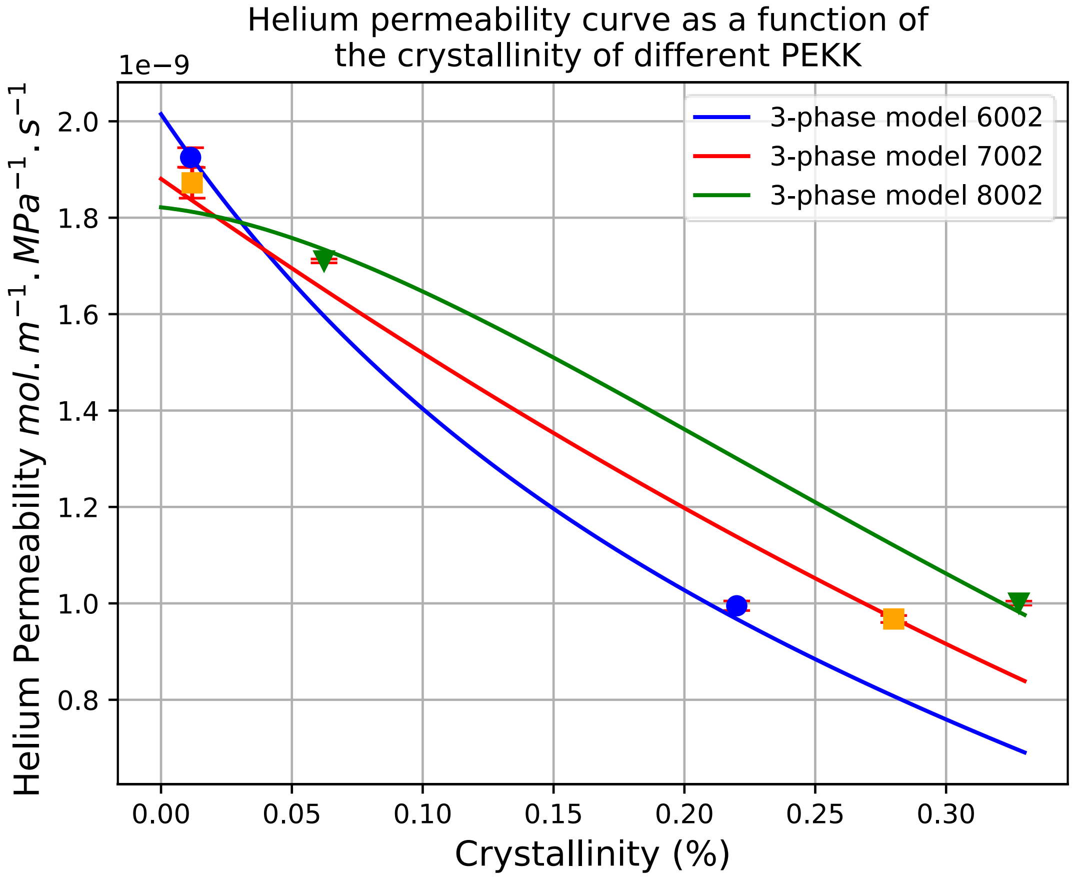
Three-Phase Model (3PM)

PEKK	6002 AR	6002 CC	7002 AR	7002 CC	8002 AR	8002 CC
Xc (%)	1.10	22.0	1.20	28.0	6.20	33.0
MAF(%)	90.3	47.0	84.6	40.0	75.4	30.0
RAF(%)	8.60	31.0	14.2	32.0	18.4	37.0

* AR = As Received ; CC = Cold Crystallized

« Three-Phase Model (3PM) » [6]

$$D_{SC} = X_{MAF}D_{MAF} + X_{RAF}D_{RAF}$$
$$S_{SC} = X_{MAF}S_{MAF} + X_{RAF}S_{RAF}$$
$$P_{SC} = D_{SC} \times S_{SC}$$



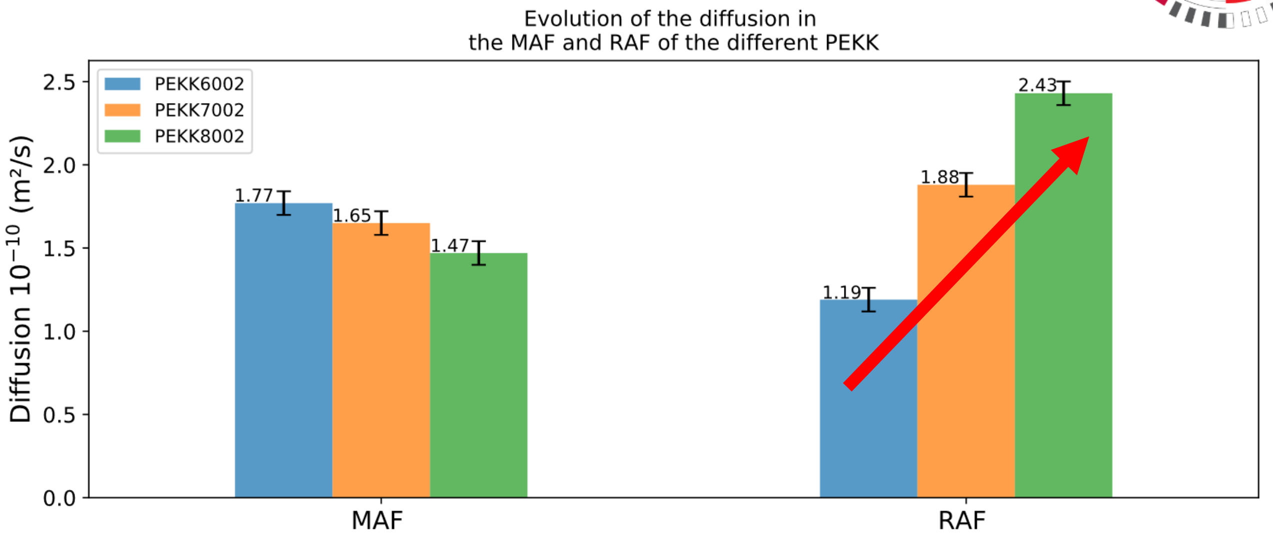
[6] : Sonchaeng et al. - Prog. Polym. Sci. Vol. 86 – 2018

Permeability vs. Crystallinity

Three-Phase Model (3PM)

PEKK	6002		7002		8002	
	AR	CC	AR	CC	AR	CC
Xc (%)	1.10	22.0	1.20	28.0	6.20	33.0
MAF(%)	90.3	47.0	84.6	40.0	75.4	30.0
RAF(%)	8.60	31.0	14.2	32.0	18.4	37.0

* AR = As Received ; CC = Cold Crystallized



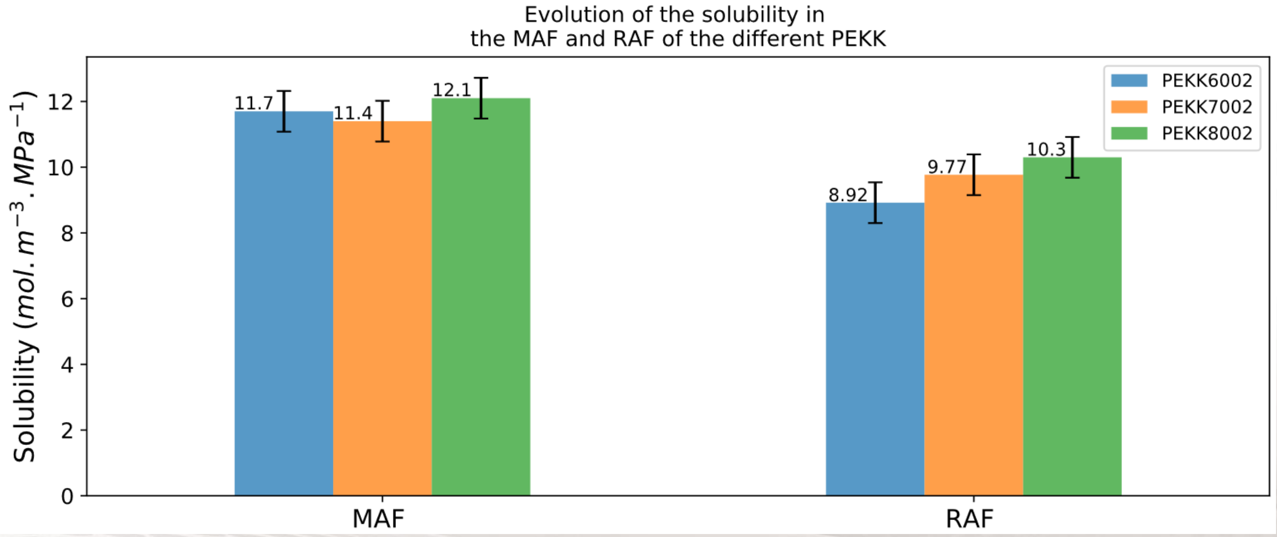
Possible explanations given in literature

$$\begin{cases} \rho_{RAF} < \rho_{MAF} \\ \rho_{RAF} > \rho_{MAF} \end{cases} ?$$

[6]

or

$$FV_{RAF} > FV_{MAF}$$



[6] : Sonchaeng et al. - Prog. Polym. Sci. Vol. 86 – 2018

Conclusions and perspectives

Conclusions

The **crystallinity** is effectively a **key factor** of gas permeability

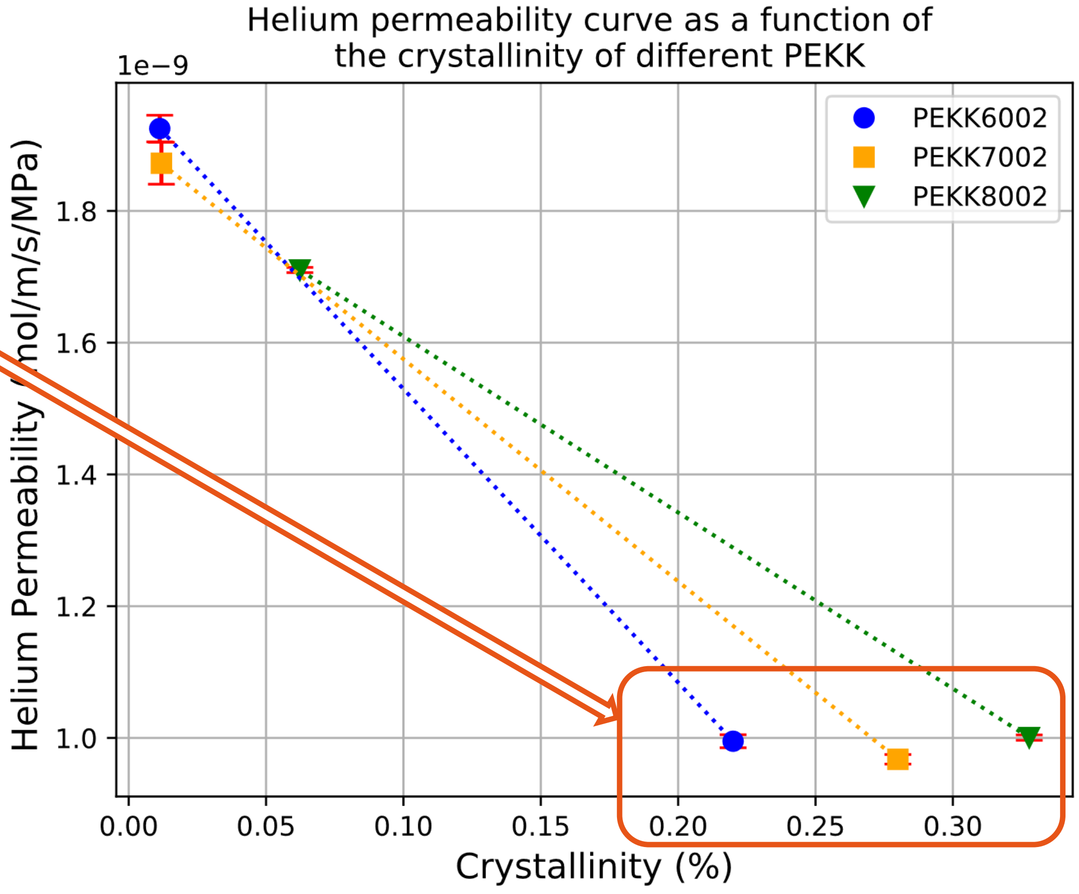
Increasing PEKK **crystallinity does not always decrease gas permeability**

RAF appears to become increasingly diffusible as the T/I ratio increases.

Perspectives

Permeability measurements of **CF/PEKK X002 Composites** are planned

The same samples will be tested in **cryogenic conditions** (down to **55K**)



INFLUENCE OF SEMI-CRYSTALLINE MICROSTRUCTURE ON HYDROGEN PERMEABILITY OF POLY(ETHER-KETONE-KETONE)

THANK YOU FOR YOUR ATTENTION

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