The application of advanced Design of Experiments for the efficient development of spin-on-carbon hard masks

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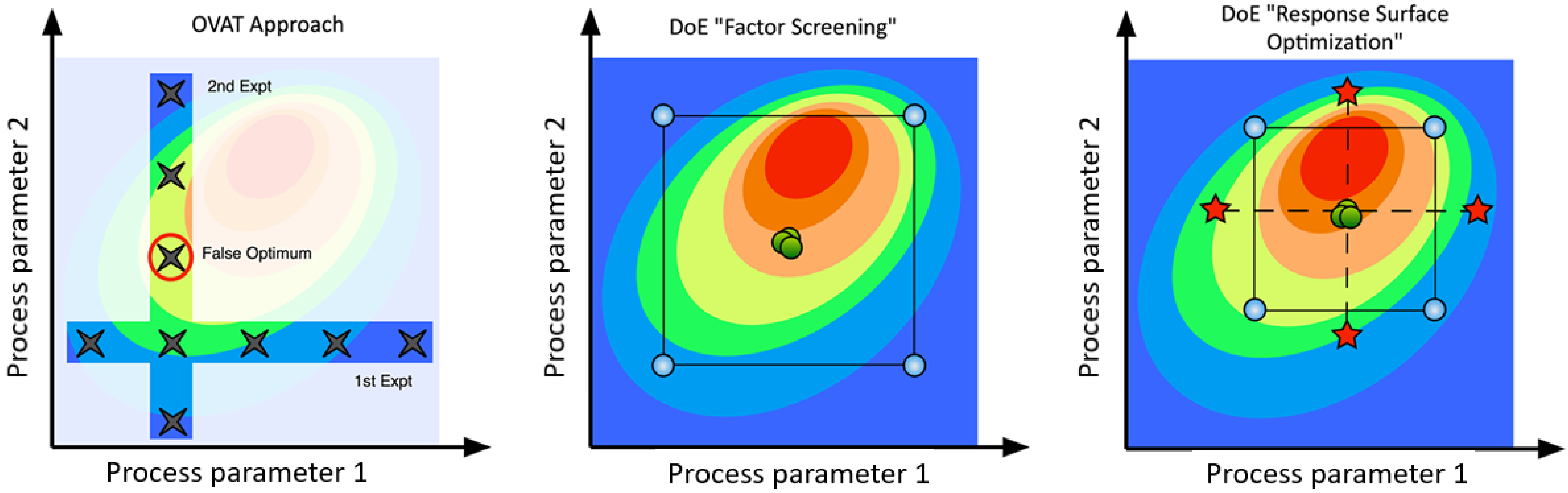
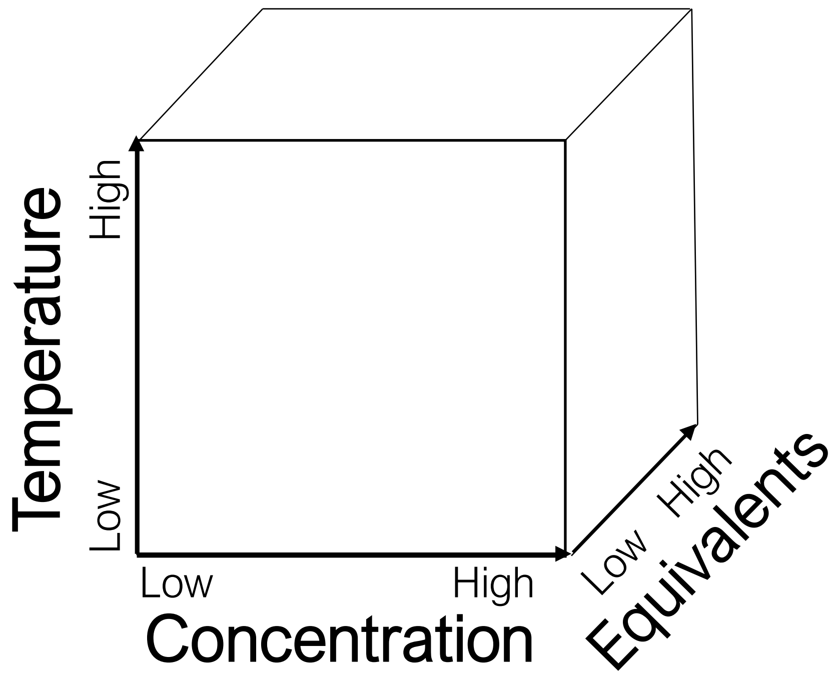
Design of Experiments

- Design of experiments (DoE) is a set of statistical tools.



Continuous factors

- When considering a chemical reaction there are continuous factors, which are easily investigated by DoE such as concentration, temperature, time, pressure, stoichiometry of reagents, catalyst loading and so on.



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Discrete factors

- There are other parameters which are also important in a chemical reaction, but are more difficult to investigate, such as **solvent, catalyst, ligand or monomer**.
- However, **it is possible to correlate these factors** by looking at their chemical and physical properties, allowing investigation by DoE.

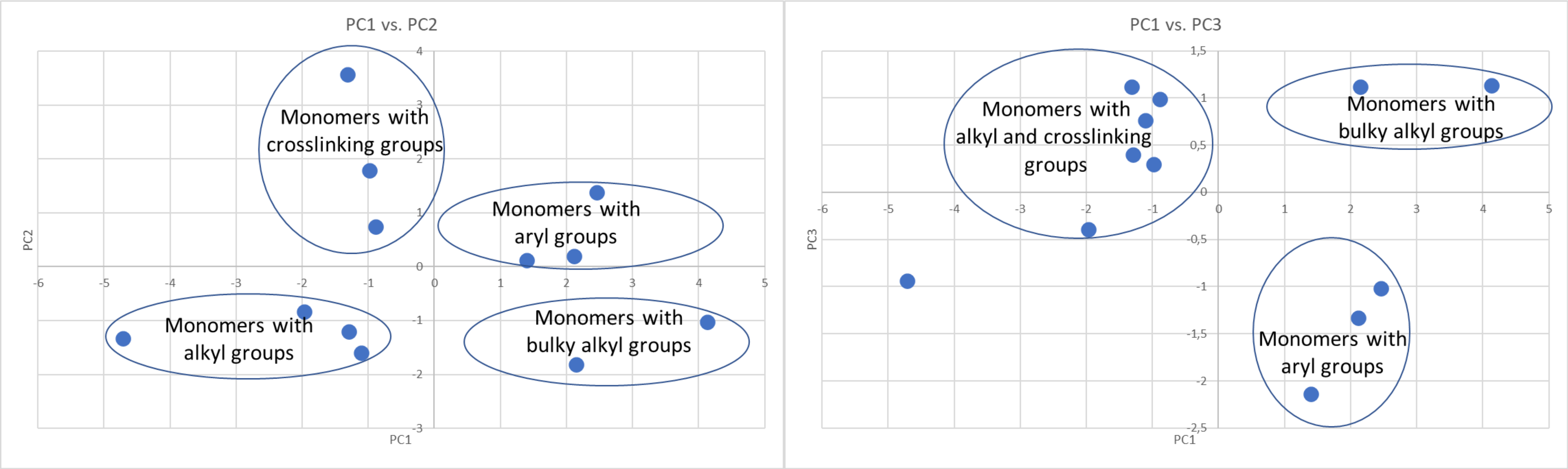
Principal component analysis

- Principal Component Analysis (PCA) is a multivariate data analysis tool.
- PCA allows the creation of new principal components from the multitude of original properties, e.g. leading to 3 properties which can explain over 90% of the variation in the data.

Monomer	Molecular weight	Boiling point	Index of Refraction	Density	Vapour Pressure	Flash Point	Molar Refractivity	Ohnishi Number	LogP	Polar Surface Area	Molar Volume	Surface Tension	Polarizability
1													
2													
3													
4													
5													
6													
7													
8													
9													
10													
11													
12													

Combining PCA and DoE

- The use of a monomer PCA map allows each monomer principal component to be studied in an experimental design just like the standard factors.



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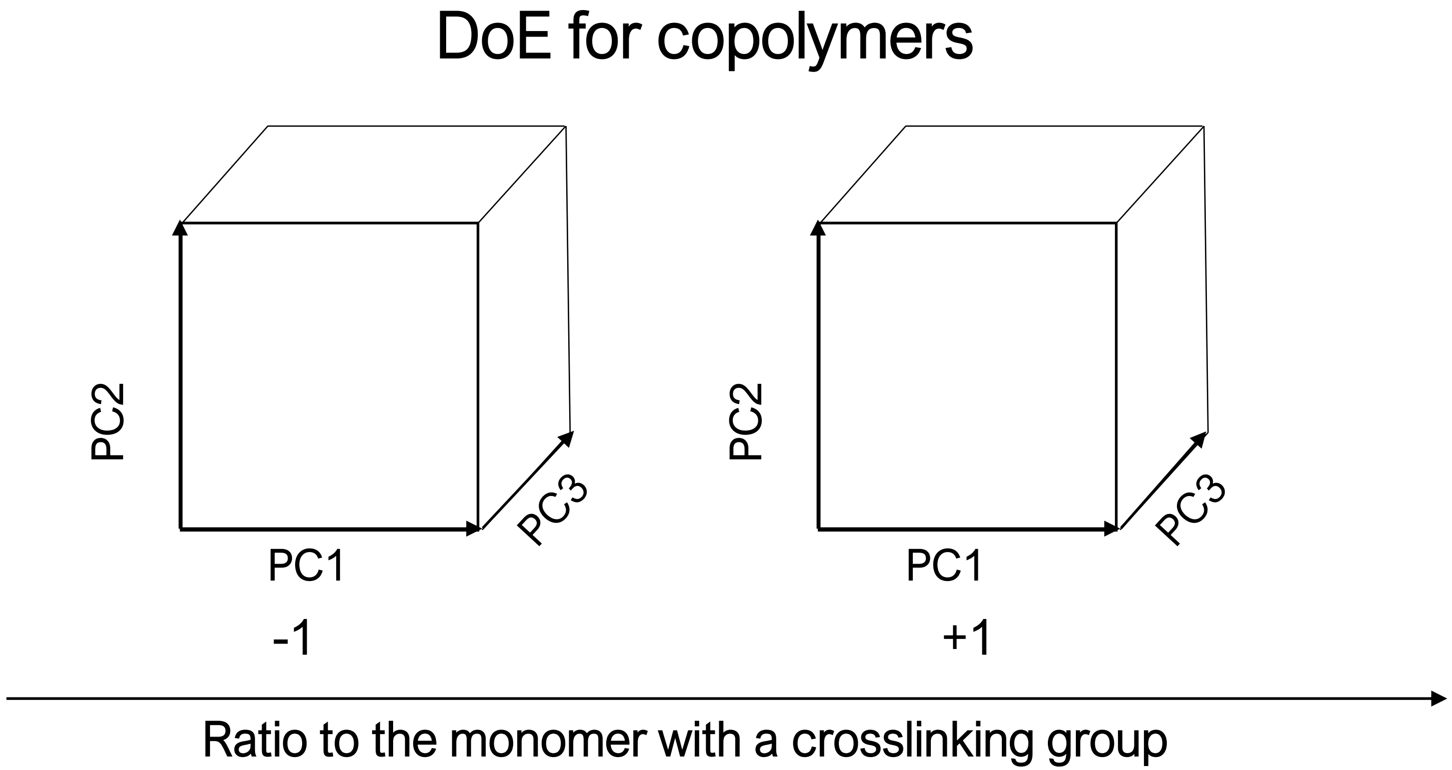
Combining PCA and DoE

- The combination of PCA with DoE allows for a very efficient investigation of the whole chemical space for a given reaction.



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Polymerization results

- 19 out of 22 copolymerizations were successful.

Monomer	PC1	PC3	PC3	Ratio of monomers	n@193nm	k@193nm	Etch rate (nm/min)
1	-4,7	-1,3	-0,9	-1	1,68	0,07	384
1	-4,7	-1,3	-0,9	1	1,69	0,06	371
2	2,5	1,4	-1,0	-1	1,65	0,58	266
2	2,5	1,4	-1,0	1	1,68	0,26	324
….				…			
10	2,1	0,2	-1,3	1	1,83	0,25	308
11	-0,9	0,7	1,0	-1	1,68	0,04	405
11	-0,9	0,7	1,0	1	1,69	0,05	380

Showcase

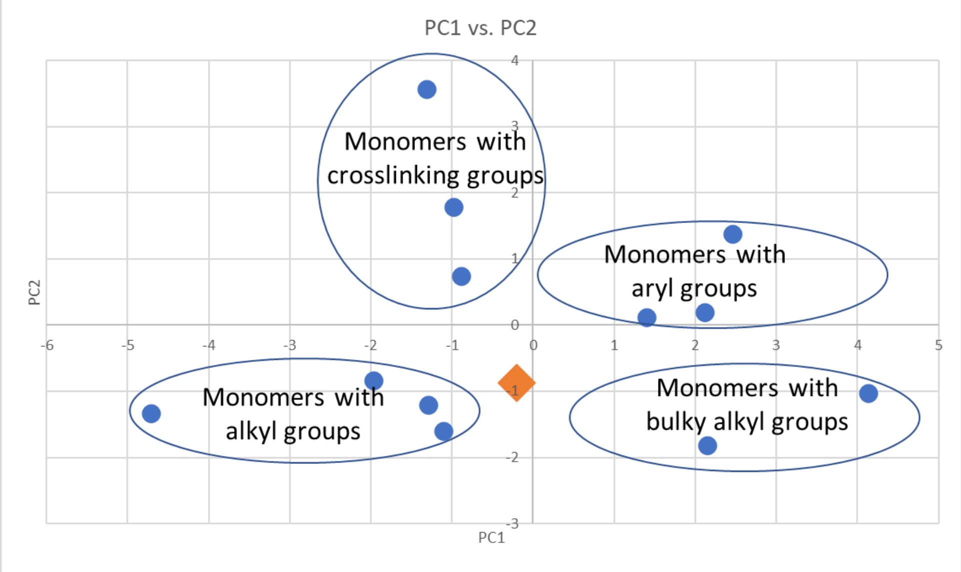
- Showcase target was to produce polymer with
  - Refractive index (n) of 1,6 at 193nm
  - As low as possible extinction coefficient (k) 193nm
  - And as low as possible etch rate.

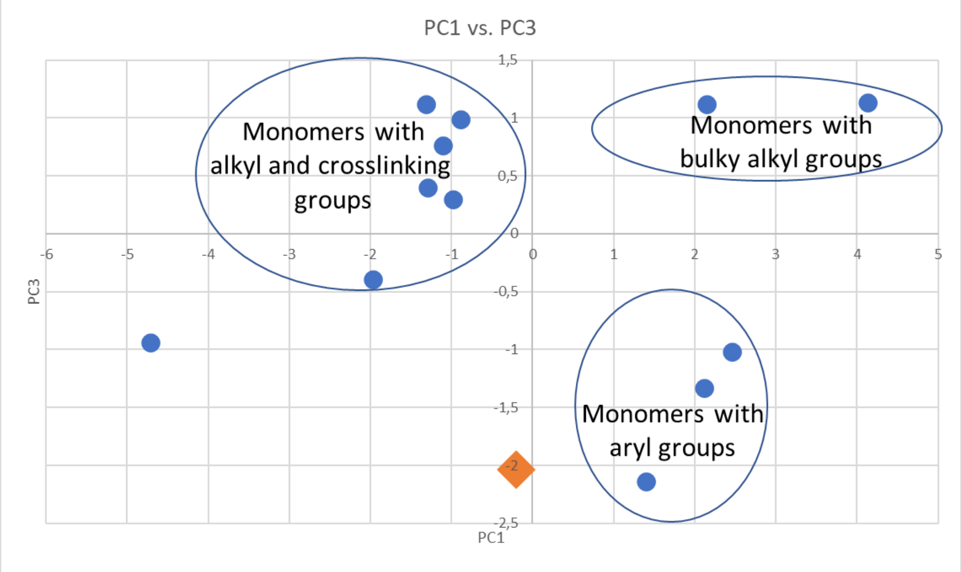
	n@193nm	k@193nm	Etch rate (nm/min)
Target	1,6	As low as possible	As low as possible

DoE model prediction

- DoE model predicts the following solution:

	PC1	PC3	PC3	Ratio of monomers	n@193nm	k@193nm	Etch rate (nm/min)
Target					1,6	As low as possible	As low as possible
Solution #1	-0,2	-0,9	-2,0	0	1,6	0,2	310





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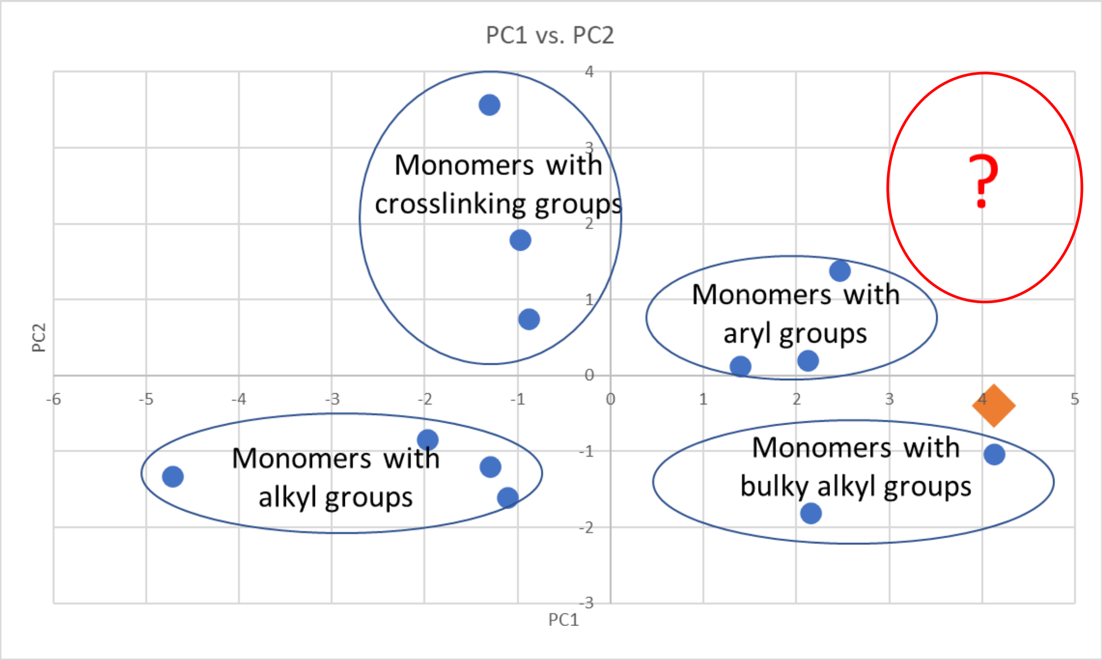
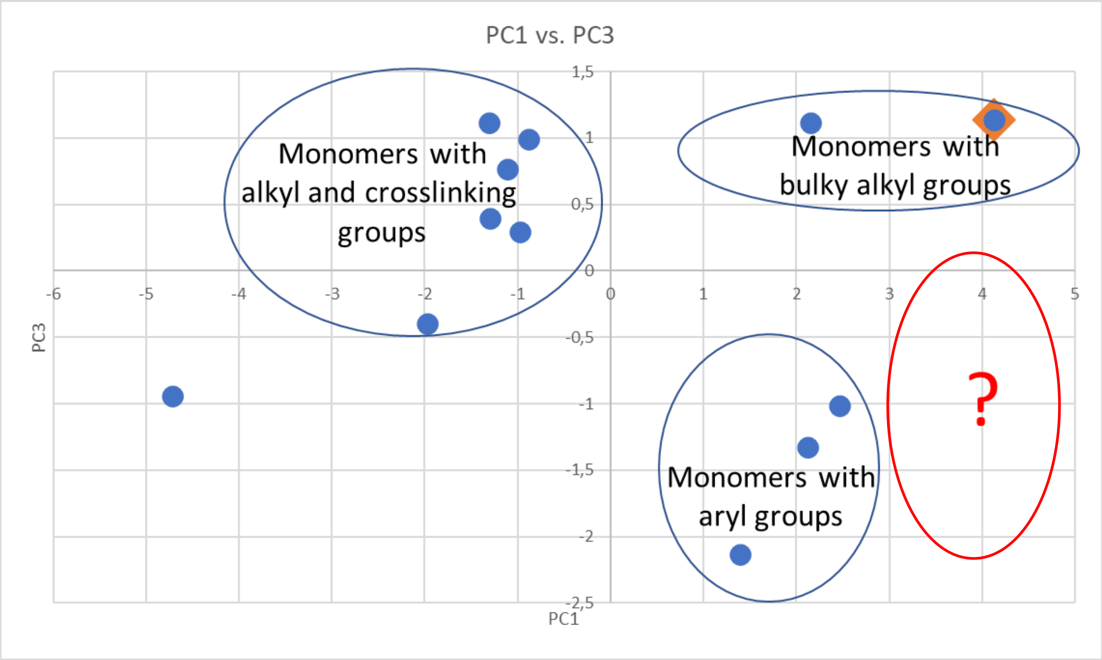
Uninvestigated regions of chemical space

- The combination of PCA with DoE also directs the future experimental effort into the regions of chemical space, where the specific chosen reaction occurs most successfully.





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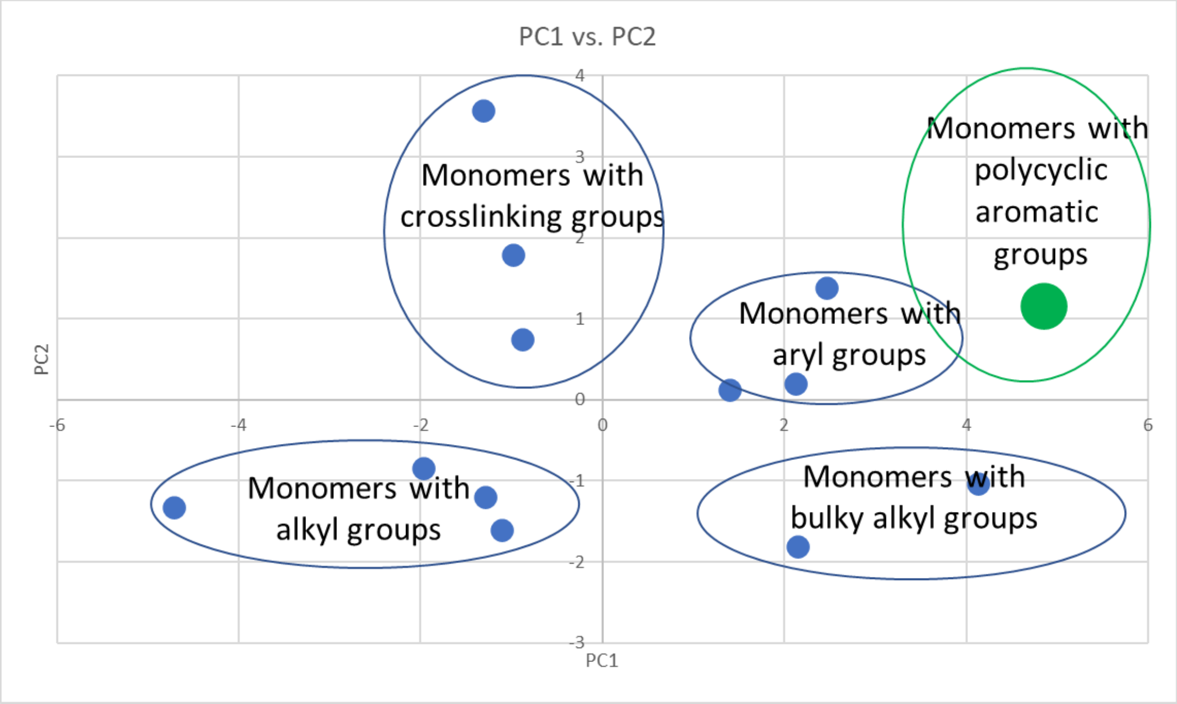
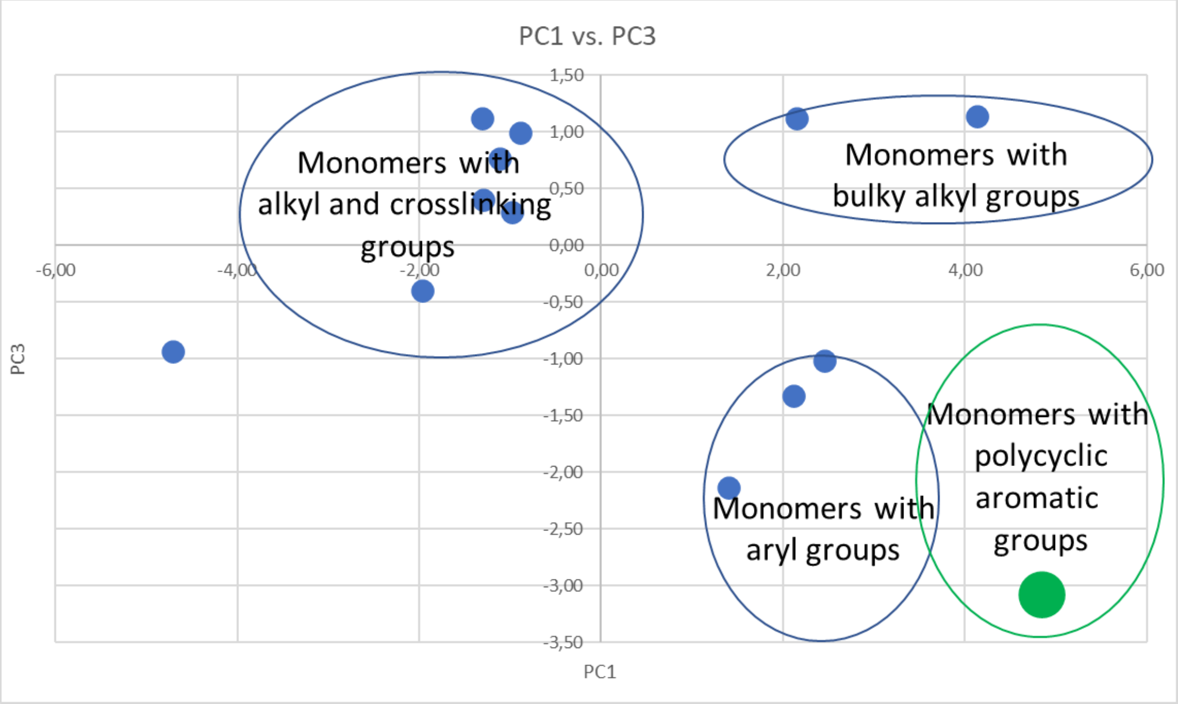
New monomer

- Based on chemical and physical properties of a new monomer, its principal components can be calculated.

Monomer	Molecular weight	Boiling point	Index of Refraction	Density	Vapour Pressure	Flash Point	Molar Refractivity	Ohnishi Number	LogP	Polar Surface Area	Molar Volume	Surface Tension	Polarizability
New 13													





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Additional polymerization results

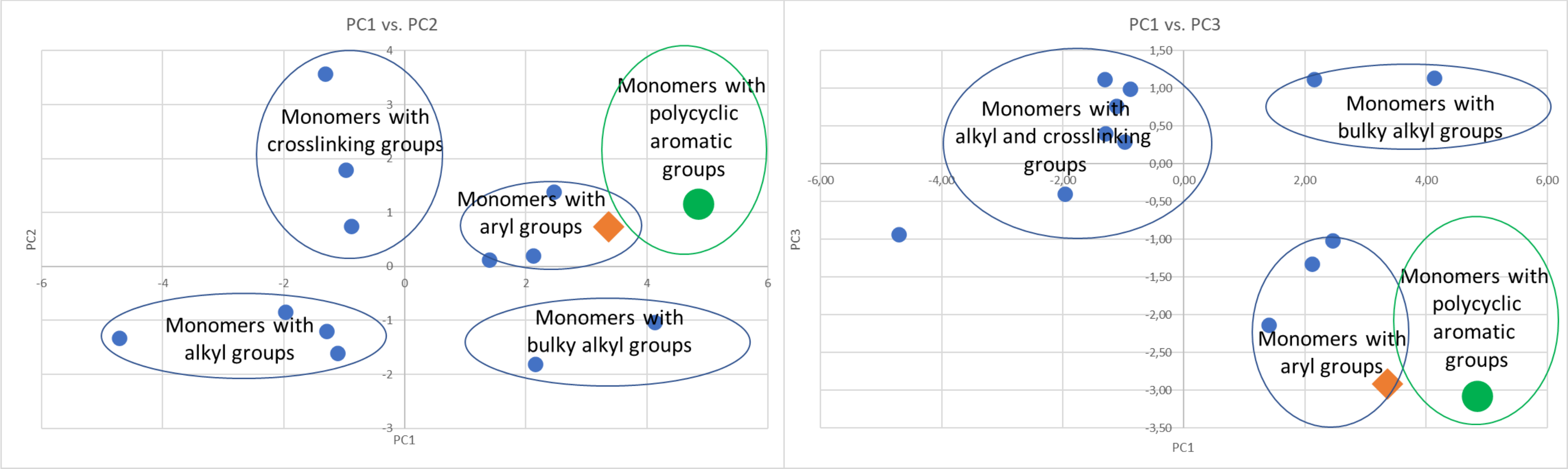
- Copolymers with new monomer showed promising balance of properties:

	PC1	PC3	PC3	Ratio of monomers	n@193nm	k@193nm	Etch rate (nm/min)
Monomer #13	4,9	1,2	-3,1	1	1,61	0,12	298
Monomer #13	4,9	1,2	-3,1	-1	1,48	0,22	190

DoE model prediction

- DoE model predicts the following solution:

	PC1	PC3	PC3	Ratio of monomers	n@193nm	k@193nm	Etch rate (nm/min)
Target					1,6	As low as possible	As low as possible
Solution #2	3,4	0,7	-2,9	-1	1,6	0,2	190



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DoE model prediction

- DoE model predicts the following solution:

	PC1	PC3	PC3	Ratio of monomers	n@193nm	k@193nm	Etch rate (nm/min)
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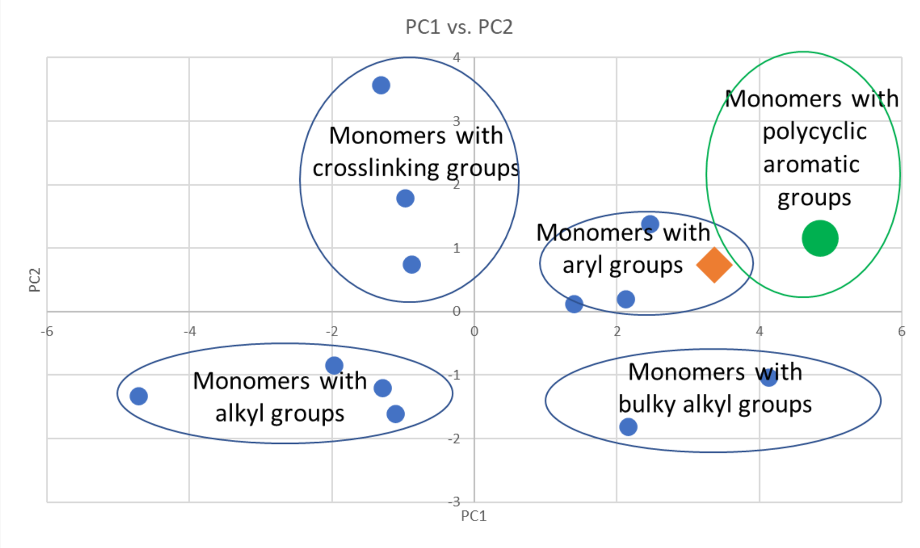

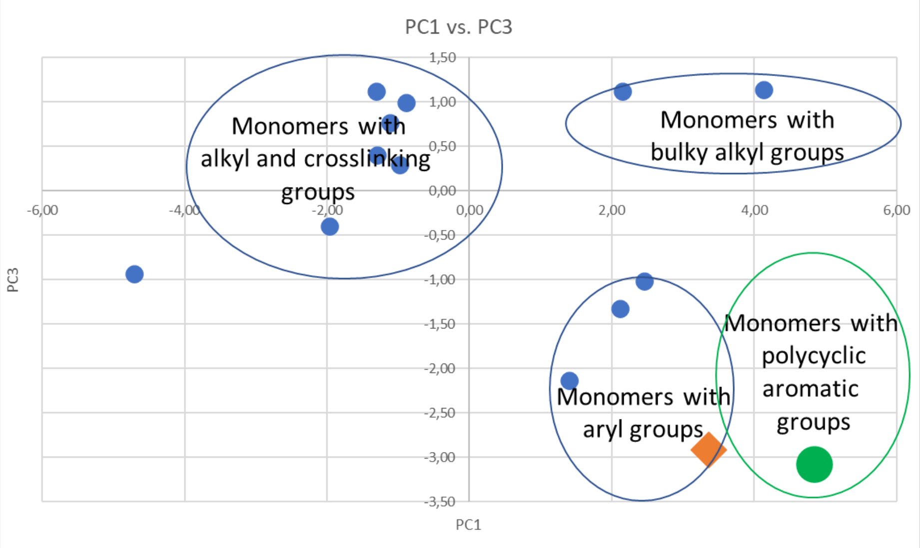

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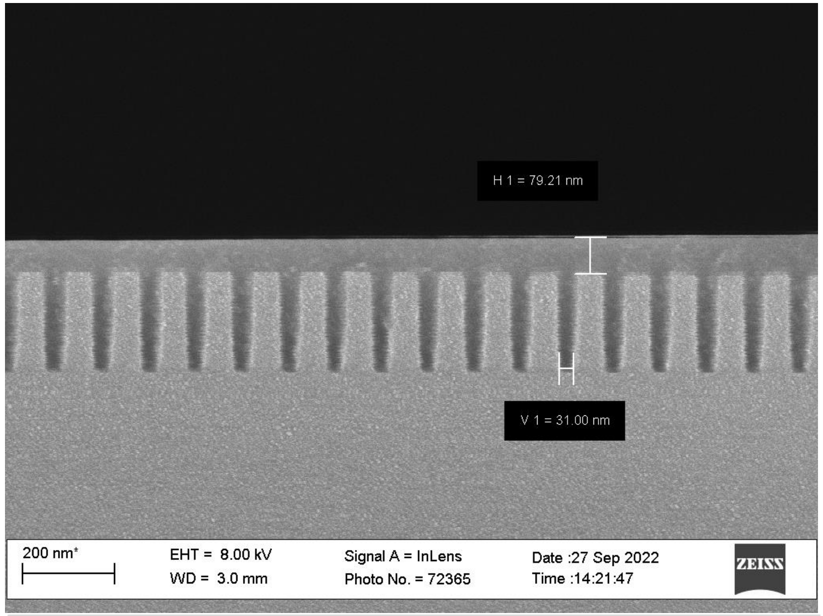
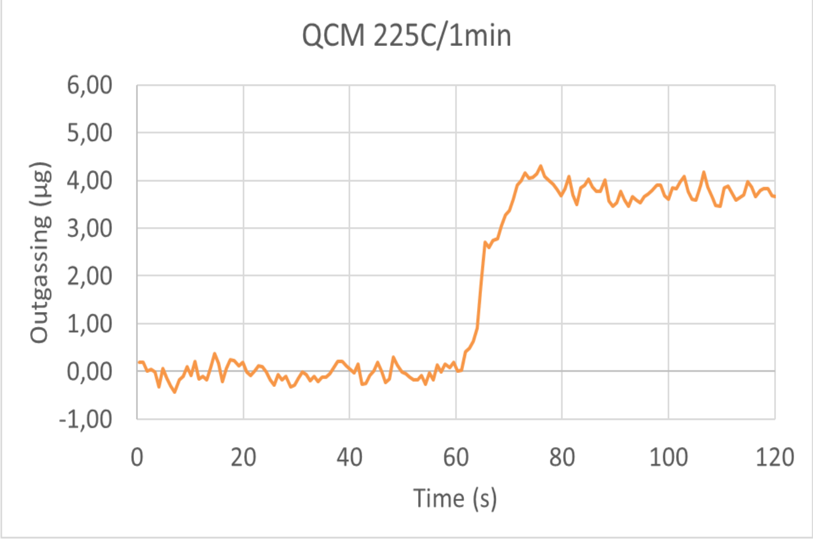
Developed spin-on-carbon hard masks

- Target n and k and etch rate.
- Good crosslinking.
- Low outgassing
- Good gap filling
- Very good solvent compatibility
- Excellent storage stability





Summary

- Terpolymer concept (monomers with crosslinking group, aryl group and polycyclic aromatic group) has been selected and optimized to have the target n and k, and etch rate values.
- The combination of Principal Component Analysis (PCA) with Design of Experiments (DoE) methods has been successfully applied for the fast and efficient development of spin-on-carbon hard masks and bottom anti-reflective coatings with tailorable optical properties and desired etch rate.

Thank You!

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