Fine-tuning polymer-based biomonitoring tools for quick and cost-effective screening of persistent, bioaccumulative and toxic contaminants (PBTs) in lipid containing matrices.

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Introductions

PBTs: persistent, bioaccumulative, toxic compounds

Examples: PolyChlorinated Dibenzo-*p*-Dioxins (PCDDs) - dioxins

PolyChlorinated Biphenyls (PCBs) - pesticides

?

¿Risk assessments?

¿Biomornitoring?

http://www.greatbarrierreefs.com.au/dugong-great-barrier-reef/
https://cbartazo.com/2013/02/09/orbit-and-alcoholic-some-sad-story/

Sampling methods

- Exhaustive extraction and solvent clean-up
- Without or only few solvent clean-up

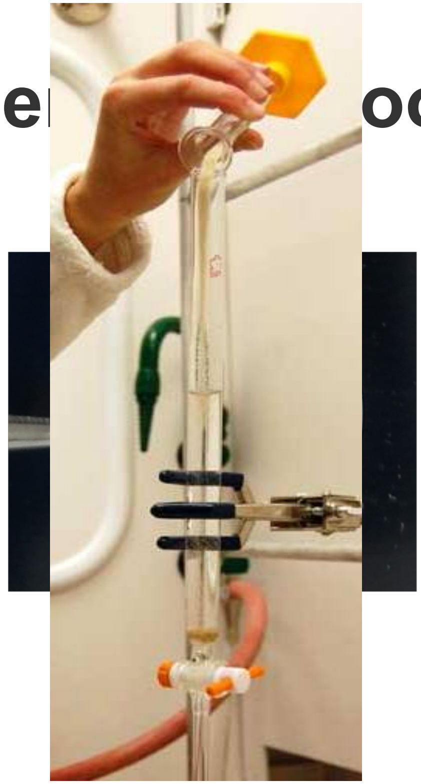
☹ time/cost consuming and laborious???

☺ Quick and cost effective screening tools

Extraction and clean-up

Samples

Polyme



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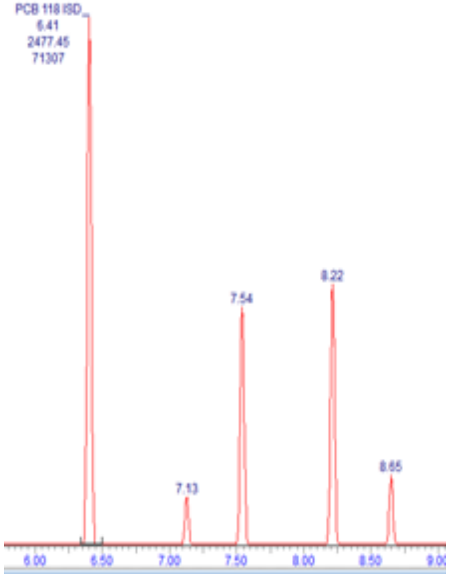
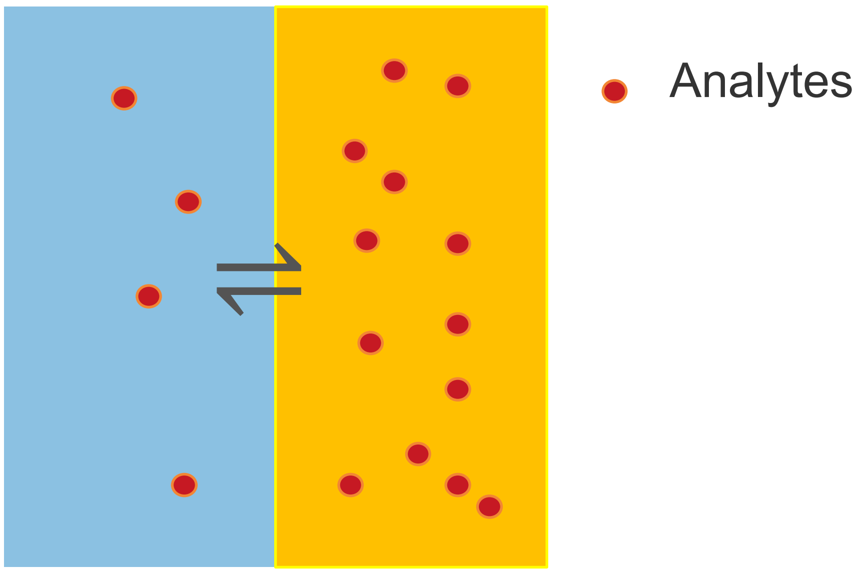
Analyses



slideplayer.com
https://cornucopiacorner.files.wordpress.com/2011/02/dugong-with-turtle-300x227.jpg
https://en.wikipedia.org/wiki/Gas_chromatography%E2%80%93mass_spectrometry

Polymer-based passive sampling
State of the art.

➤ **Passive sampler:** polydimethylsiloxane (PDMS)



Partitioning coefficients (K value)

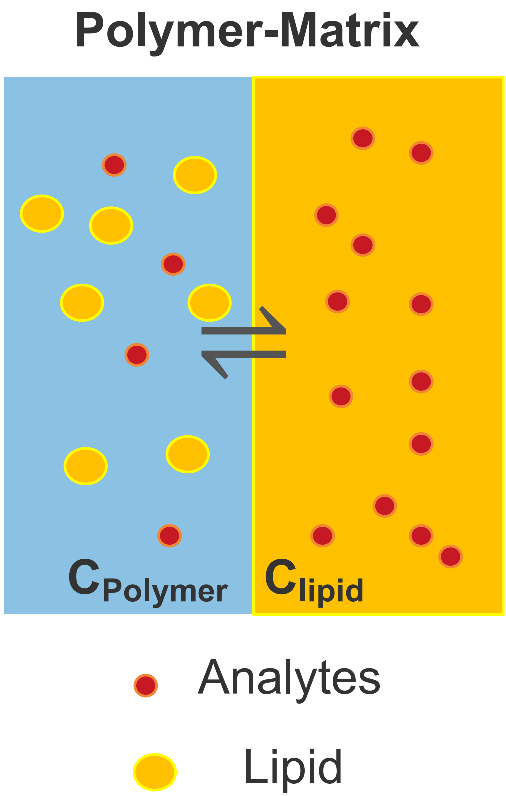
$$K_{lipid-polymer} = \frac{C_{lipid}}{C_{polymer}}$$

Figure: Polymer inserted into fish tissues (Jahnke et. al. 2009)

Limitation of current PDMS-based passive sampling in lipid rich tissue.

Low sorptive capacity:

$K_{lipid\text{-}PDMS}$ = 37 (PCDDs) (Jin et al 2013)



High volume of samplers

↓

High lipid swelling

?

- **Good polymers:** ✓
- **☺ Low $K_{lipid\text{-}polymer}$ ☺ Low lipid swelling**

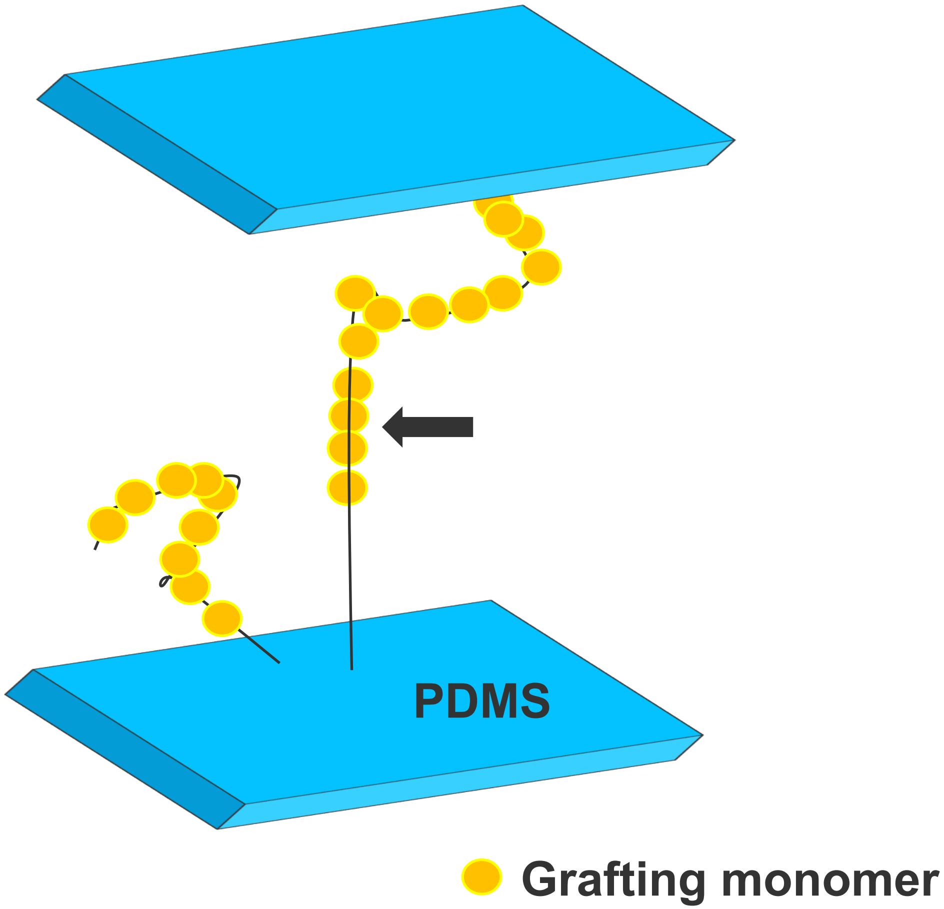
http://animaldiversity.org/accounts/Dugong_dugon/

www.foodsafetynews.com

Solution: Custom-made polymers

E.g. (poly)*tert*-butyl methacrylate (PtBuMA) grafting on PDMS

(Dürig et al. 2016)



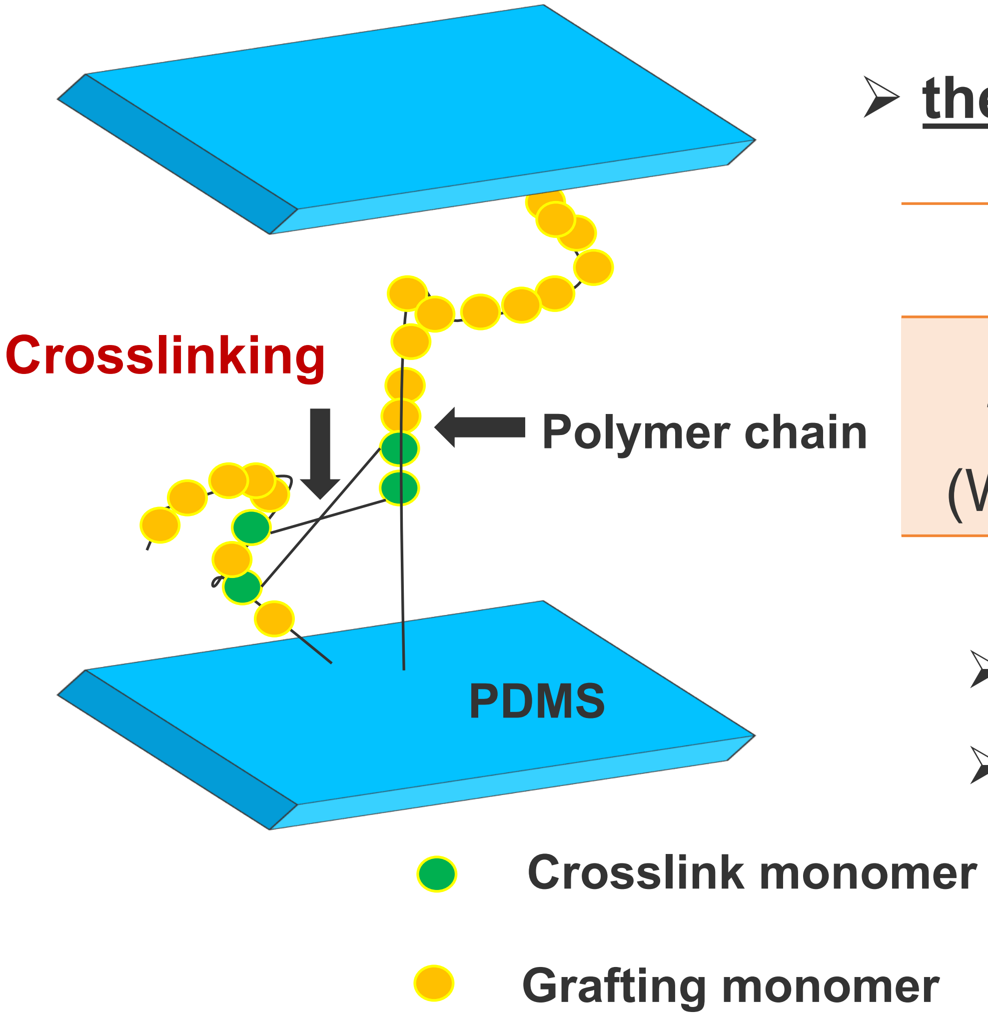
☺ **Lower $K_{lipid\text{-}PtBuMA} = 7$**

(PDMS, $K_{lipid\text{-}PDMS} = 37$)

☹ **Higher lipid swelling**

(compared with PDMS)

Solution: Custom-made polymers



- the difference in molecualer sizes

Lipids	PBTs
20 to 200 Å	< 15 Å
(Welson 2006)	(Suter 2008)

- excluding lipid molecules
- selecting PBTs based on their size

Fine-tuning polymer-based biomonitoring tools (Done by AIBN, UQ)

❖ ***Aims: seek for the better performing polymer***

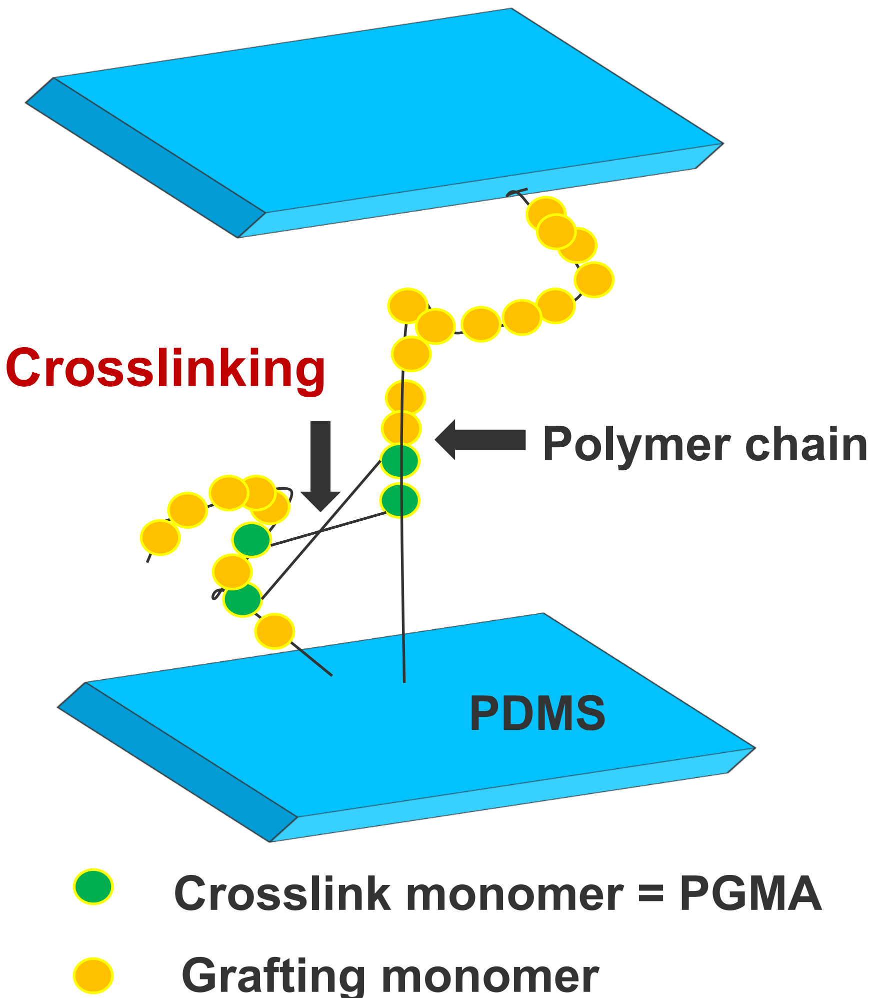
✓ ***Limited lipid swelling***

✓ ***Low $K_{lipid\text{-}polymer}$***

1. **Different type of monomers**

PBMA, PtBMA, PMMA

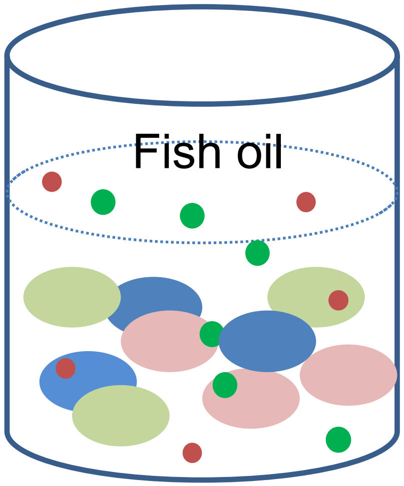
2. **Increase crosslinking degrees**
3. **Higher concentration of monomers**



Methods: How to find the best polymer?

❖ Screen polymers

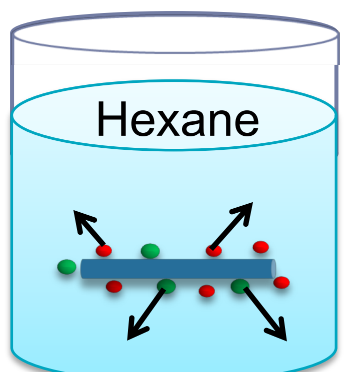
Sampling



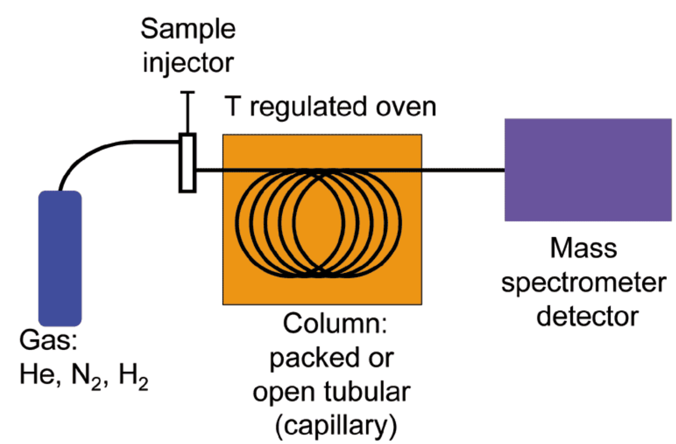
Methanol wipping

Weight

Extraction



Analyses GC-MS

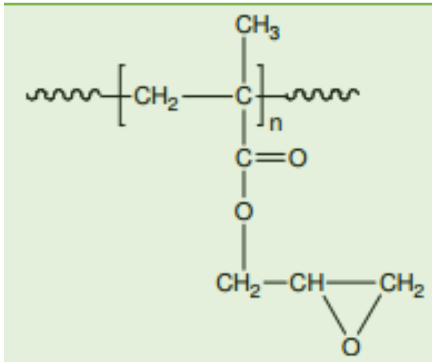


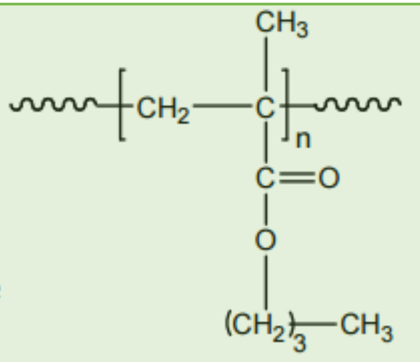
- PCDDs
- PCBs
- Polymers

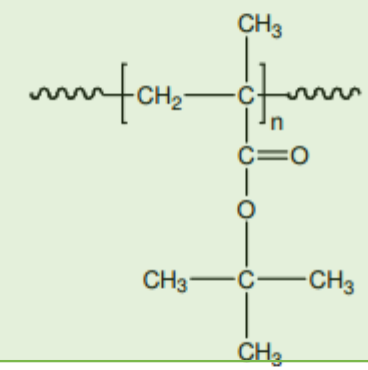
Materials

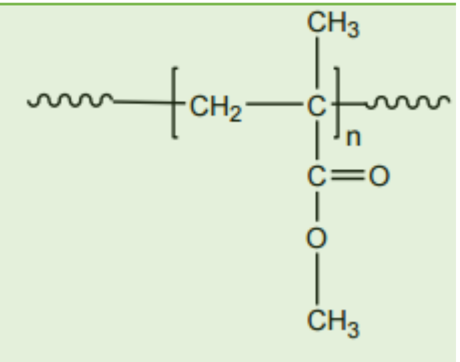
Table 1: Chemical structures of monomers (PBMA, PtBMA and PBMM)

PolyGlycidyl methacrylate (PGMA)	PolyButyl methacrylate (PBMA)	Polytert-Butyl methacrylate (PBtMA)	PolyMethyl methacrylate (PMMA)







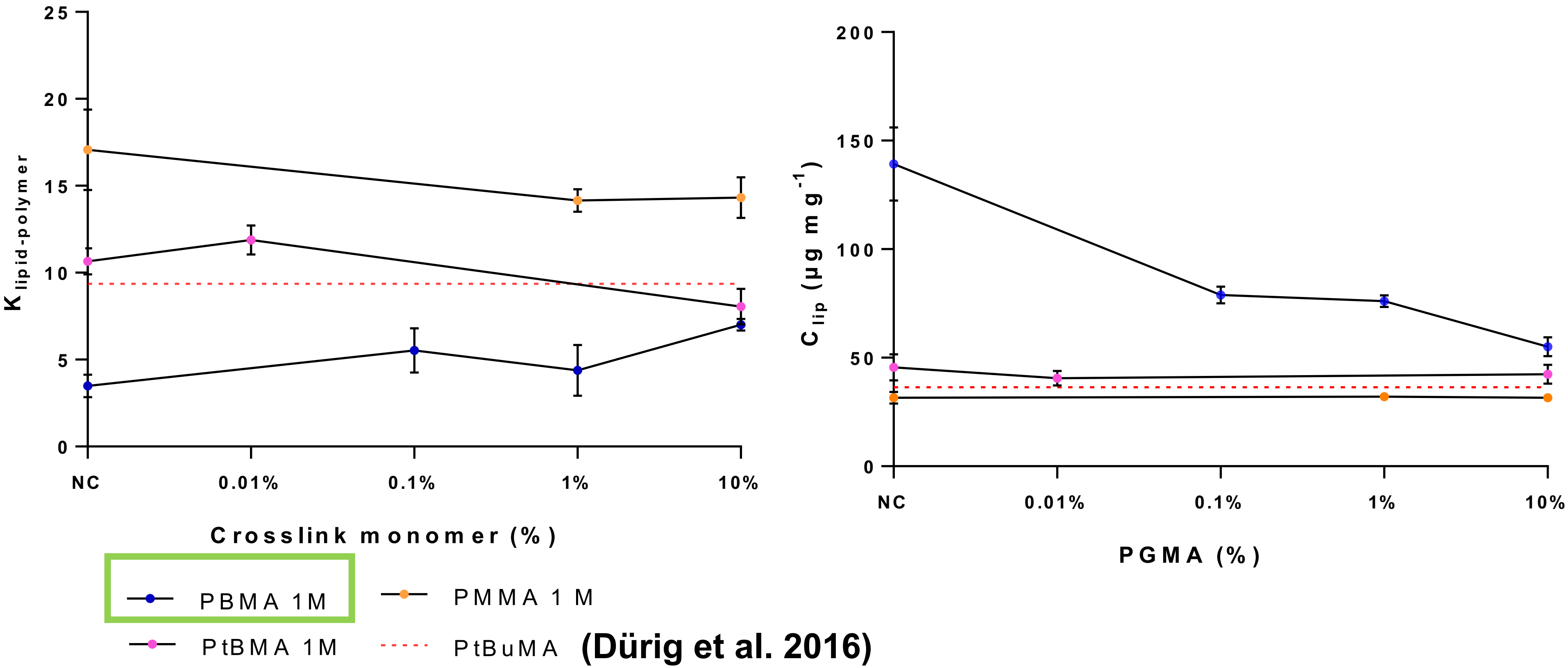


from Pubchem

Table 2: Polymer grafts with different monomers (PBMA, PtBMA and PBMM), n = 3

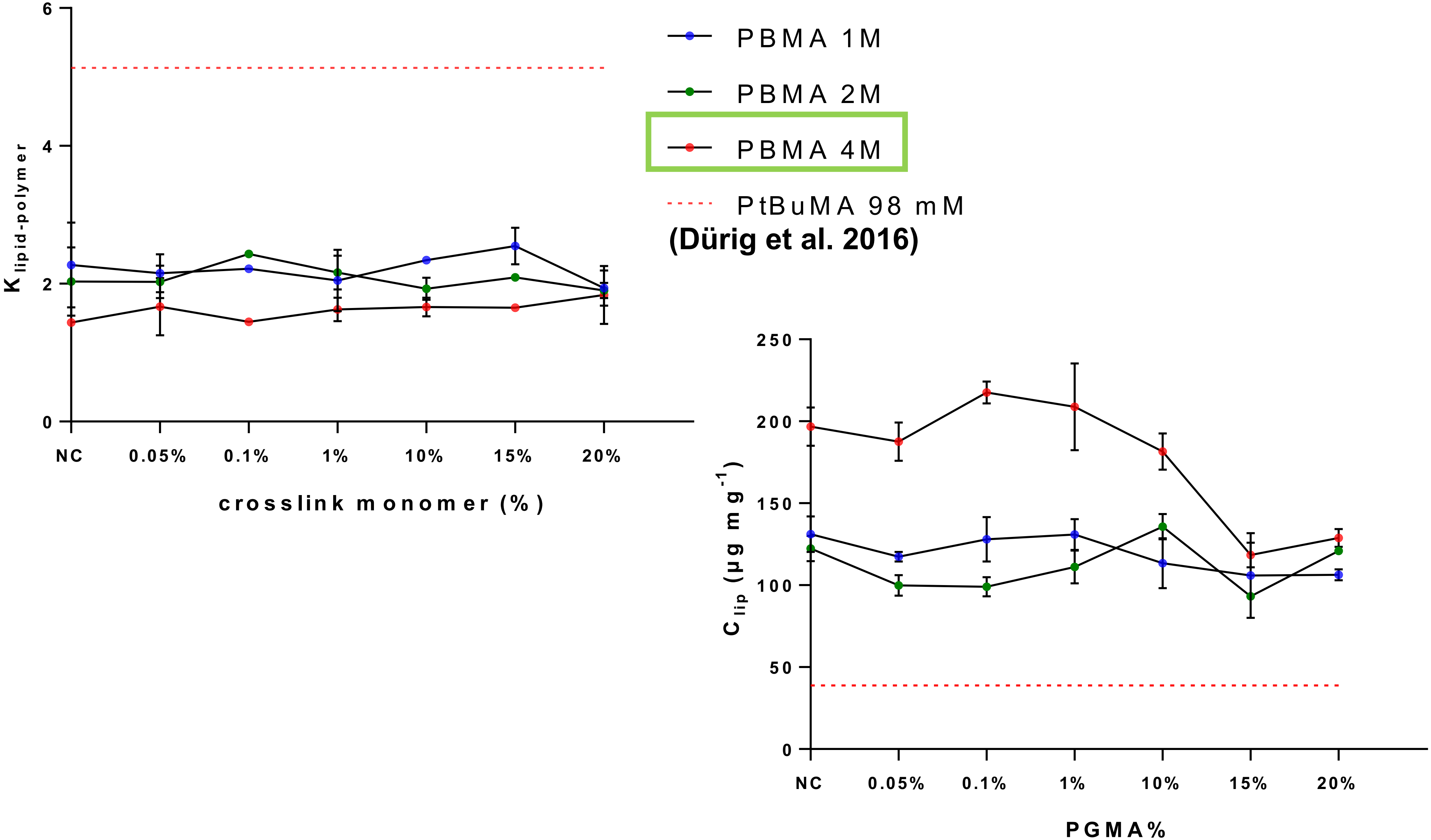
	Phase I: Prioritization (10 days)			Phase II: Fine tuning (15 days)		
PGMA(%)	**PBMA 1 M**	**PtBMA 1 M**	**PMMA 1 M**	**PBMA 1 M**	**PBMA 2 M**	**PBMA 4 M**
NC	✓	✓	✓	✓	✓	✓
0.01%	×	✓	×			
0.05%				✓	✓	✓
0.10%	✓	×	×	✓	✓	✓
1%	✓	×	✓	✓	✓	✓
10%	✓	✓	✓	✓	✓	✓
15%				✓	✓	✓
20%				✓	✓	✓

Results. Phase I: Prioritisation



➔ **PBMA give lowest K value.** ➔ ⬆ **crossliniking reduces lipid swelling.**

Results. Phase 2: Fine-tuning



Implications

LOD = 0.1 pg/µL, V extract = 20 µL Low contaminated (TCDD) → higher contaminated (OCDD)					
Ci lipid	pg/g lipid	1	10	100	1000
PDMS, K=37, Clipid/polymer = 9 mg/g (Jin et al. 2013)					
V polymer	g	**74**	7.4	0.74	0.074
% Mi from lipid	%	25%	25%	25%	25%
PBMA 4 M, K=1.3, Clipid/polymer = 118 mg/g					
V polymer	g	**2.6**	0.26	0.026	0.0026
% Mi from lipid	%	13%	13%	13%	13%

2,3,7,8-tetrachloro-dibenzo-p-dioxin (TCDD),
1,2,3,4,5,6,7,8,9-octachloro-dibenzo-*p*-dioxin (OCDD)

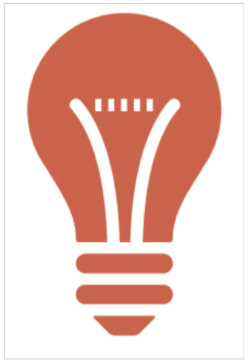
Conclusions

1. PBMA 4 M

- $K_{lipid\text{-}polymer}$ = 1.3 ± 0.028 (PCDDs) and 1.7 ± 0.034 (PCBs)
- 3 folds # PtBuMA (Dürig et al. 2016)

2. Crosslinking > 15%

- Lipid swelling reduction by a half (C_{lipid} = 118 ± 7.5 $\mu g_{lipid}/mg_{polymer}$)



Outlooks

- **further minimize the lipid swelling**

? trying with different crosslinking agents