

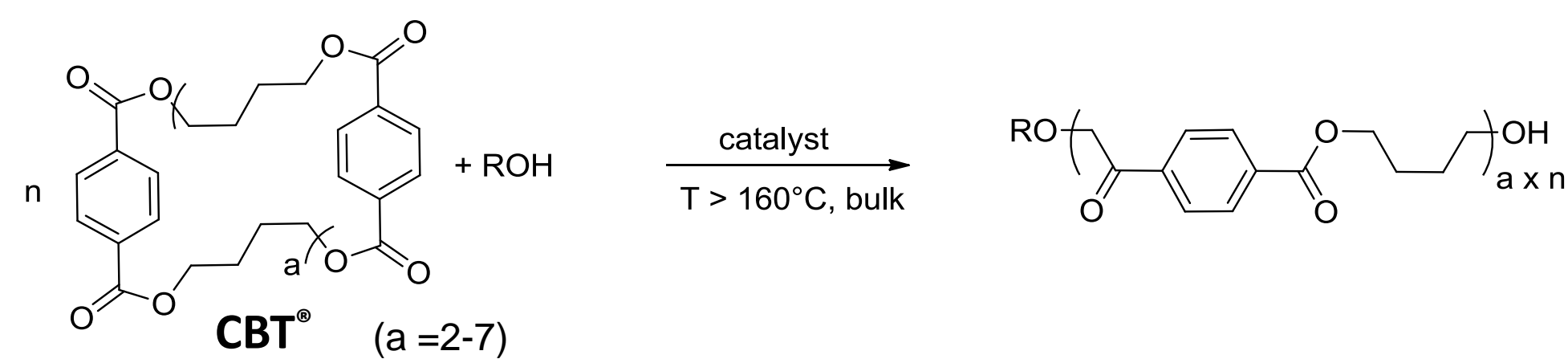
Organocatalyzed Ring Opening Polymerization of Cyclic Butylene Terephthalate Oligomers

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All about Cyclic Butylene Terephthalate Oligomers (CBT®)¹



CBT®:

- Tm = 120-160°C
- Low Melted state viscosity (17 mPa.s)
- Polymerized by ROP in 3-5 min with no by-products

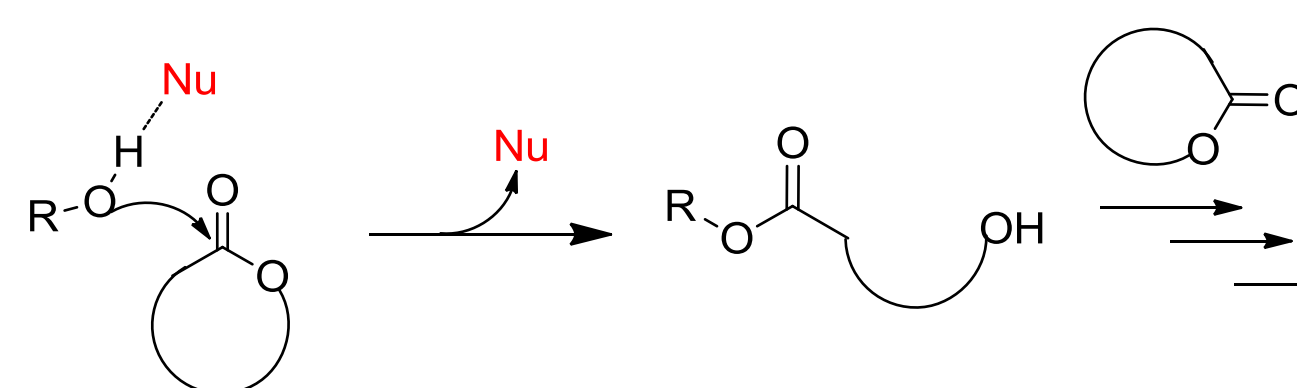
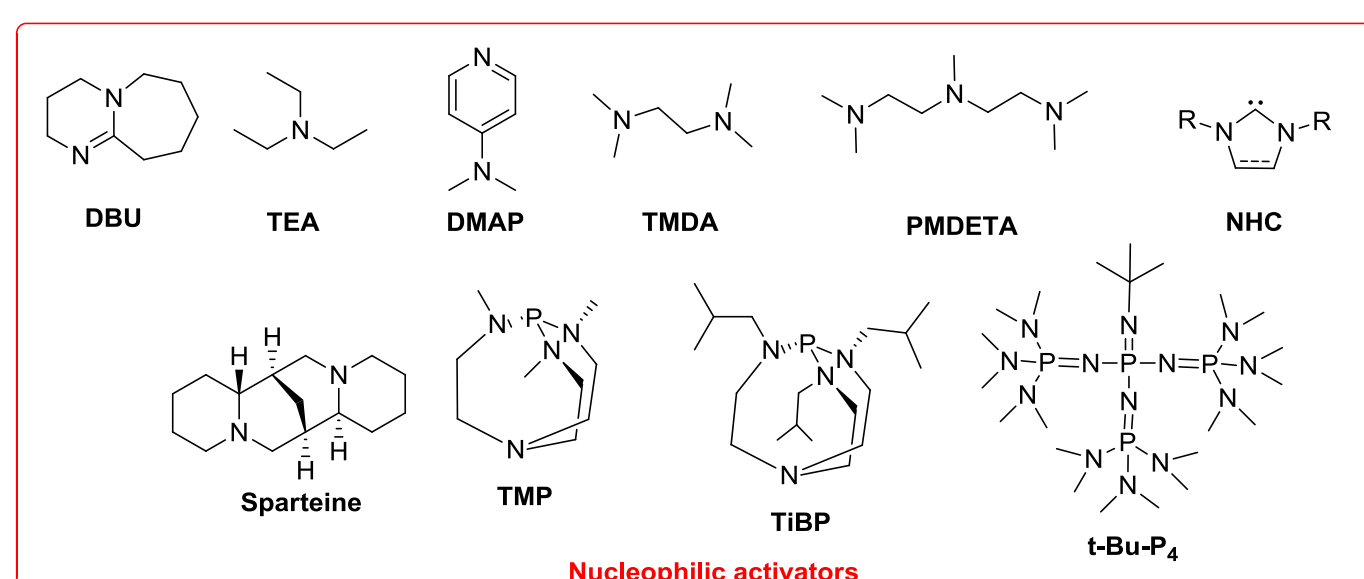
PCBT = PBT:

- High Tm polymer (Tm = 220°C)
- Fast-crystallizing polymer
- Recyclable

Suitable matrix for engineering thermoplastic composites processed by impregnation

¹ Tripathy AR, Elmoumni A, Winter HH and MacKnight WJ, *Macromolecules*, **2005**, *38*, 709–715.

Context

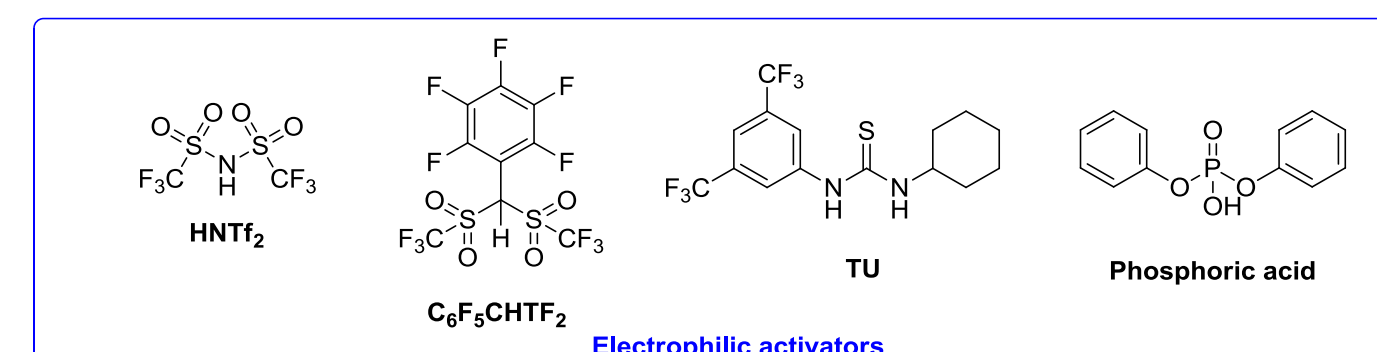
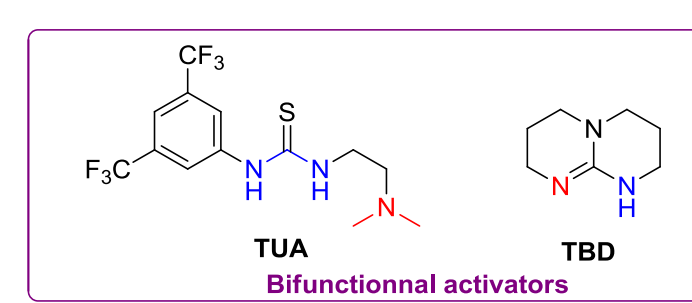


Control of Mn and *D*; Control of macromolecular architectures; Avoid metallic species (biomedical or microelectronic)
Similar or better performances than organometallic species. → Is it possible with CBT®?

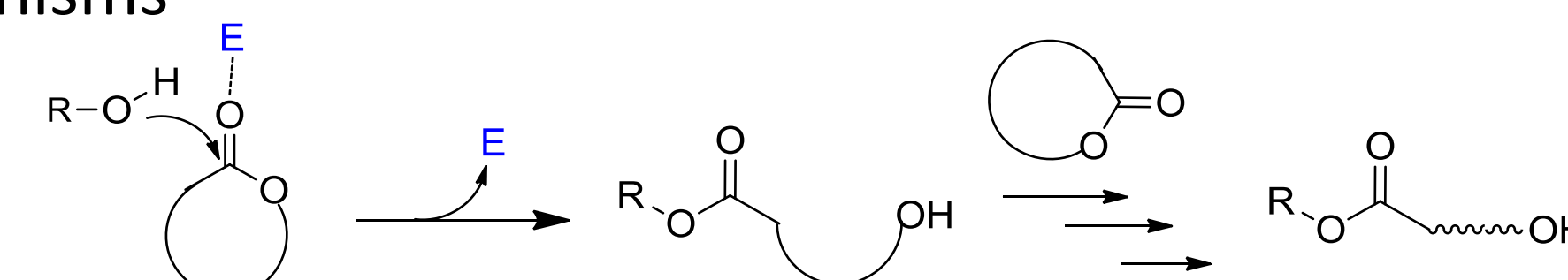
²Kiesewetter, M. K.; Shin, E. J.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2010**, *43*, 2093.

Organocatalyzed Ring-Opening Polymerization (ROP)

Organocatalysts

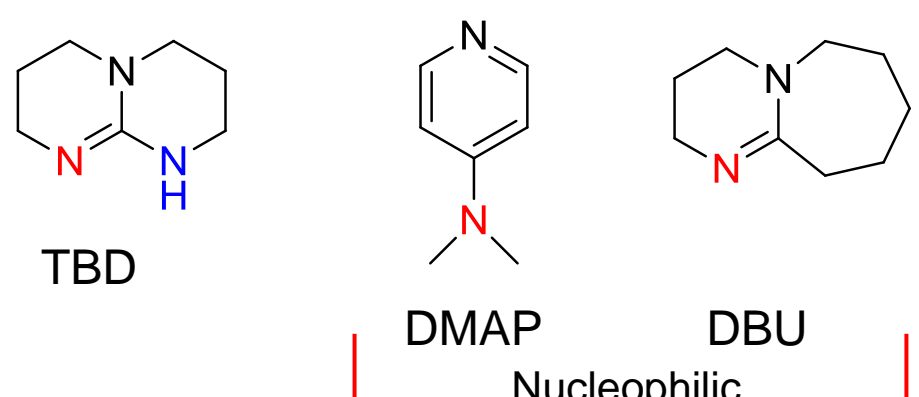
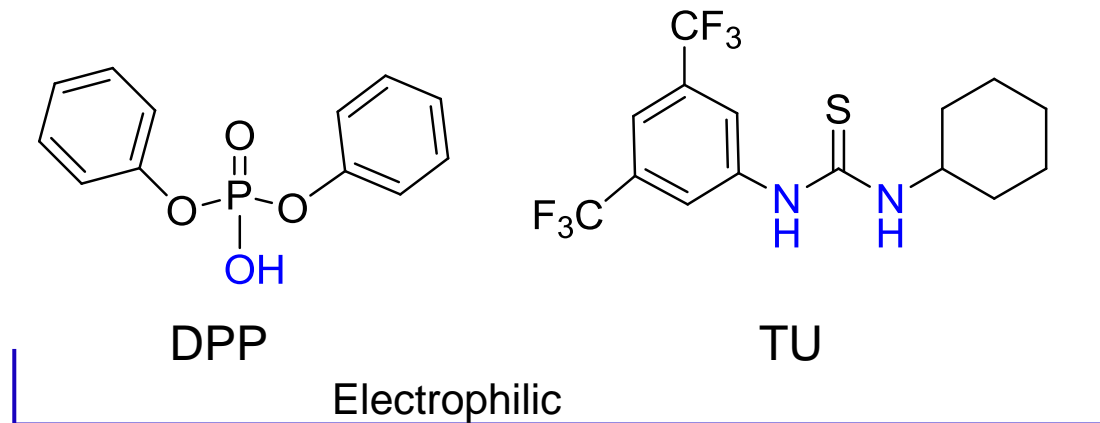


ROP mechanisms



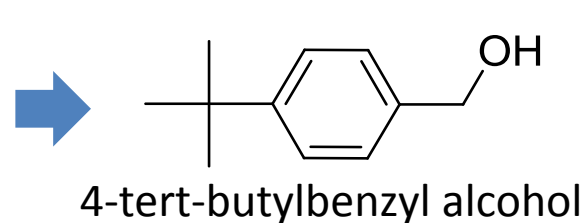
Catalysts selection

- Robust, non sensitive to air and moisture
- Must stand temperature > 220°C (reaction temperature)



Initiator choice

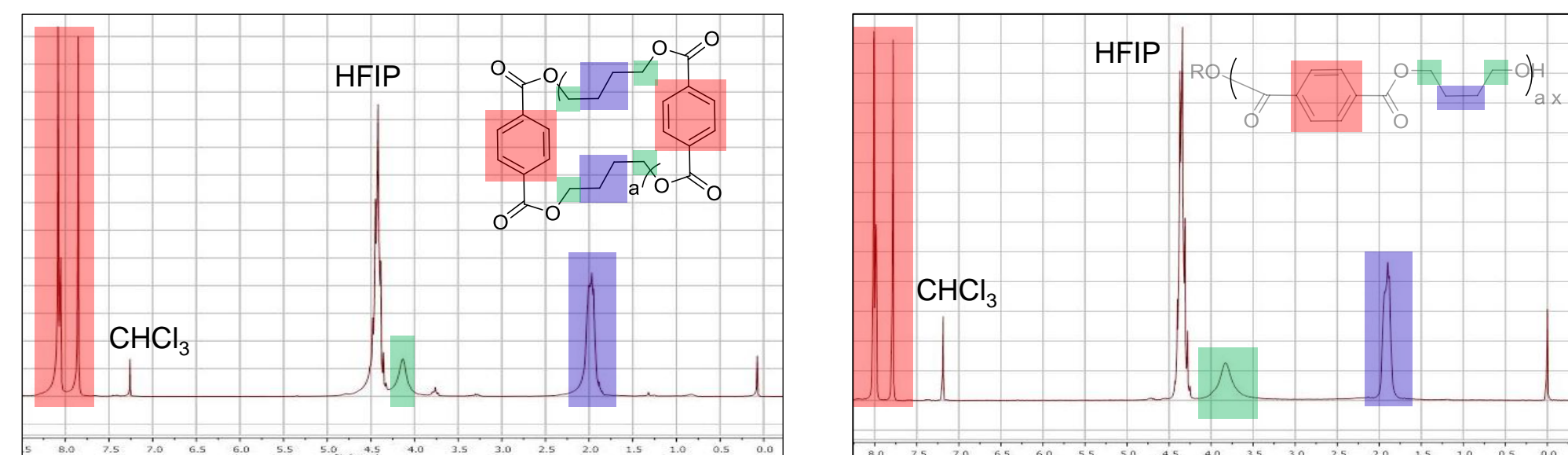
- Similar to initiator usually employed (benzyl alcohol)
- Must stand temperature > 220°C (reaction temperature)



Influence of the type of catalyst on the ROP of CBT in bulk

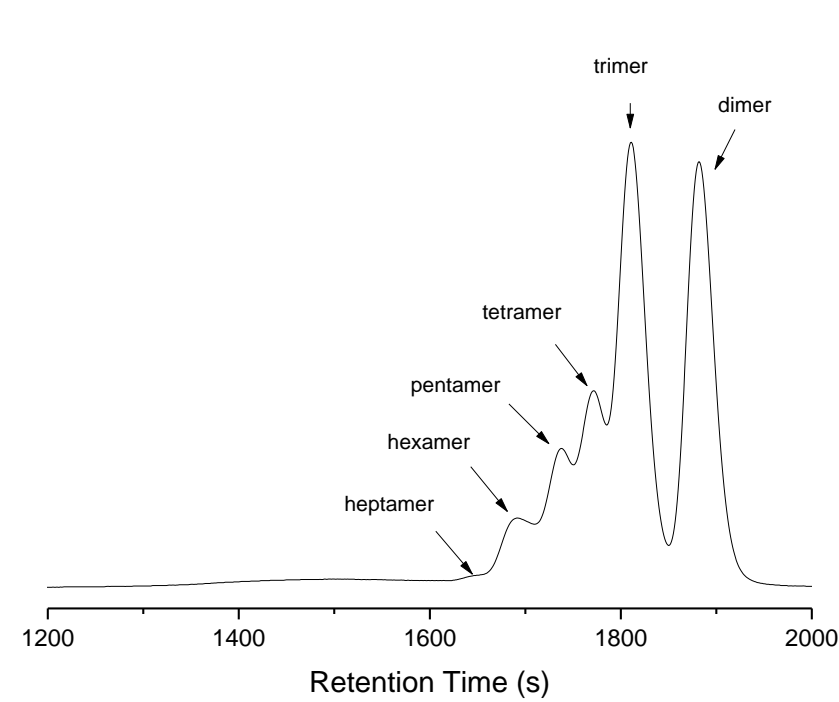
Determination of monomer conversion

¹H NMR spectra of a) CBT® and b) PBT in CDCl₃/HFIP

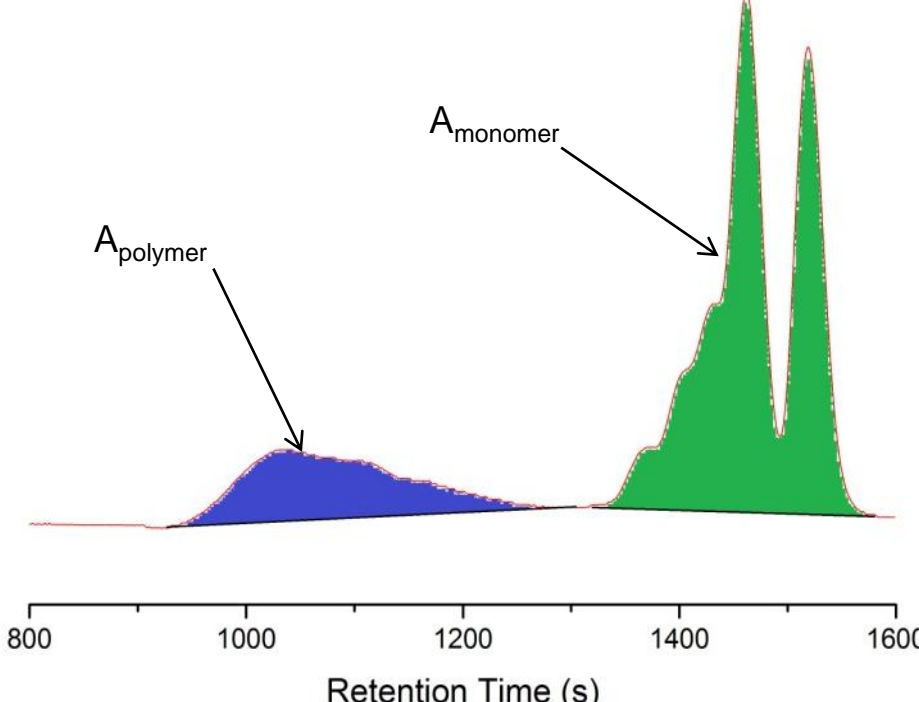


Not possible to determine monomer conversion by NMR
→ Determination by SEC

Typical SEC trace of PCBT



Typical SEC trace of CBT®



$$\text{Equation 1: } \text{conv. (\%)} = \left(1 - \frac{A_{\text{monomer}}}{A_{\text{polymer}} + A_{\text{monomer}}} \right) * 100$$

Catalysts effect

ROP of CBT in bulk with various organocatalysts^a

Exp	Catalyst	M _{n th} (g/mol)	M _{n SEC} (g/mol) ^b	D ^b	Conv. (%) ^b
1	DBU	10000	13760	2,01	93
2	DBU	30000	30130	1,40	24
3	DBU	50000	32760	1,53	29
5	DPP	10000	9120	1,16	16
6	DPP	30000	-	-	0
7	DPP	50000	-	-	0
9	DMAP	10000	28630	1,69	78
10	DMAP	30000	56010	1,54	67
11	DMAP	50000	57120	1,52	40
13	TBD	10000	11870	2,14	99
14	TBD	30000	29910	1,76	92
15	TBD	50000	15600	1,49	26
17	Thiourea/DMAP	10000	12220	1,50	44
18	Thiourea/DMAP	30000	53690	1,30	20
19	Thiourea/DMAP	50000	47270	1,44	29
xx ¹	Stannoxane	?	50100	2,6	97

^a Polymerizations were carried out in the molten state at 208 °C under nitrogen atmosphere after drying CBT® and the initiator under vacuum at 100 °C. Under efficient stirring, 1 eq. of catalyst as compared to initiator was then added to the reaction mixture which was let to polymerize for 30 min at 208 °C. ^b As determined by SEC in CHCl₃ according to PS standards. ^c As determined by SEC in CHCl₃ according to Eq. 1.

¹ Tripathy AR, Elmoumni A, Winter HH and MacKnight WJ, *Macromolecules*, **2005**, *38*, 709–715.

Conclusion:

- Nucleophilic catalysts appear to be the most effective

- Lower *D* are obtained with organic catalysts than with organometallic catalysts.

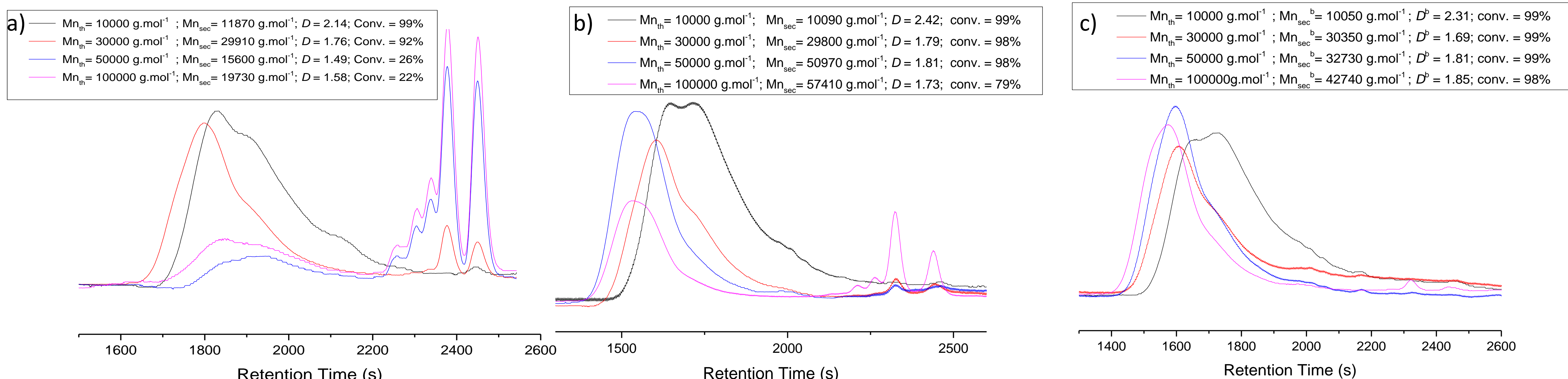
- TBD chosen for the remainder of the study

- Decrease of conversion with increase of targeted Mn → necessary to optimise catalysts content

- Only 3 min necessary to polymerise with stannoxane → how much with TBD?

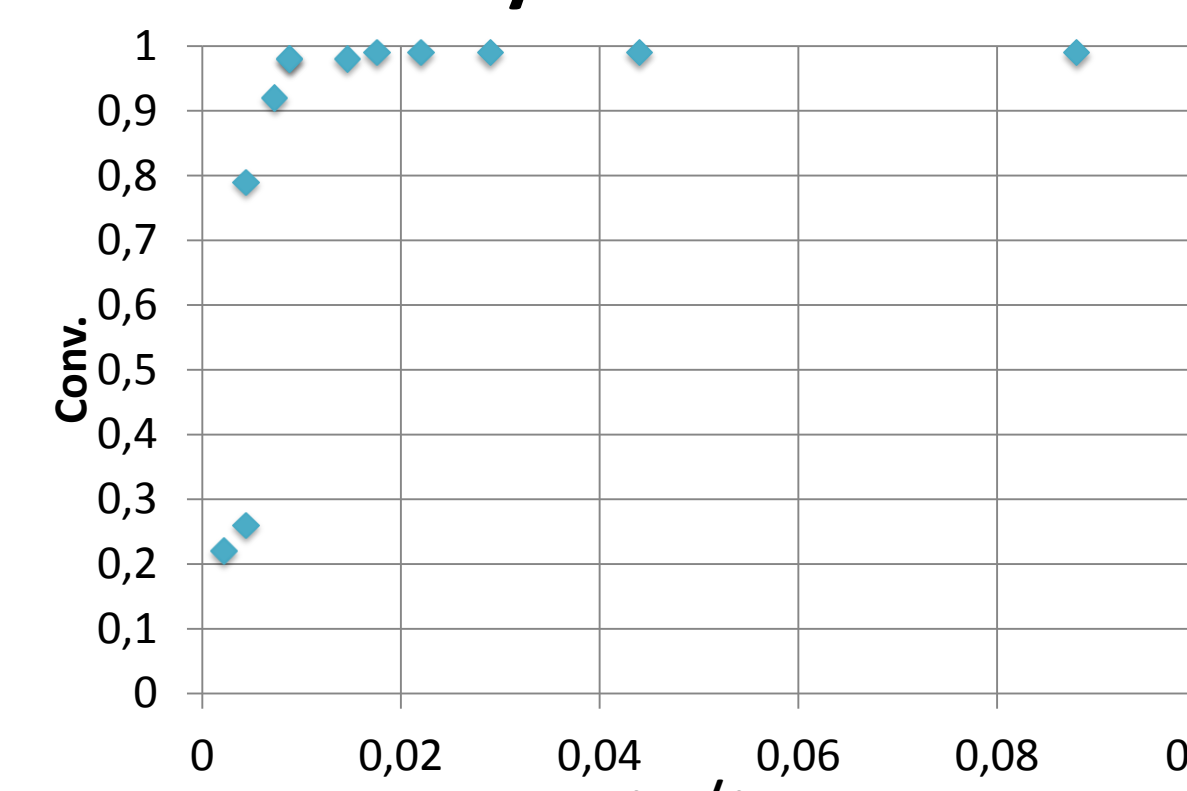
Influence of TBD content on the ROP of CBT in bulk

SEC traces of PCBT in CHCl₃ obtained with a) [Cat]/[Ini] = 1, b) [Cat]/[Ini] = 2 and c) [Cat]/[Ini] = 4^a



^a Samples taken after 30 min of polymerizations. SEC traces are normalized according to total peaks area. M_{n SEC} and *D* were determined from PS standards. Conv. Was determined according to Eq. 1.

Monomer conversion as a function of the molar ratio of catalyst over monomer unit.^a

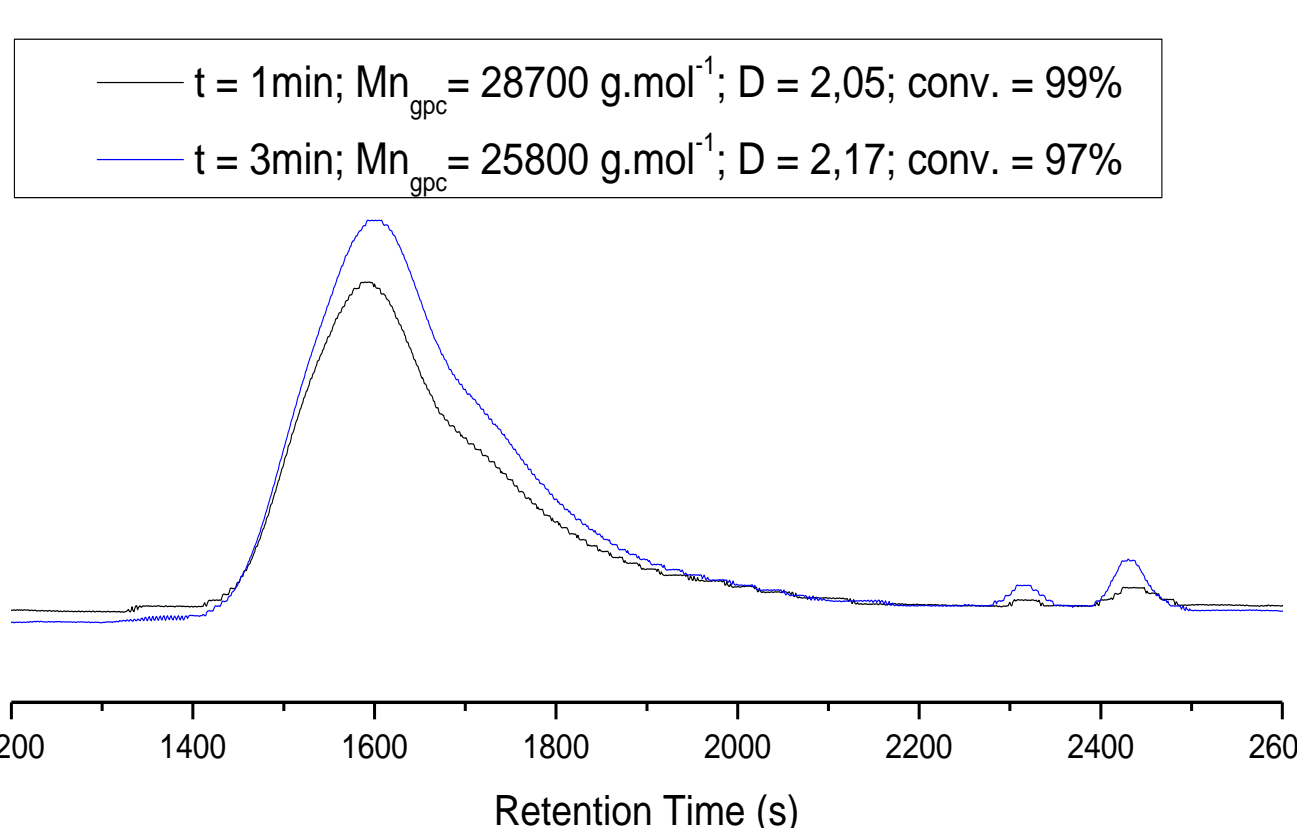


^a Monomer conversions determined after 30 min of polymerizations according to Eq. 1.

→ 1%_{mol} of TBD (as compared to monomer units) necessary to get full monomer conversion.

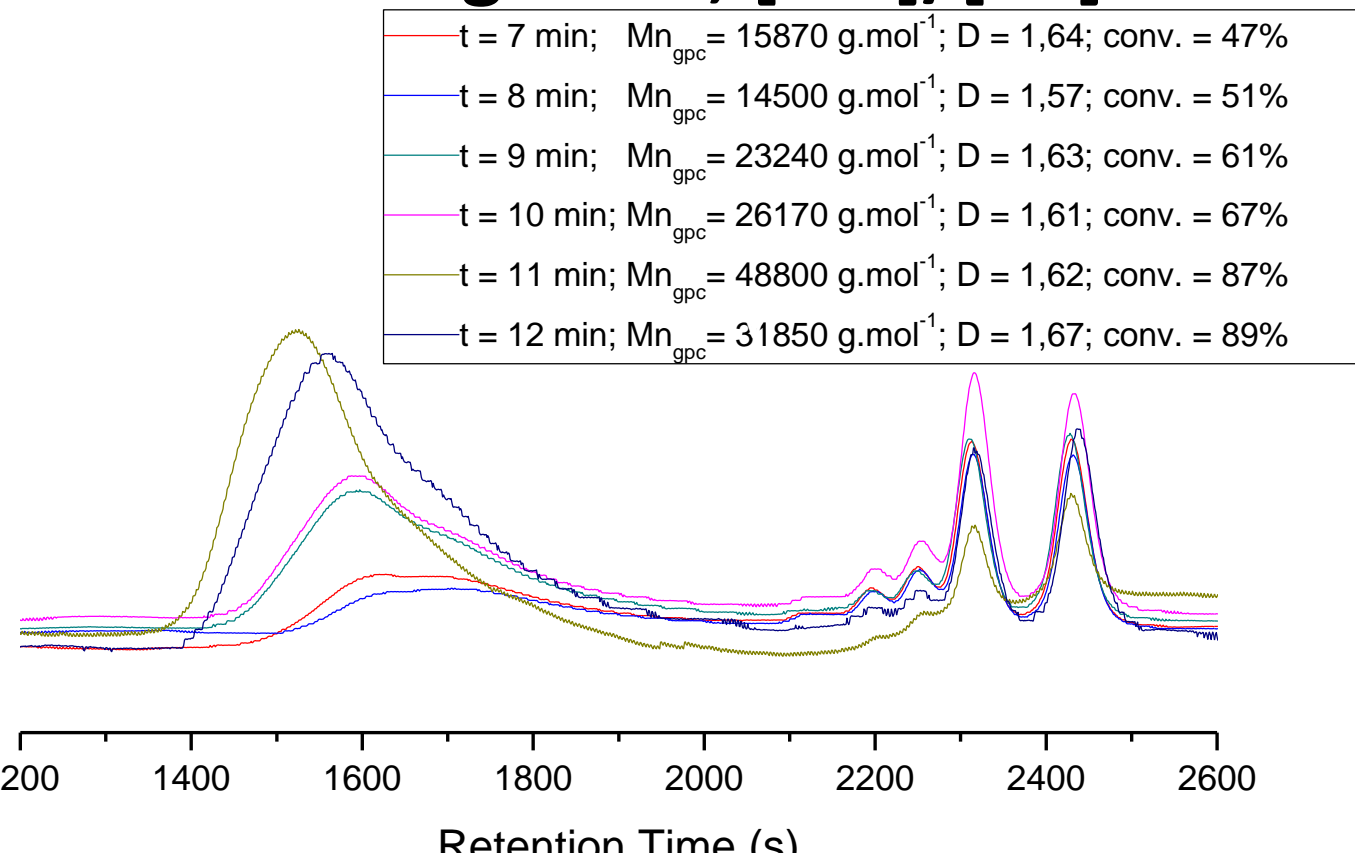
Optimisation of polymerization kinetics

SEC traces of PCBT in CHCl₃; targeted Mn = 30000g.mol⁻¹; [Cat]/[Ini] = 2.^a



a. M_{n SEC} and *D* were determined from PS standards. Conversion was determined according to Eq. 1.

SEC traces of PCBT in CHCl₃; targeted Mn = 50000g.mol⁻¹; [Cat]/[Ini] = 2.^a



a. M_{n SEC} and *D* were determined from PS standards. Conversion was determined according to Eq. 1.

ROP of CBT in bulk with [Cat]/[Ini] = 2; targeted Mn = 50000g.mol⁻¹.^a

Exp.	M _{n SEC} ^b (g.mol ⁻¹)	D ^b	Conv. ^c	Time(min)
34	0	0	0%	5
35	47000	1,60	92%	10
36	38350	1,72	94%	15
37	37700	1,73	93%	20
38	21800	1,84	97%	25

a. M_{n SEC} and *D* were determined from PS standards. Conversion was determined according to Eq. 1.

→ Increase in *D* and decrease in Mn suggests transfer reactions

Conclusion and perspectives

Conclusion:

- TBD is the most active organocatalyst and more active than organometallic catalysts usually employed.
- Only 1%_{mol} (0.05%_w) (vs monomer) of catalyst for full conversion (0.25%_w for organometallic catalysts)
- M_n up to 50 000 g.mol⁻¹ (similar to organometallic catalyst)
- Control of M_n and low *D*
- Polymerization times similar to ROP with organometallic catalysts

Perspectives:

Block copolymers of PBT for thermoplastic elastomers

