

On Electron Beam-Cured Polymer Networks: Formation Process & Other Chemical Phenomena



Coatings Trends & Technologies Summit
The Westin Lombard (IL - US) • Sept. 6th - 8th 2023

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Nemho Innovations BV - Eindhoven University of Technology

nemho next material house

TU/e EINDHOVEN UNIVERSITY OF TECHNOLOGY

Agenda

- **Introduction**

EB Technology & Applications

EB-Curable Coatings

- **Results**

Collateral EB Reactions

Acrylic Polymer Network

Formation

(Fundamentals of) Cationic Epoxy

EBC

- **Conclusions**

Implications & Outlook

nemho



TU/e



TU/e × nemho

Introduction

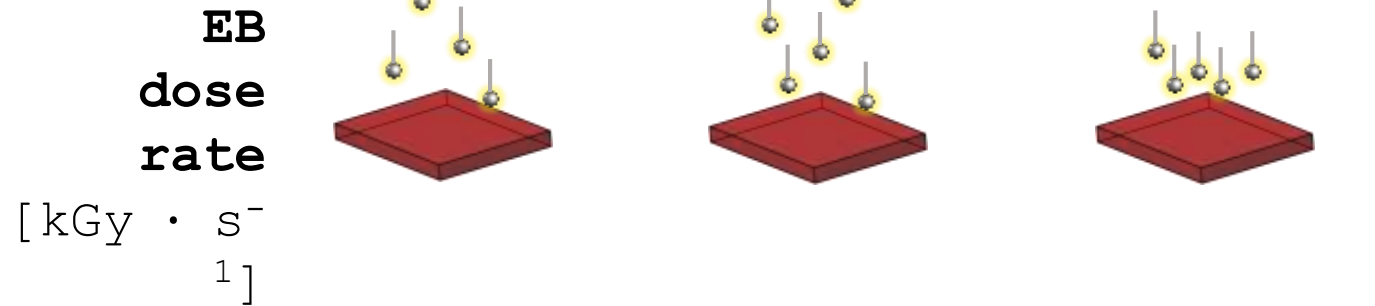
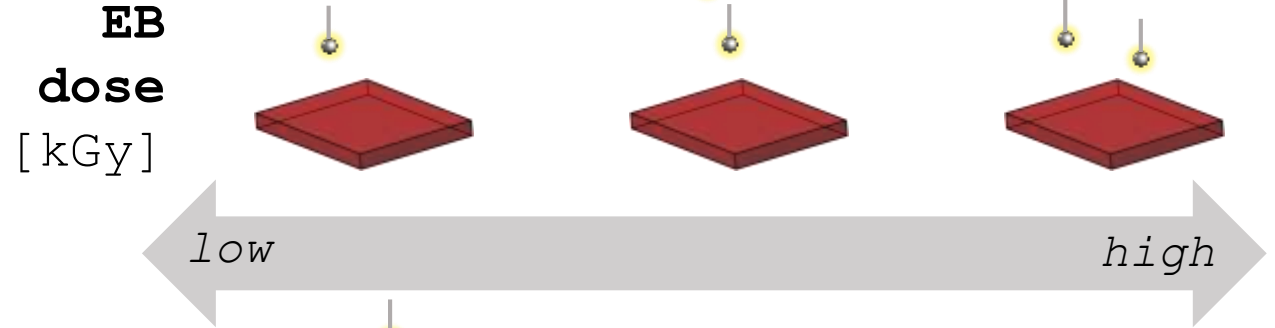
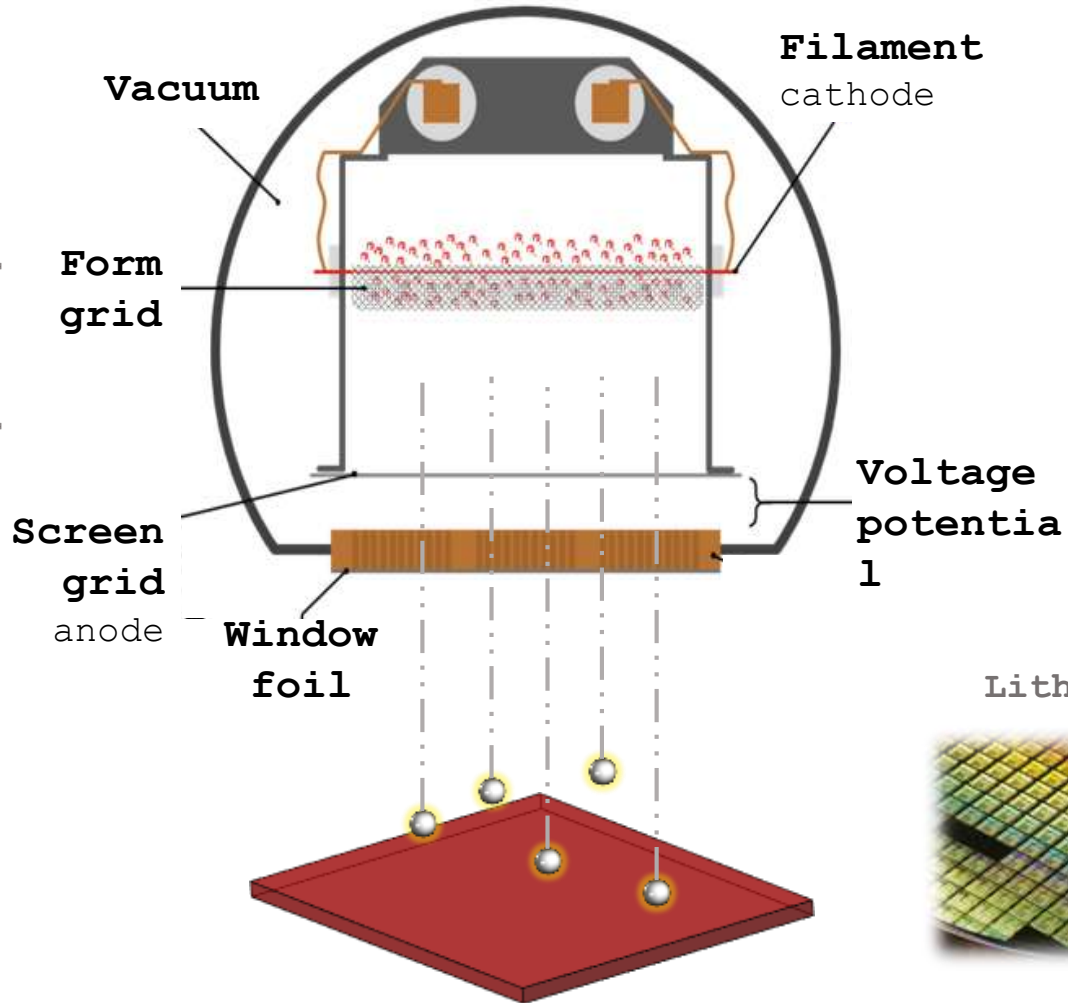
- *EB Technology & Applications*
- *EB (UV)-Curable Coatings*
- *Research Questions*



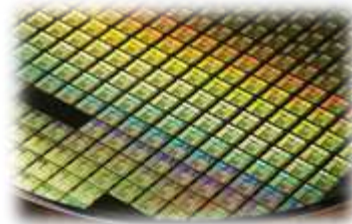
EB Technology & Applications

Introduction

adapted from ptcieb.com



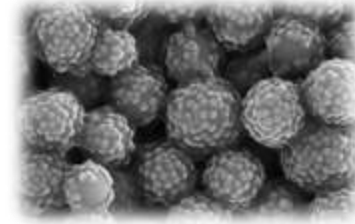
Lithography



Welding



Microscopy

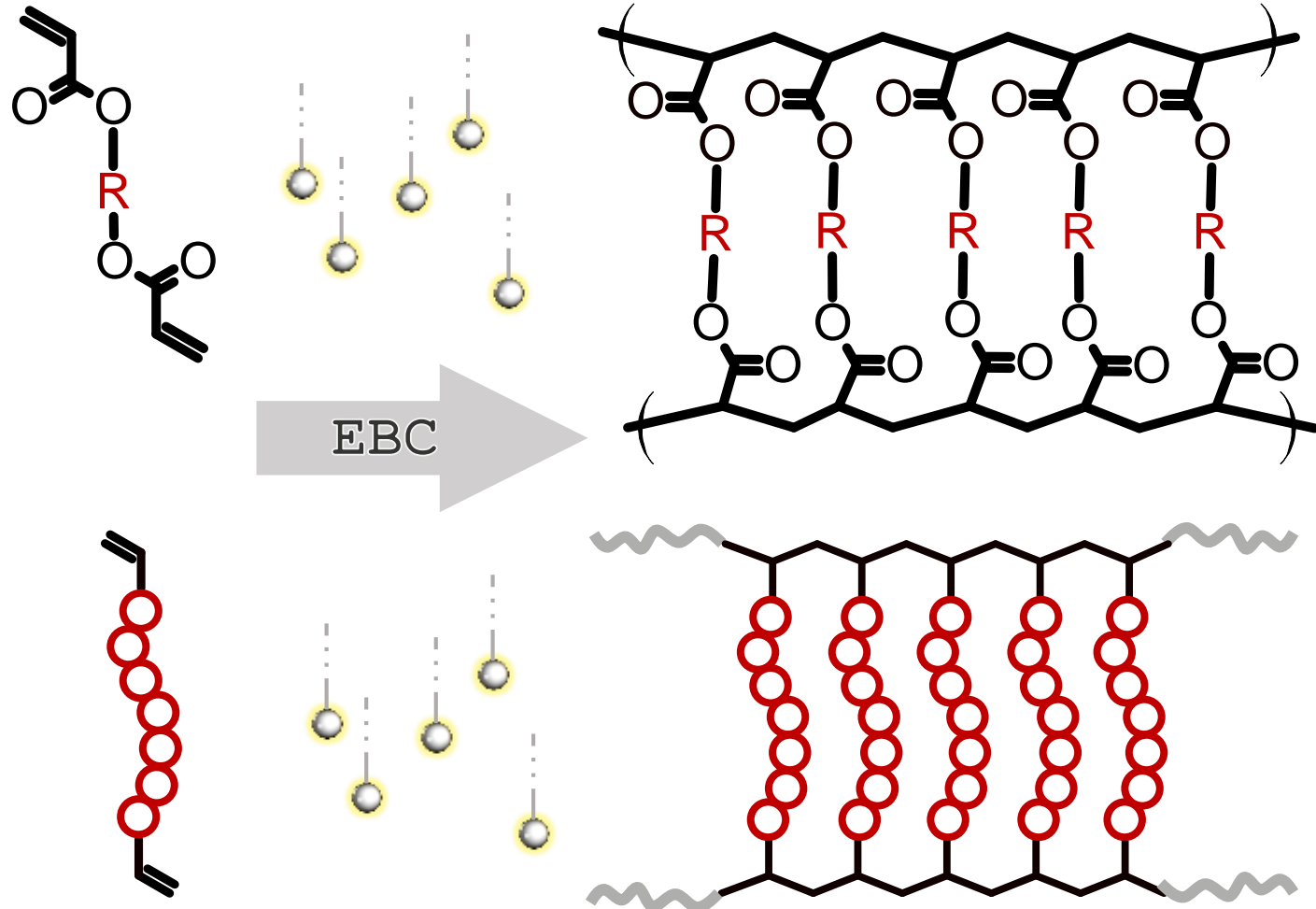


Coatings



EB (UV)-Curable Coatings

Acrylates



Advantages:
(compared to UV)



No photoinitiator needed
Electrons are energetic enough to directly radicalize most organic molecules.



Ultrafast curing
Curing time < ms.



Intrinsically greener technique
VOC- and solvent-free formulations, higher productivity, lower energy consumption (up to 90%)

EB (UV)-Curable Coatings

Epoxies

Epoxy Cationic Curing - Pro's:



No oxygen inhibition



Reduced film shrinkage



Epoxy Cationic Curing - Con's:



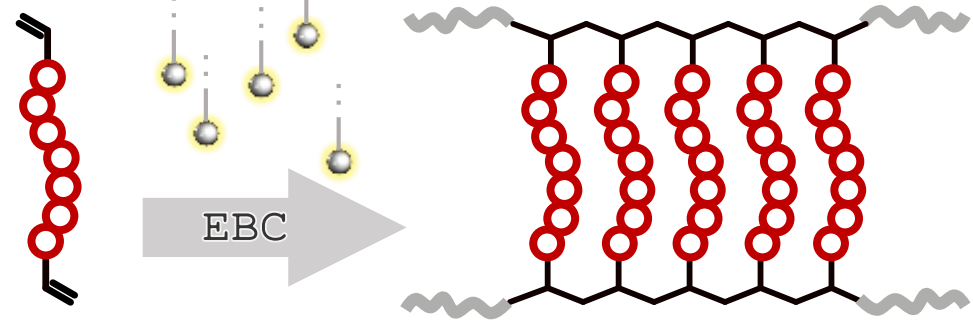
Need for cationic photoinitiators (PI)



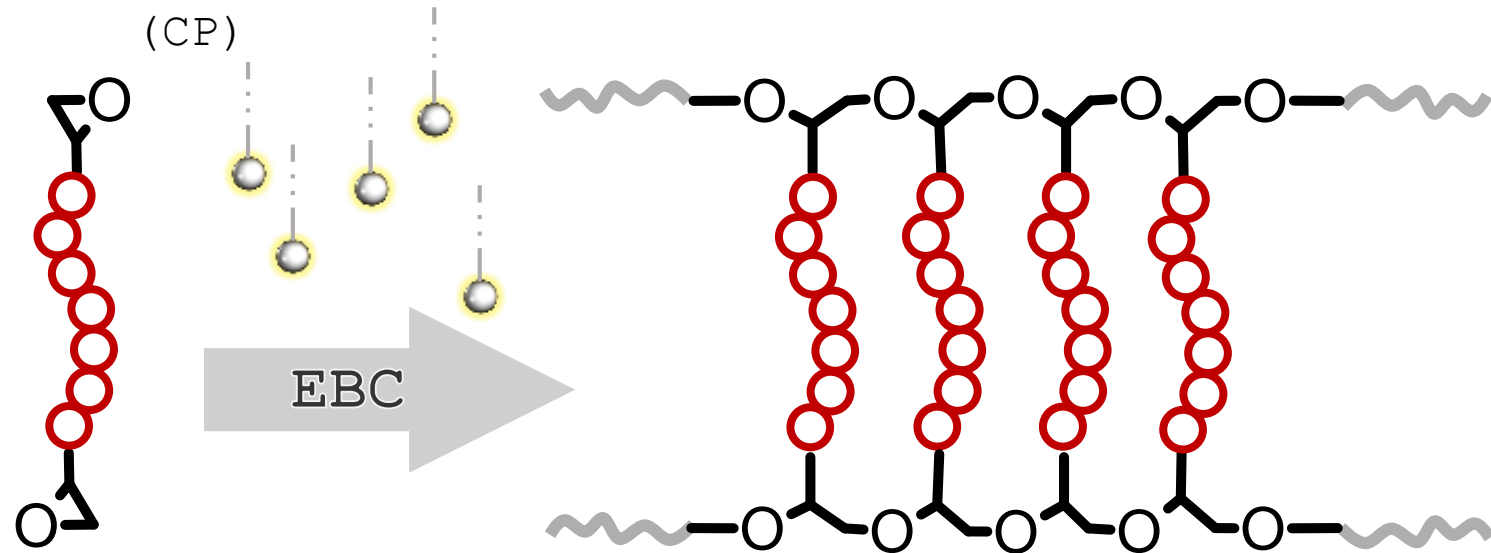
Slower curing and incomplete conversions



Acrylate Resins: Free Radical Polymerization (FRP)



Epoxy Resins: Cationic Polymerization (CP)



EB-Curable Coatings

Hurdles & Research Questions



EBC Hurdles:
(compared to UVC)



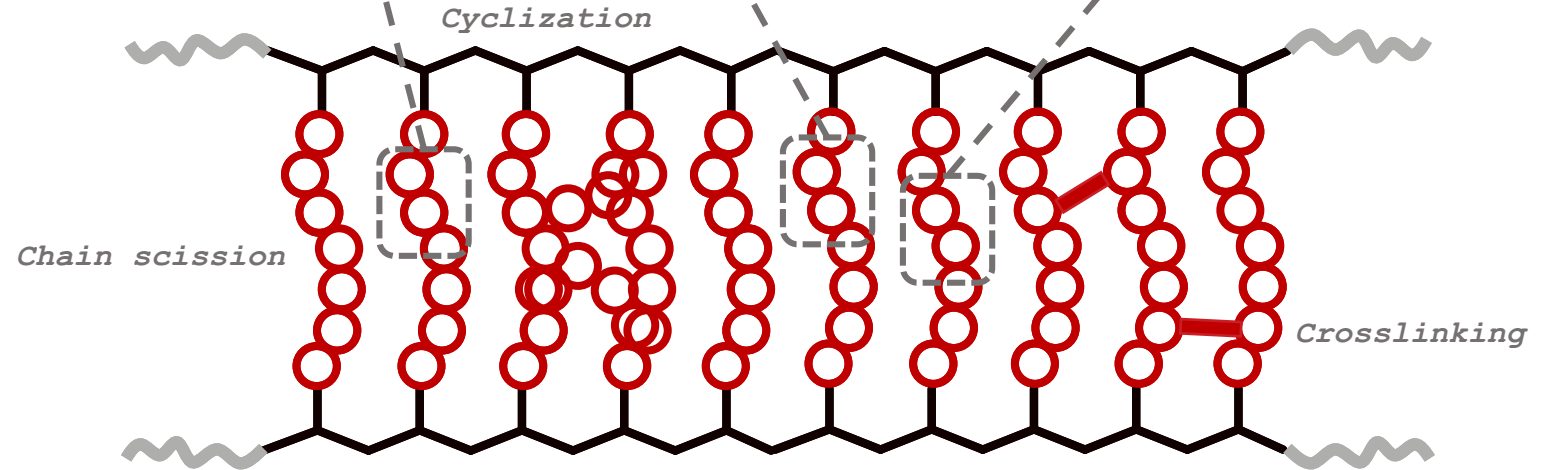
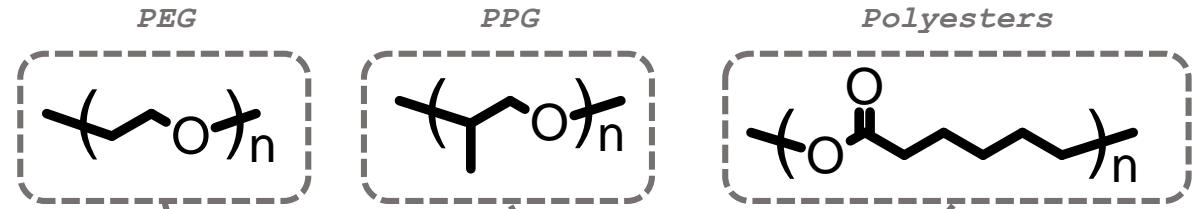
Chaotic radical generation
Possibility of triggering collateral EB chemical reactions.



Effect on material properties
Reduction of final product performance.



Understudied topic
Scarce knowledge - both in patents and academic journals.



Research Goals:

- Identify collateral EB chemical reactions;
- Relate EB process parameters - chemical phenomena - polymer network formation and properties;
- Explore and deploy less conventional EB-curable chemistries.

EBC – Acrylates

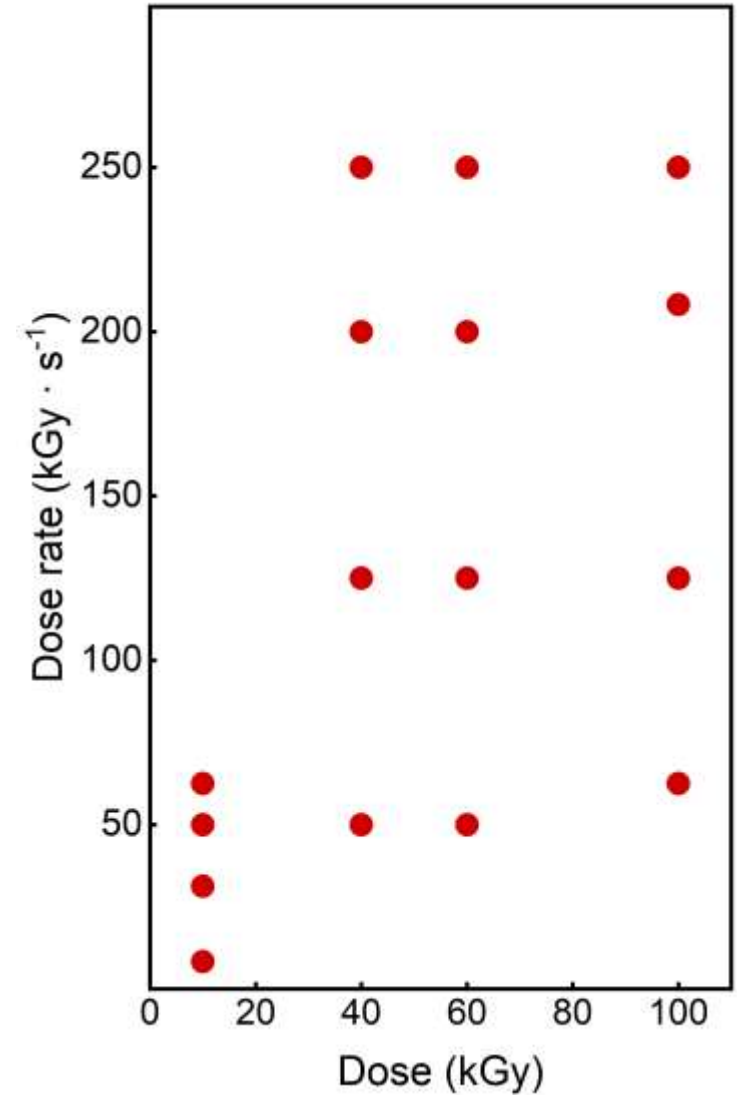
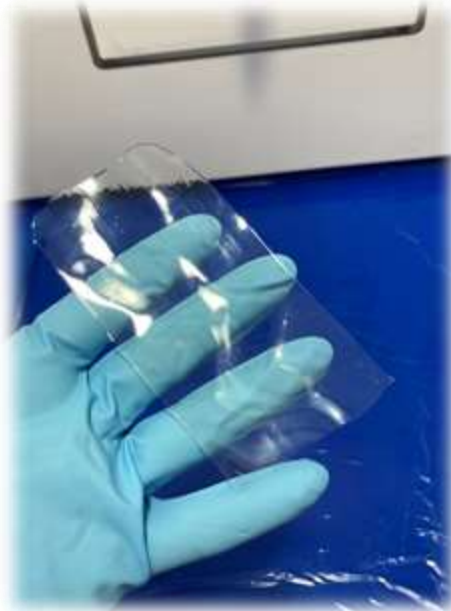
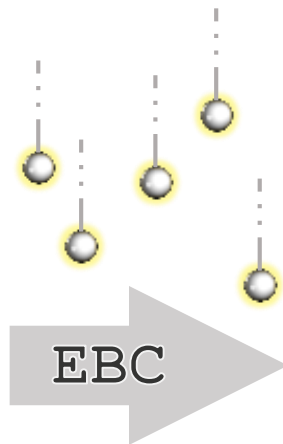
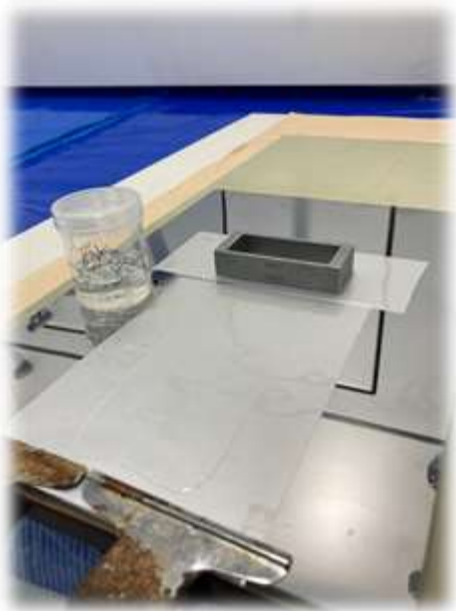
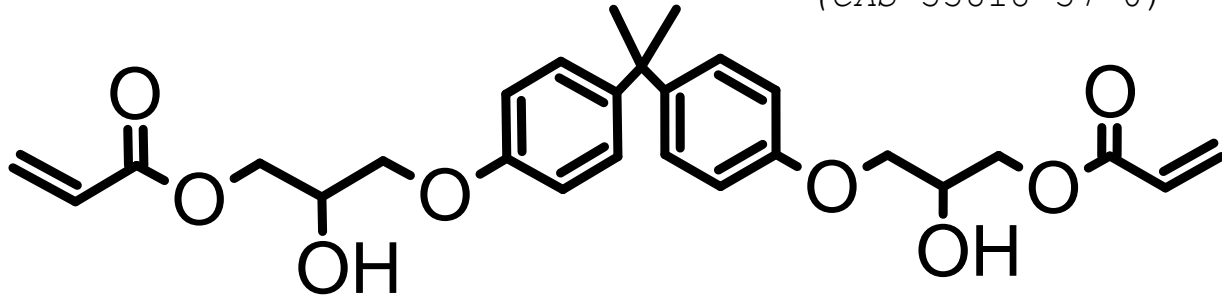
- *Collateral EB Reactions*
- *Acrylic Network Formation & Features*



Experimental Materials & EB Scan



Aromatic epoxy diacrylate
(CAS 55818-57-0)

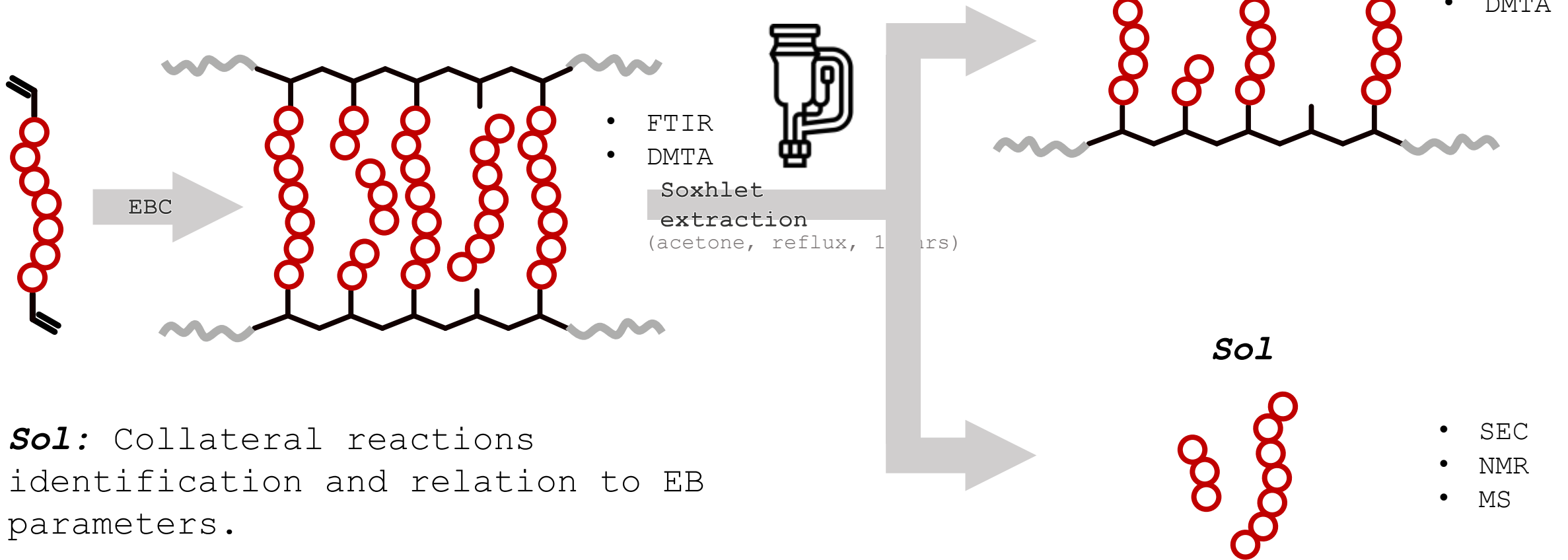


Sample naming:

Dxx DRyy = cured with xx kGy at yy kGy

Experimental

Workflow & Methodology

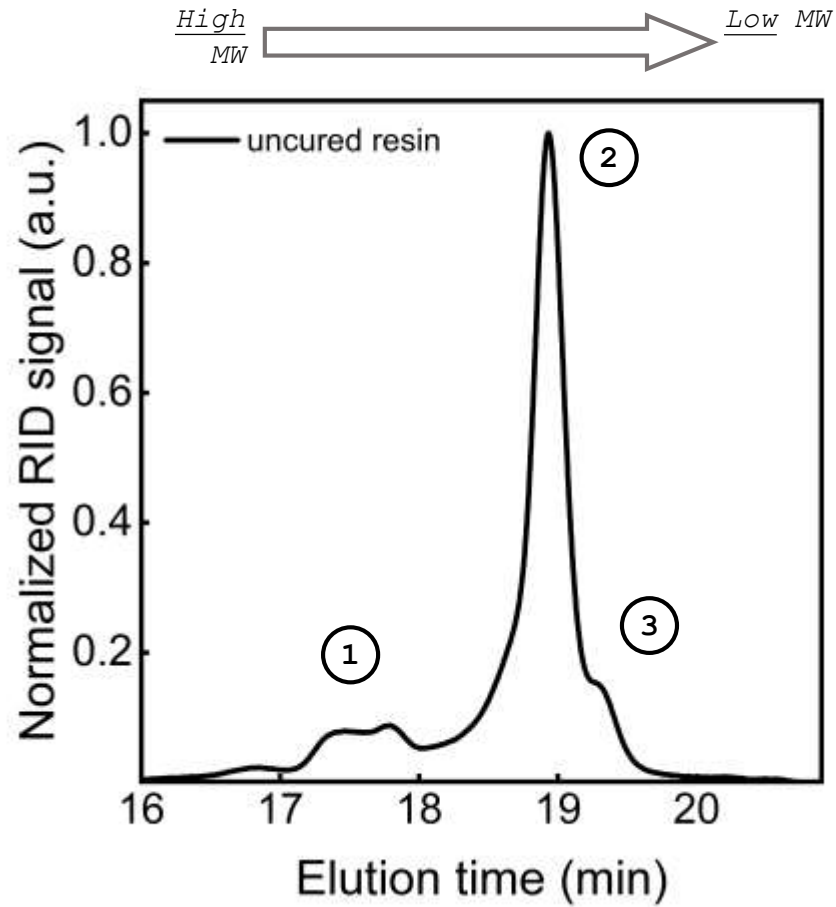
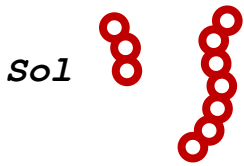


Sol: Collateral reactions identification and relation to EB parameters.

Gel: Polymer network formation and features.

Identification of Collateral EB Reactions

SEC on Sol-Fractions



① = dimer and higher MW species

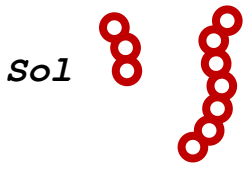
② = monomer

③ = impurities and lower MW species



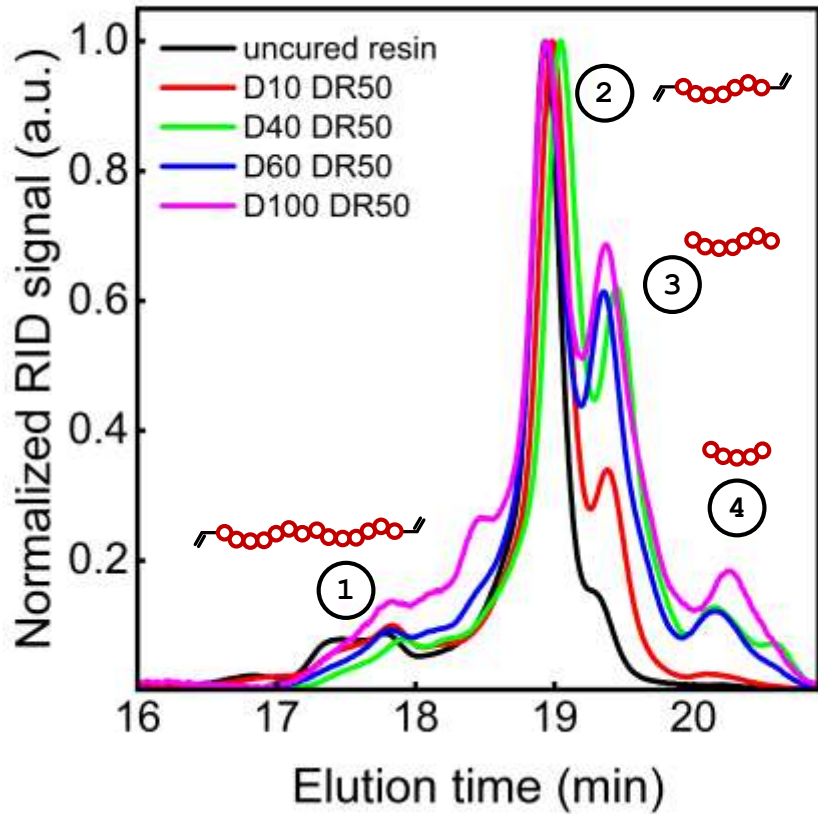
Identification of Collateral EB Reactions

SEC on Sol-Fractions



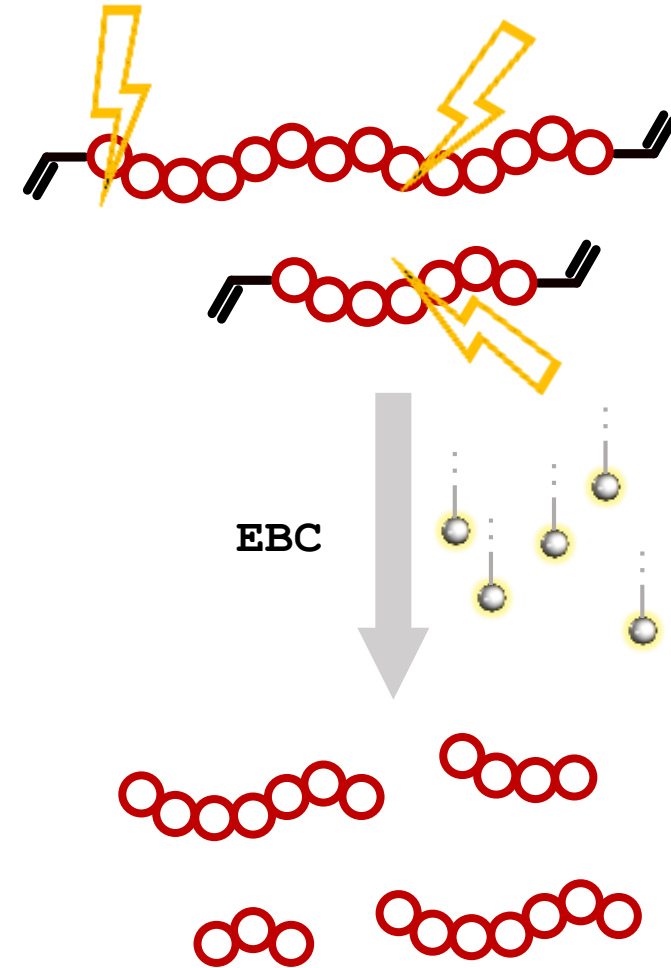
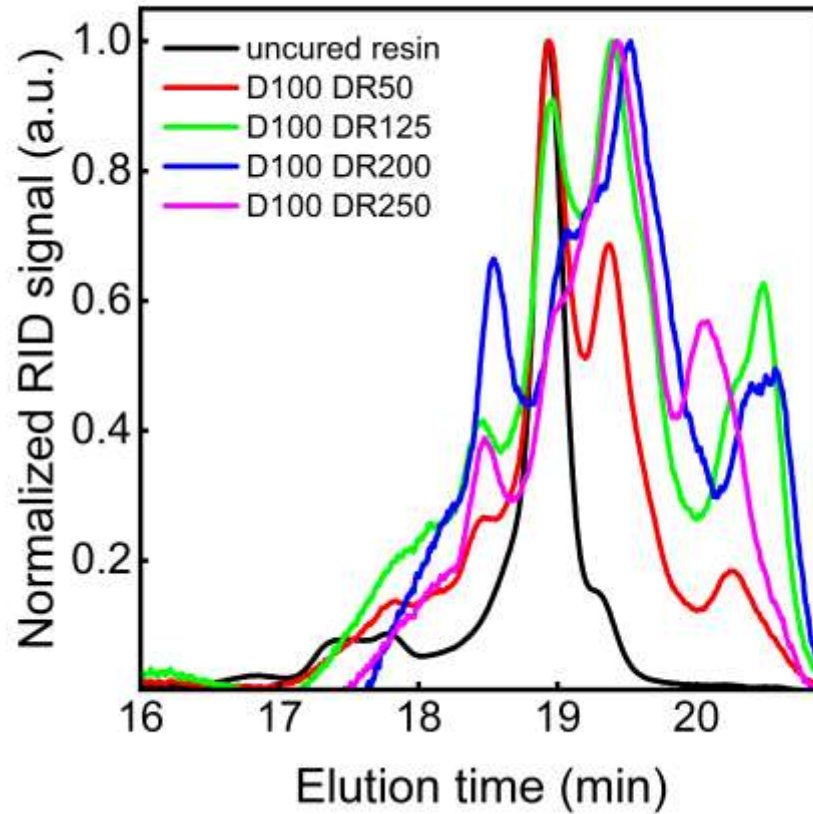
EB dose effect:

High MW \longrightarrow Low MW

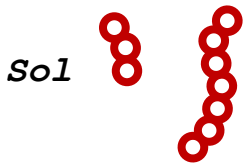


EB dose rate effect:

High MW \longrightarrow Low MW

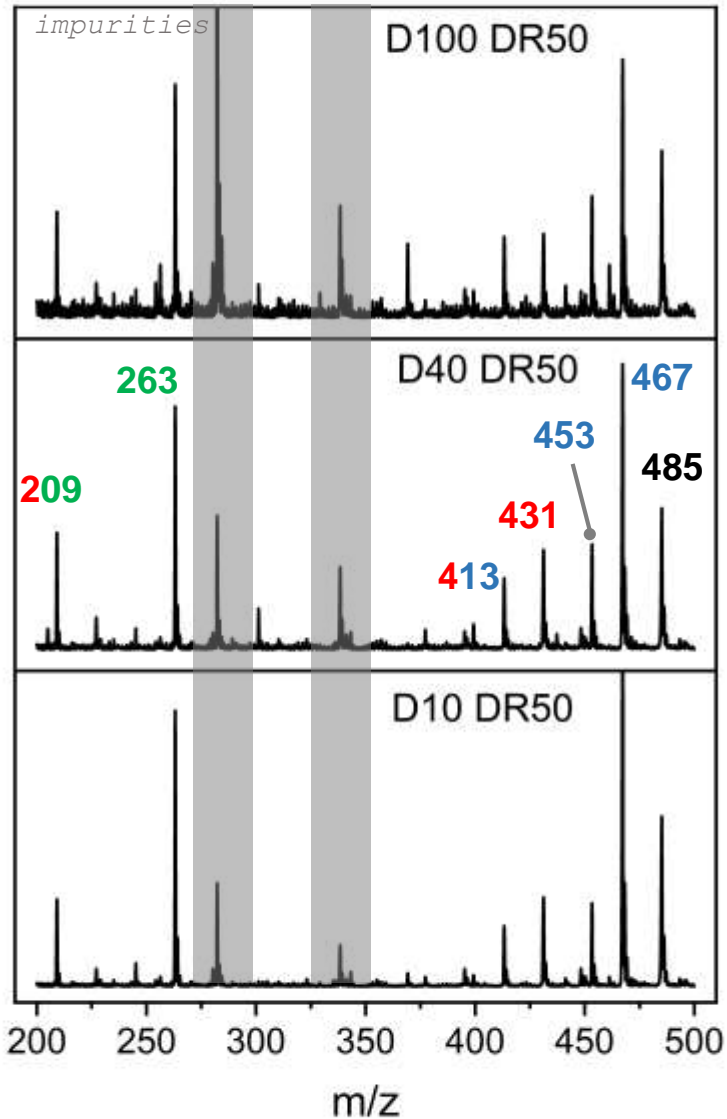


Identification of Collateral EB Reactions

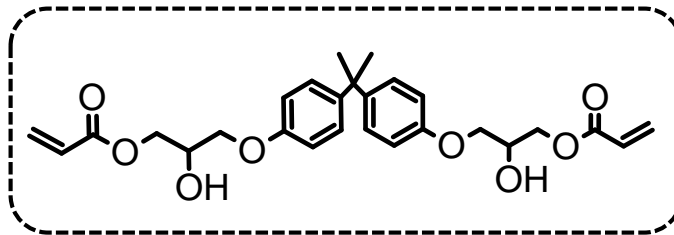


MS on Sol-Fractions

Structures were identified by simulating monomer fragmentation:

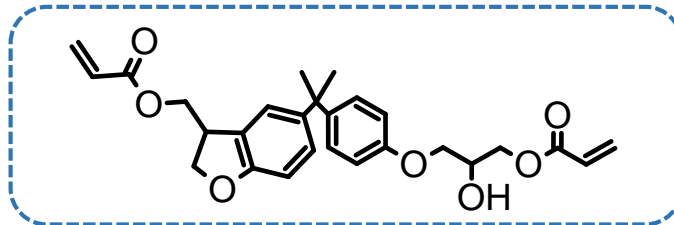


m/z = 485



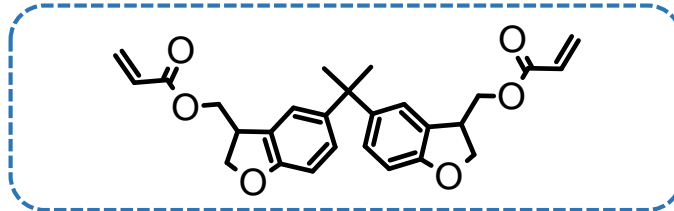
Monomer

m/z = 467



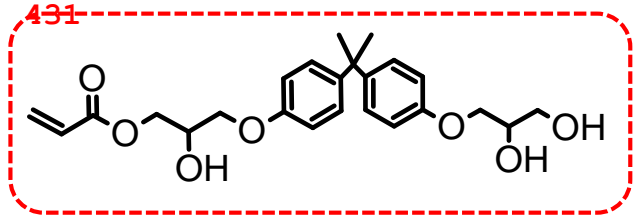
Dehydration

m/z = 453



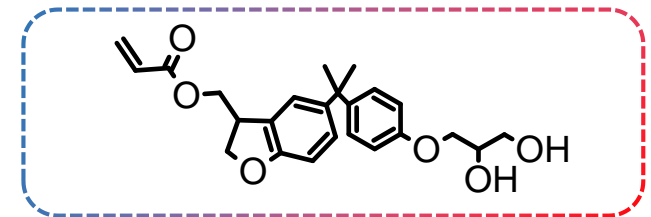
Dehydration

m/z =



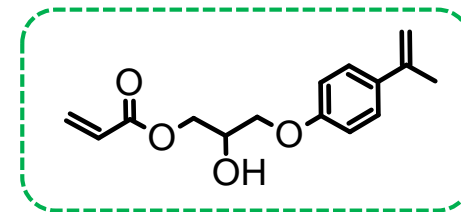
Ester hydrolysis

m/z = 413



Ester hydrolysis + dehydration

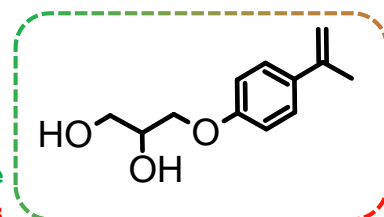
m/z = 263



C-C cleavage

C-C cleavage + ester hydrolysis

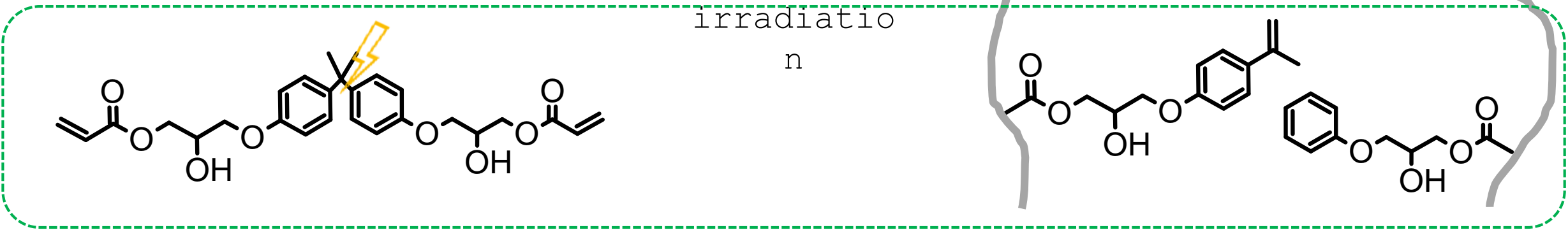
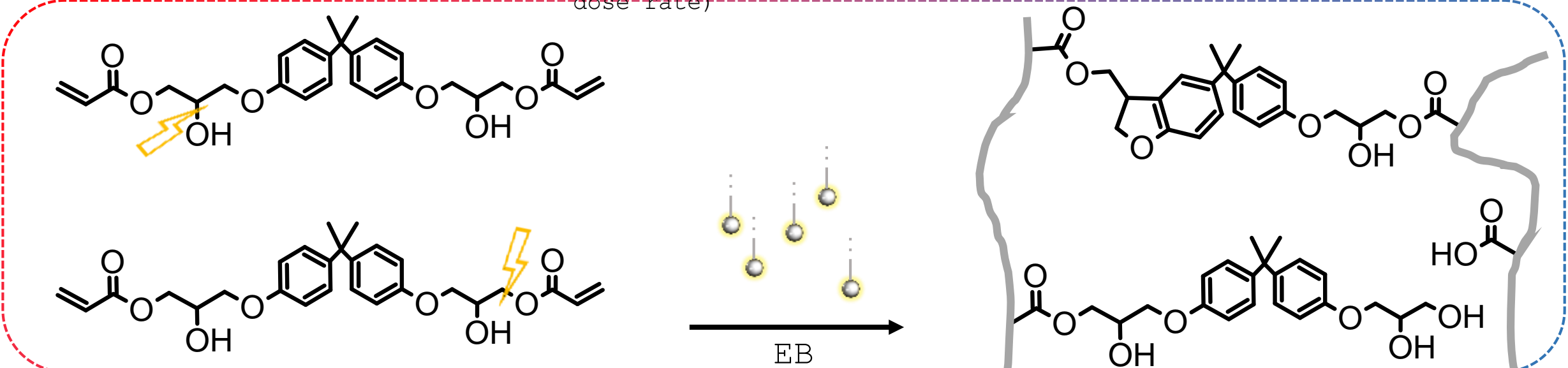
m/z = 209



Identification of Collateral EB Reactions

Resume

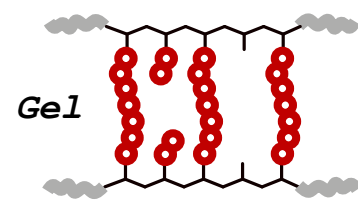
Dehydration & ester hydrolysis when increasing **EB doses** (constant dose rate)



C-C cleavage when increasing **EB dose rate** (constant dose)

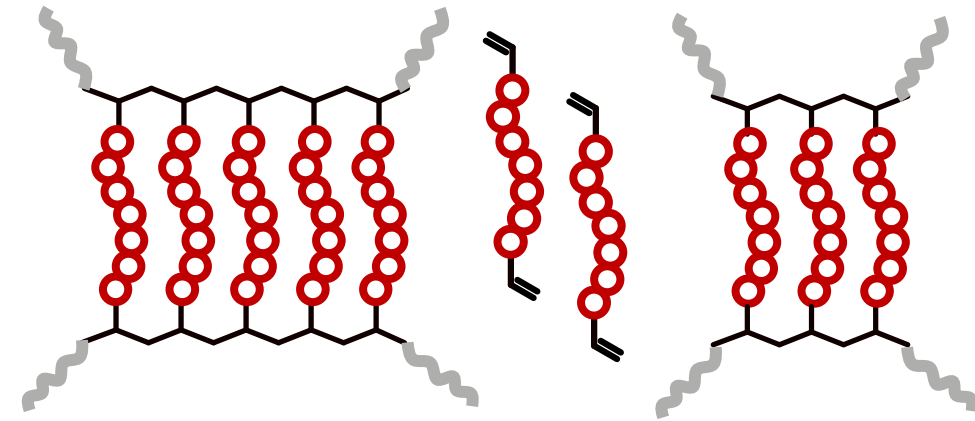
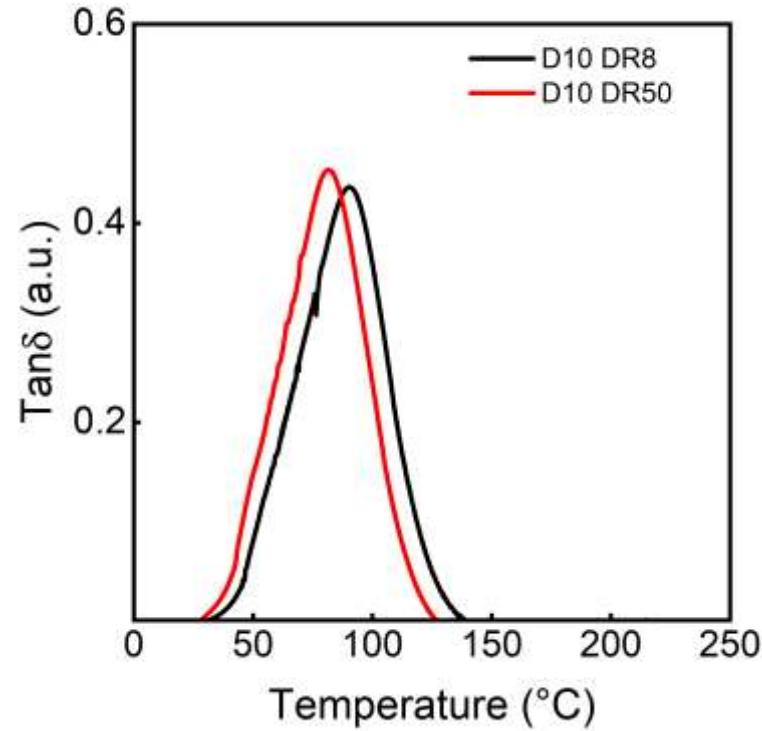
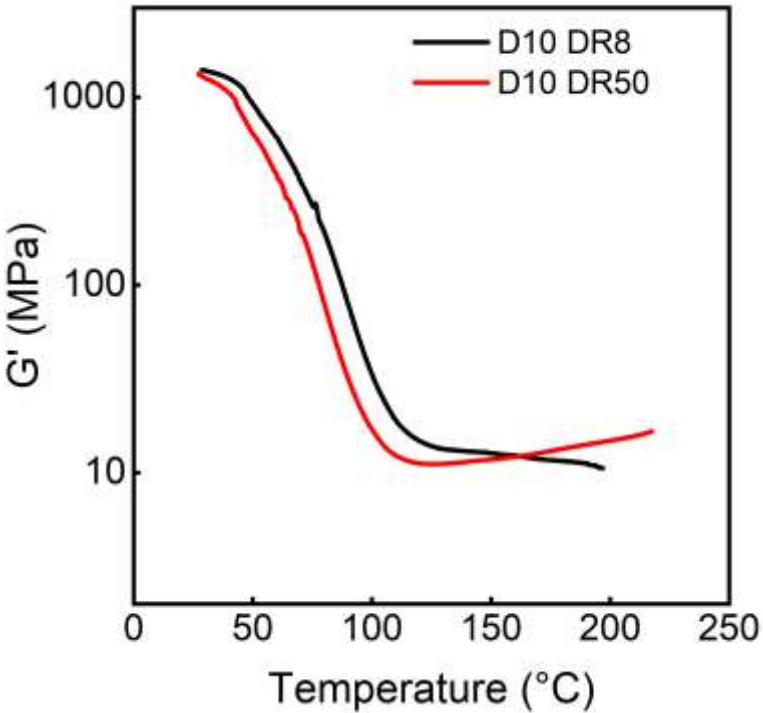
Acrylic Network Formation & Features

Attribution to EB reactions



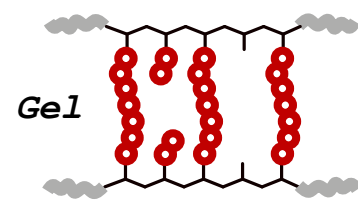
EB Dose = 10
kGy

Before extraction
After extraction



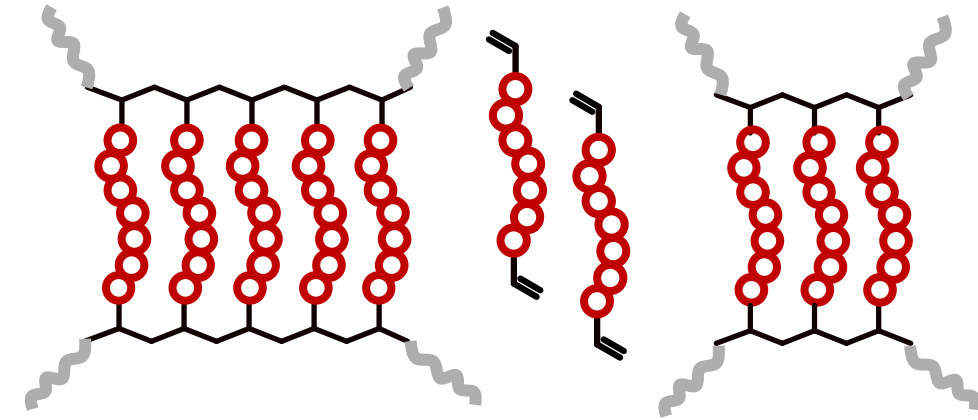
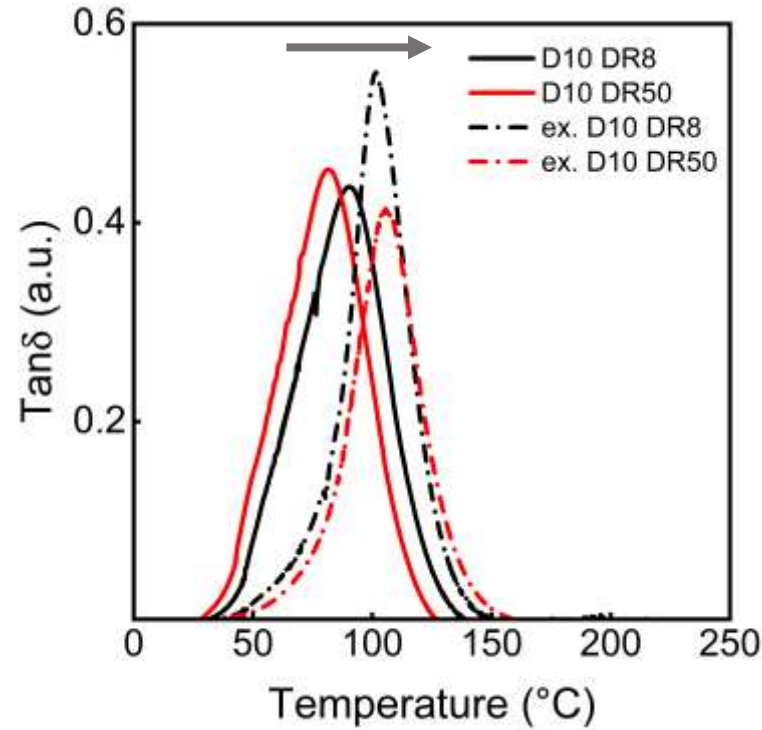
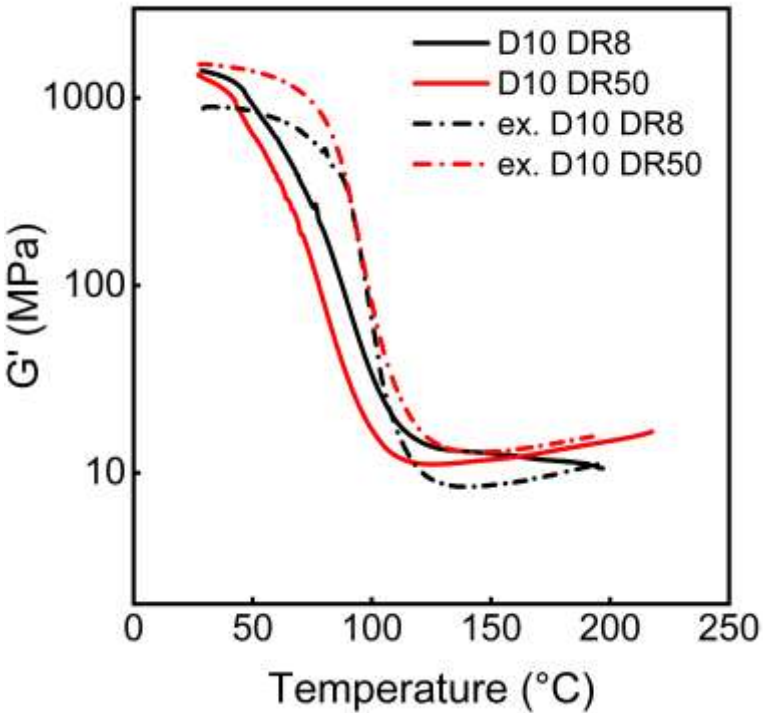
Acrylic Network Formation & Features

Attribution to EB reactions



EB Dose = 10
kGy

Before extraction
After extraction

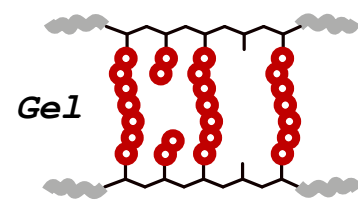


Plasticizing effect of sol-fraction

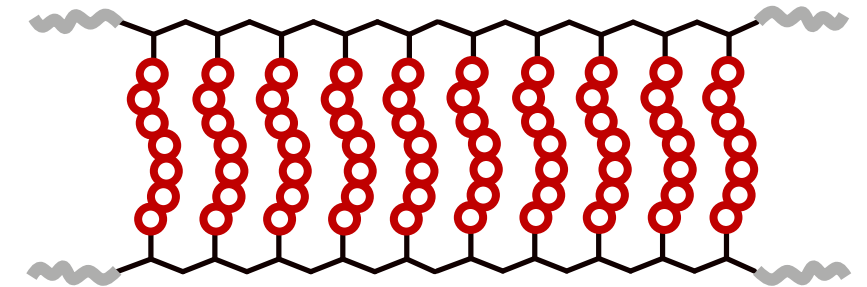
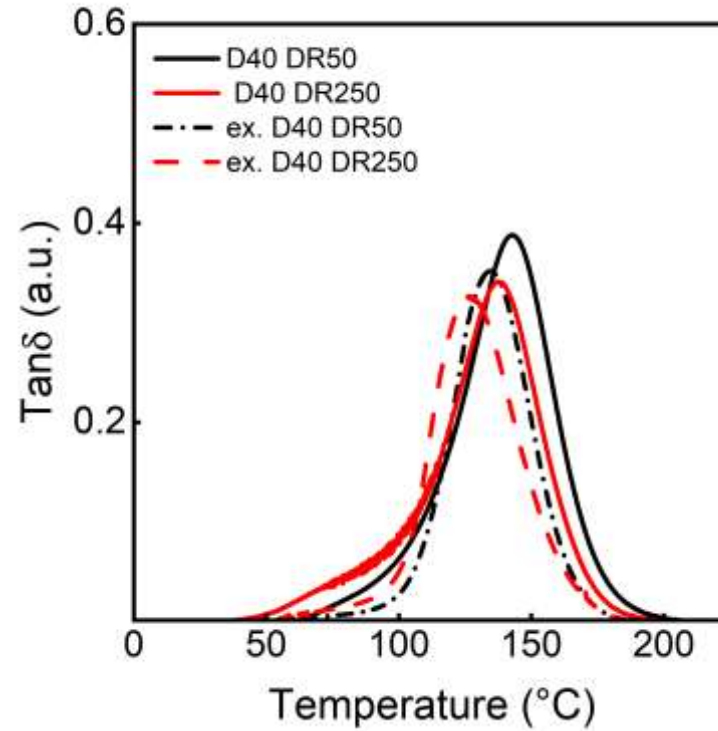
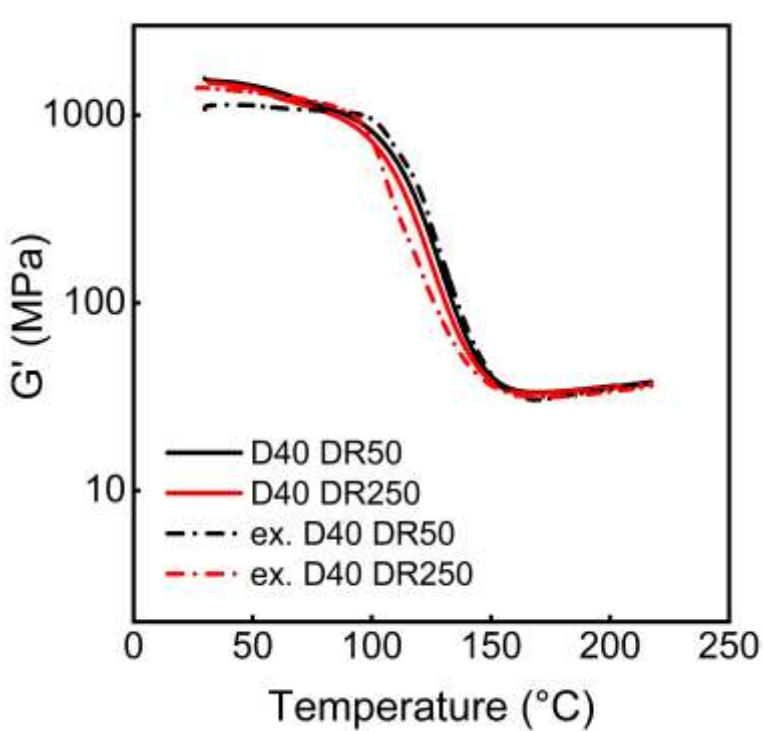
→ T_g increase

Acrylic Network Formation & Features

Attribution to EB reactions



 EB Dose = 40 kGy

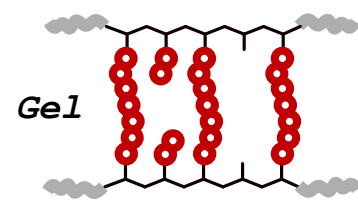


Optimal monomer conversion

→ T_g unchanged

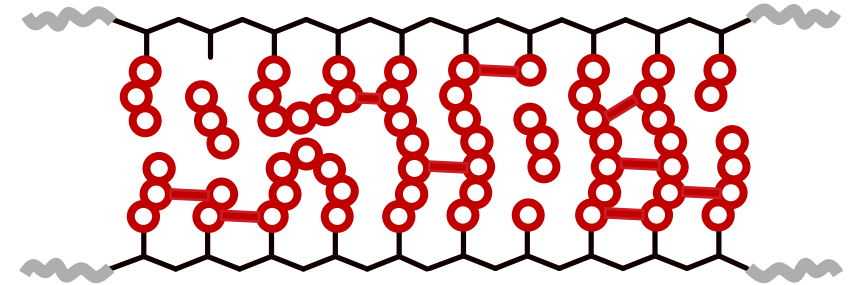
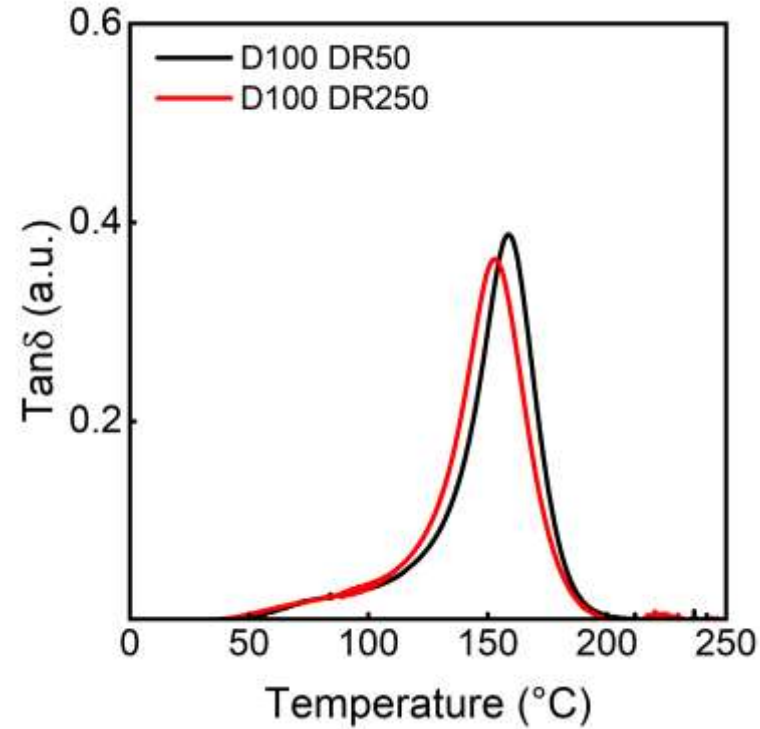
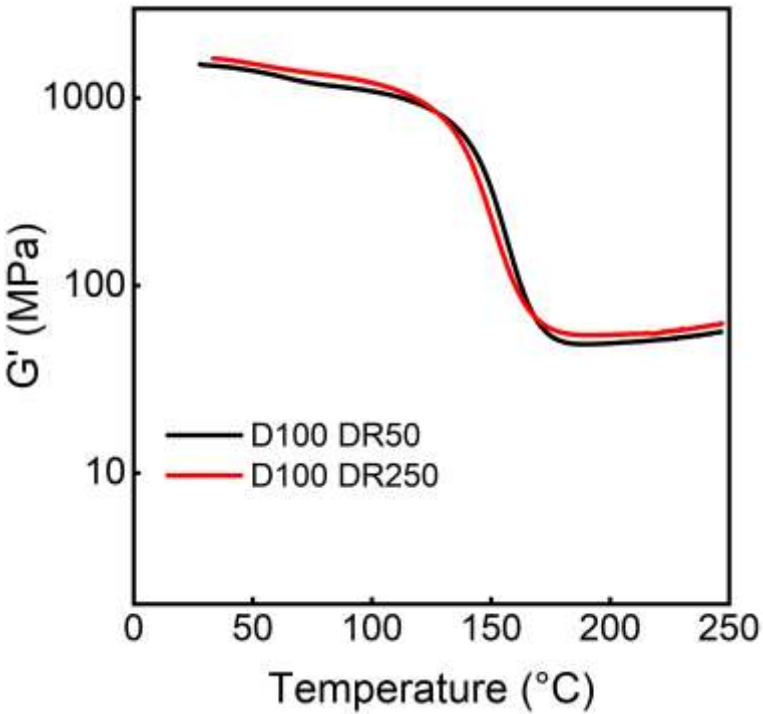
Acrylic Network Formation & Features

Attribution to EB reactions



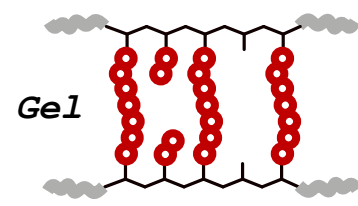
EB Dose = 100
kGy

Before extraction
After extraction



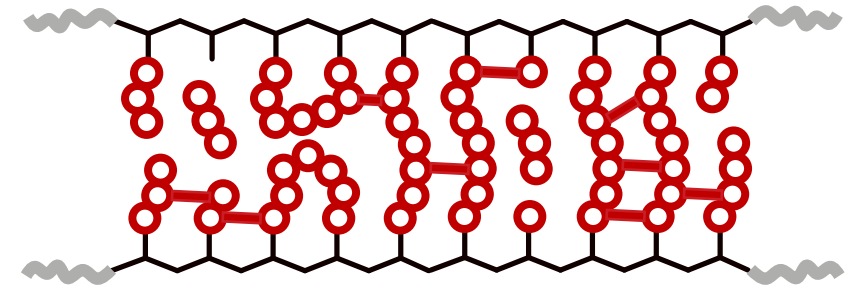
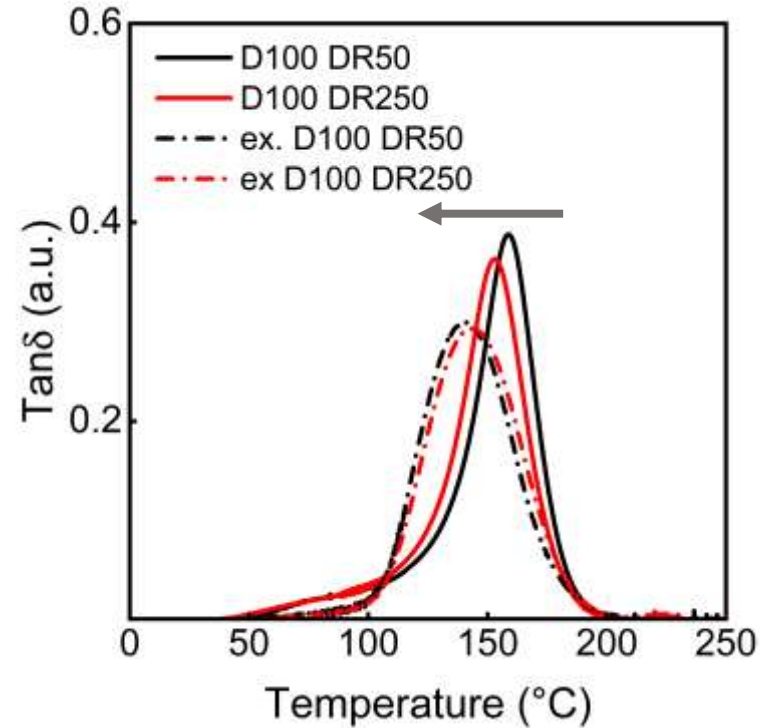
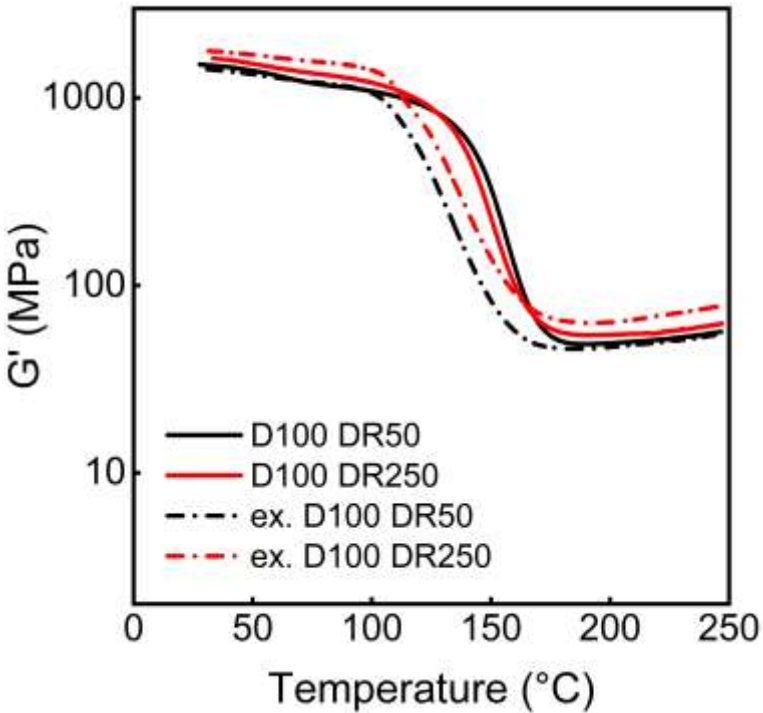
Acrylic Network Formation & Features

Attribution to EB reactions



EB Dose = 100
kGy

Before extraction
After extraction



Extraction shows
introduction of network
defects

→ T_g decrease

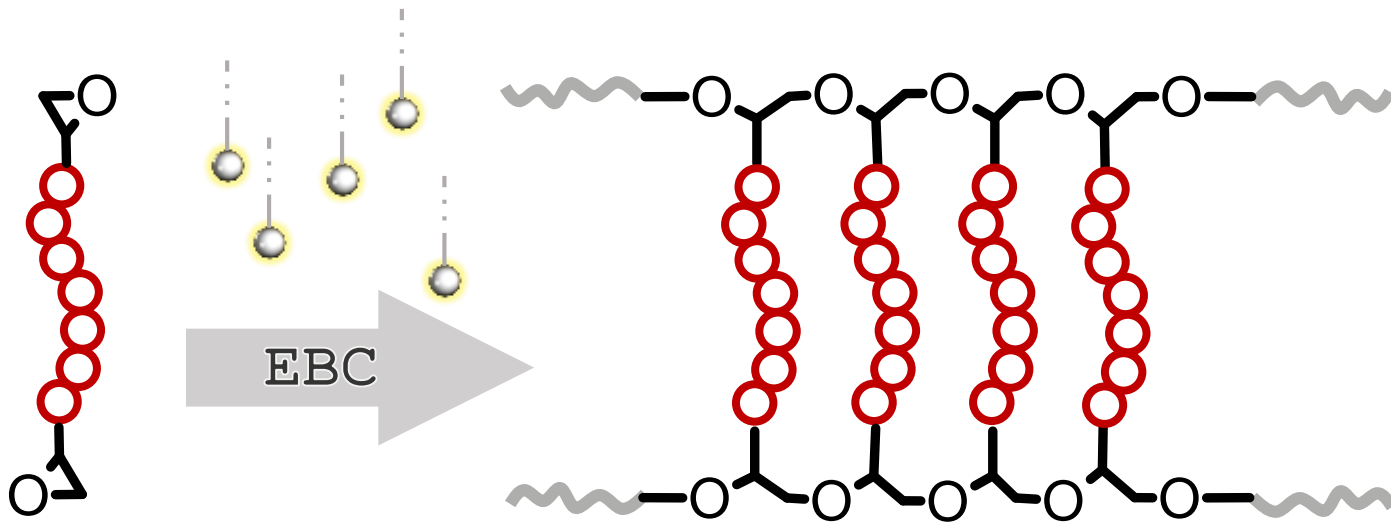
EBC – Epoxies

- *Cationic Curing:
Conditions & Kinetics*
- *Preliminary Epoxy
(Coatings) Characteristics*

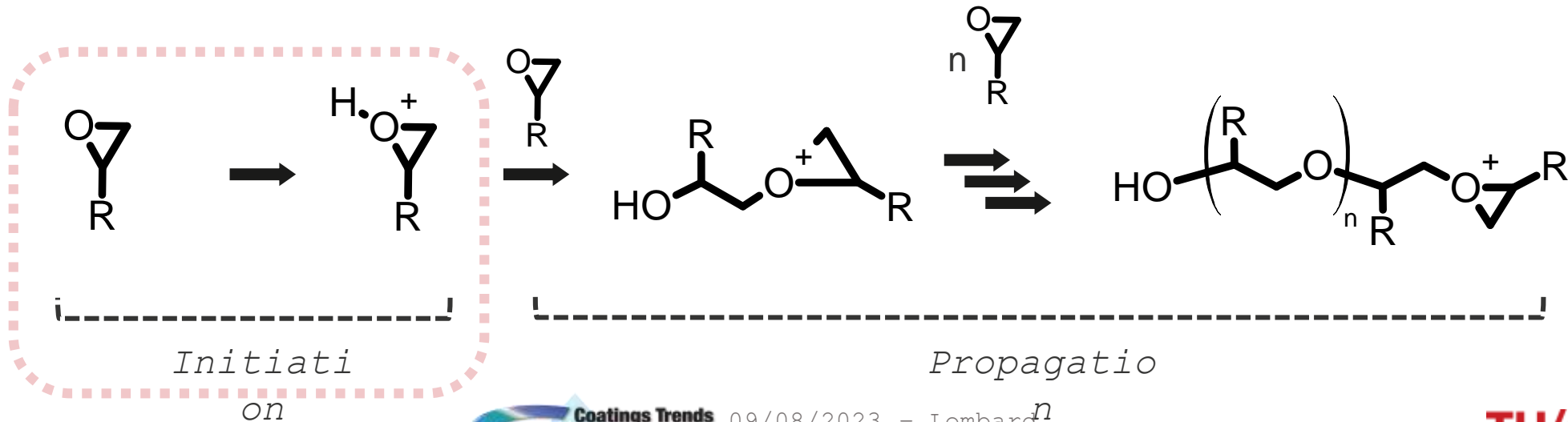
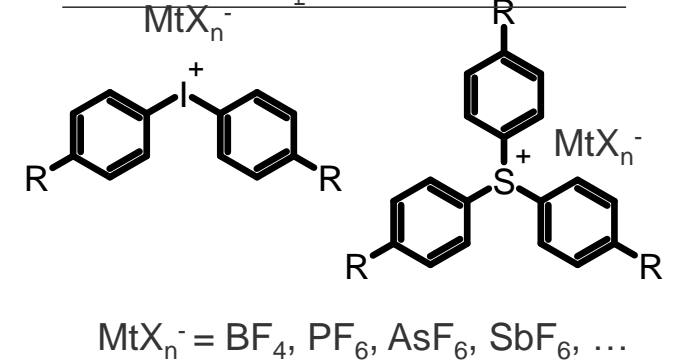


Epoxy Cationic EBC

Introduction



Onium salts: photoacid generators employed as cationic photoinitiators



Epoxy Cationic EBC

Features & Research Questions



Epoxy – Pro's:



Reduced film shrinkage
Due to ring opening polymerization.



Absence of oxygen inhibition
No need for inerting in cationic polymerizations.



Better coating properties
E.g. chemical resistance, abrasion resistance, adhesion, ...



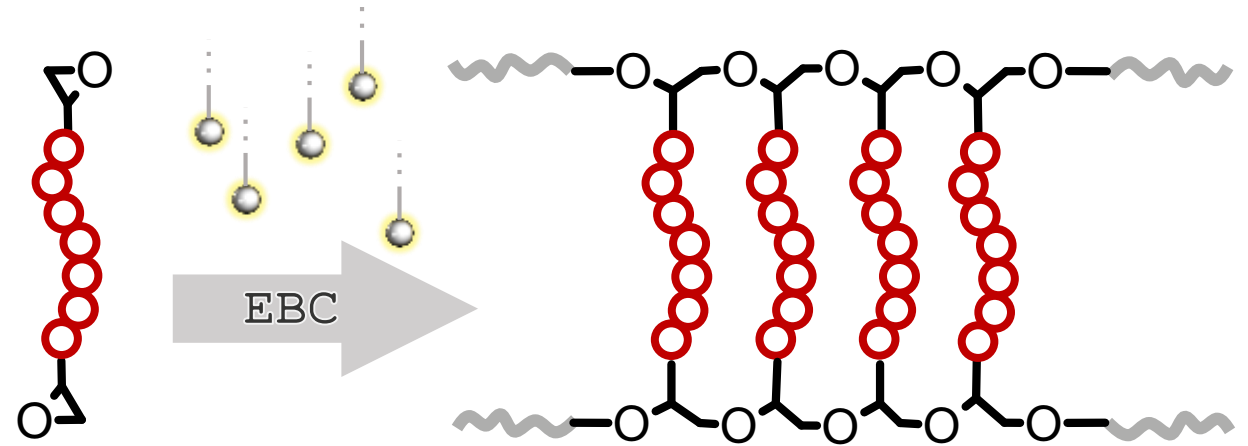
Epoxy – Con's:



Cationic PI needed
Photoacid generators trigger cationic curing.



Slower curing rate
EBC alone might not be sufficient to attain full cure.



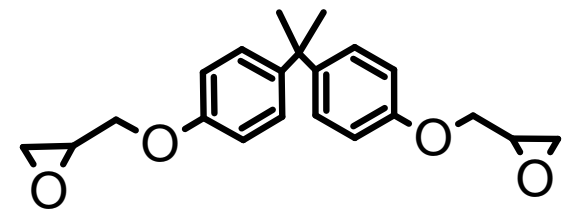
Research Goals:

- Determine EB epoxy curing kinetics.
- (Fundamental) characterization of different epoxy polymer films.
- Assess added value and specific potential applications for different epoxies.

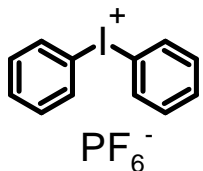
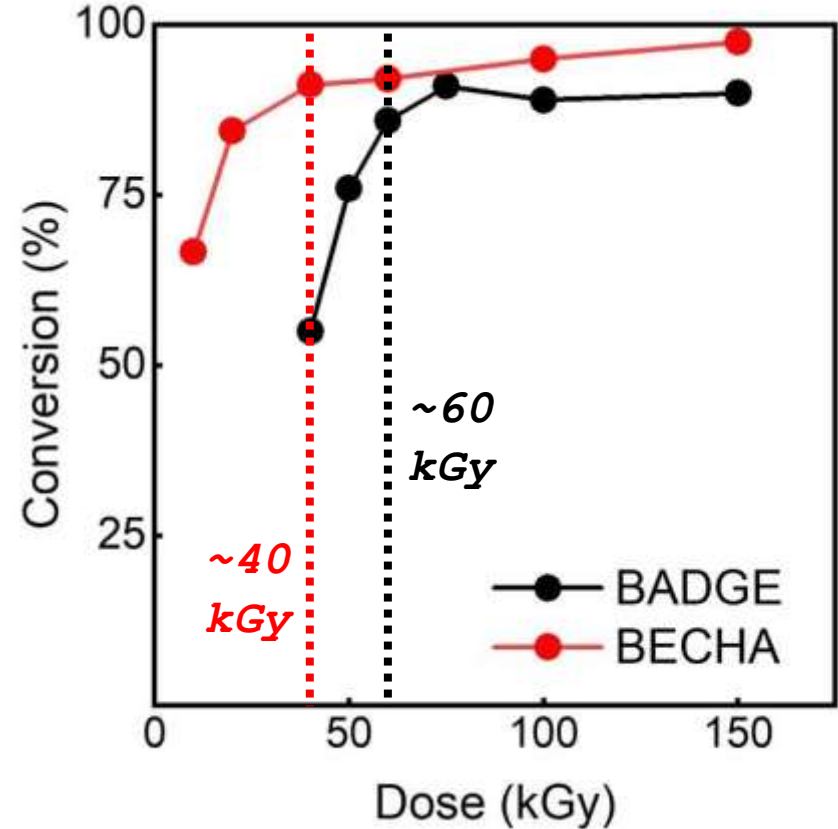
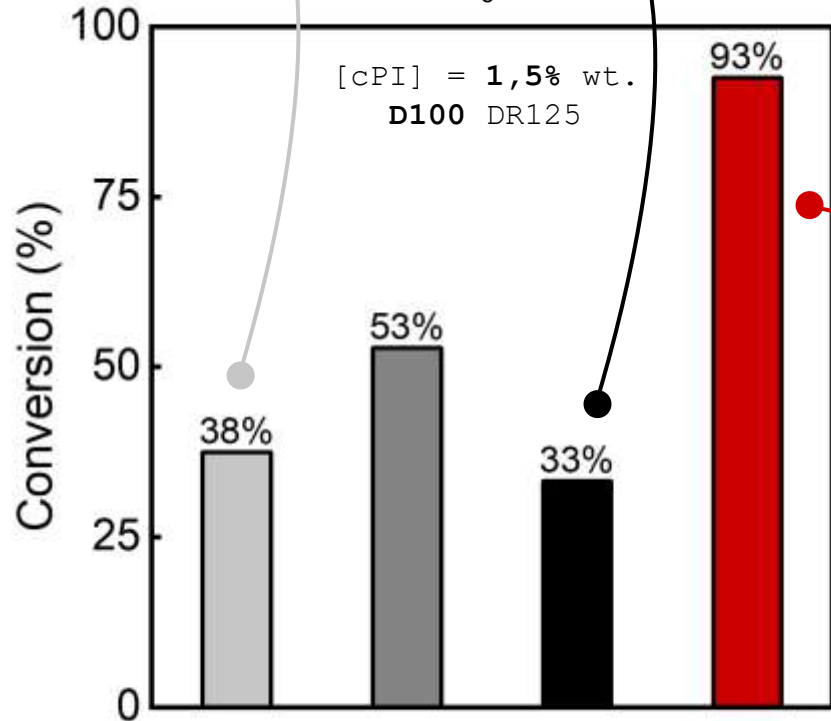
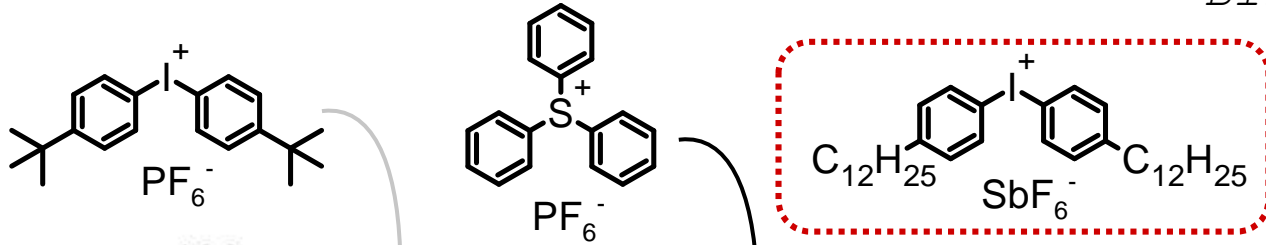
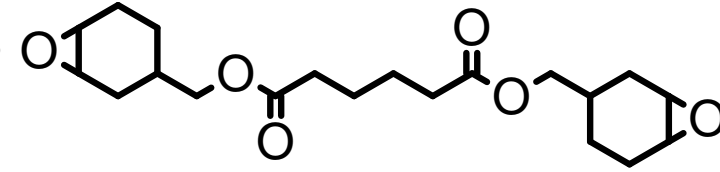
Epoxy Cationic EBC

PI Selection & Kinetics

Bisphenol-A diglycidyl ether
(**BADGE**)
(CAS 1675-54-3)

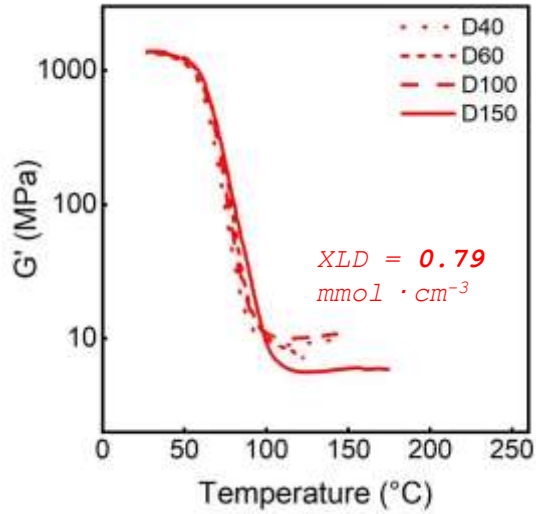
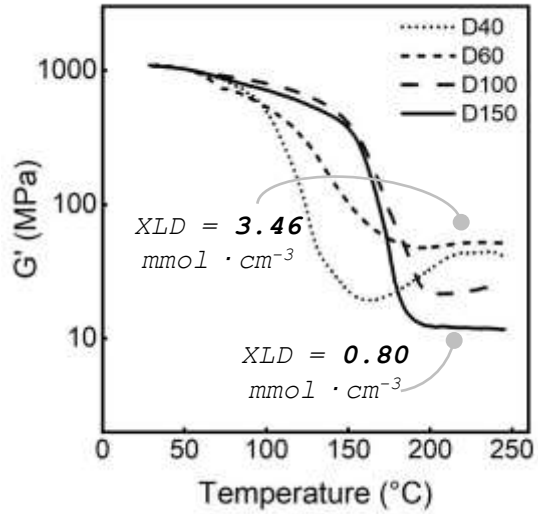
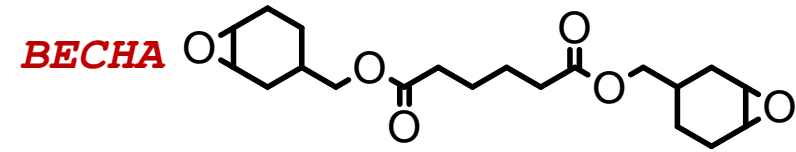
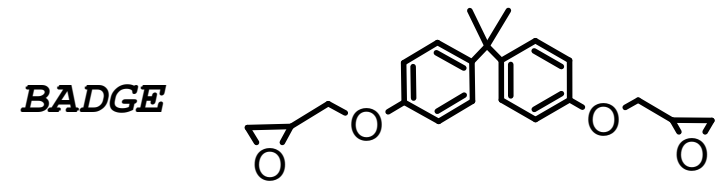


Bis(epoxycyclohexylmethyl) adipate
(**BECHA**)
(CAS 3130-19-6)



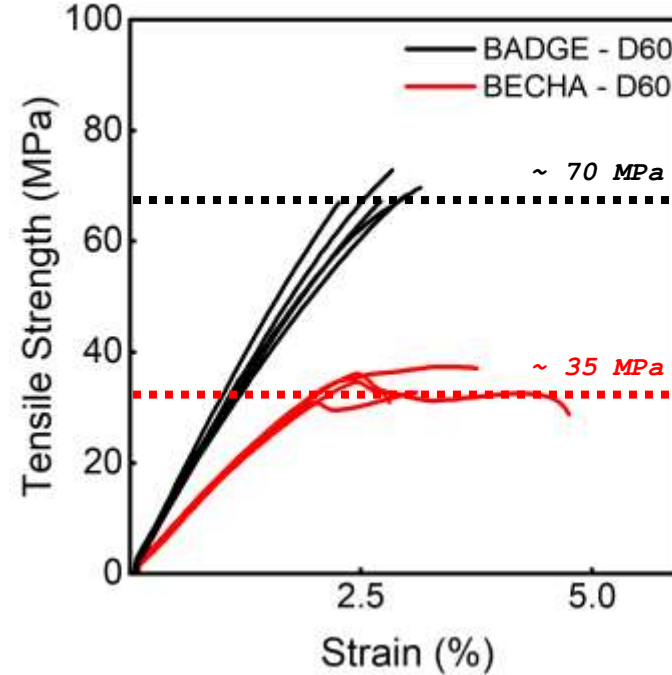
Epoxy Cationic EBC

Polymer & Coating Characterization



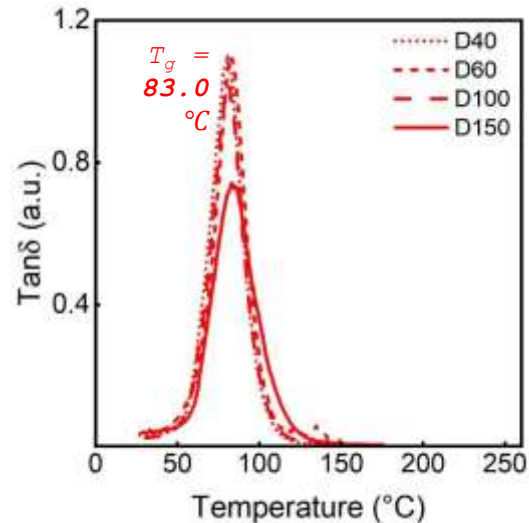
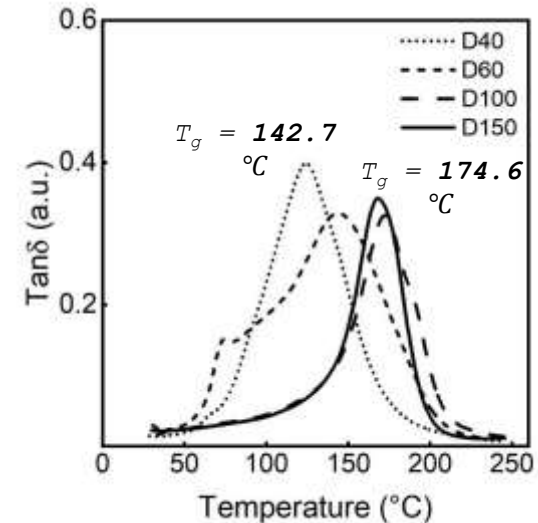
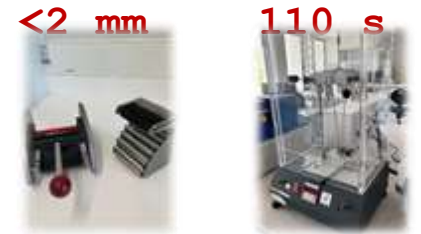
Crosslink density =

$$XLD = \frac{G'}{3 \cdot \rho \cdot R \cdot T}$$



Cylindrical mandrel flexibility
Konig hardness

	Cylindrical mandrel flexibility	Konig hardness
BADGE		
-	>32 mm	240 s
D60		
BECHA		
-	<2 mm	110 s
D60		



Conclusions

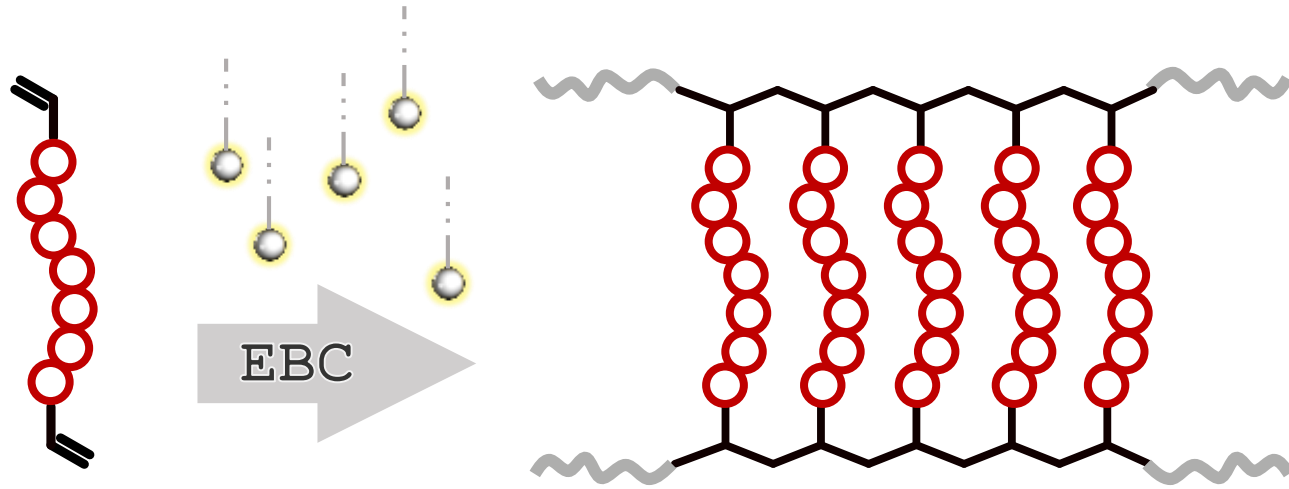
- Meaning & Implications
- Outlook

- Acknowledgements

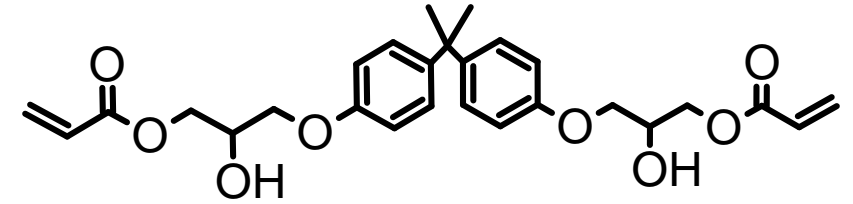


EB Acrylic Networks - Conclusions

Learnings & Implications

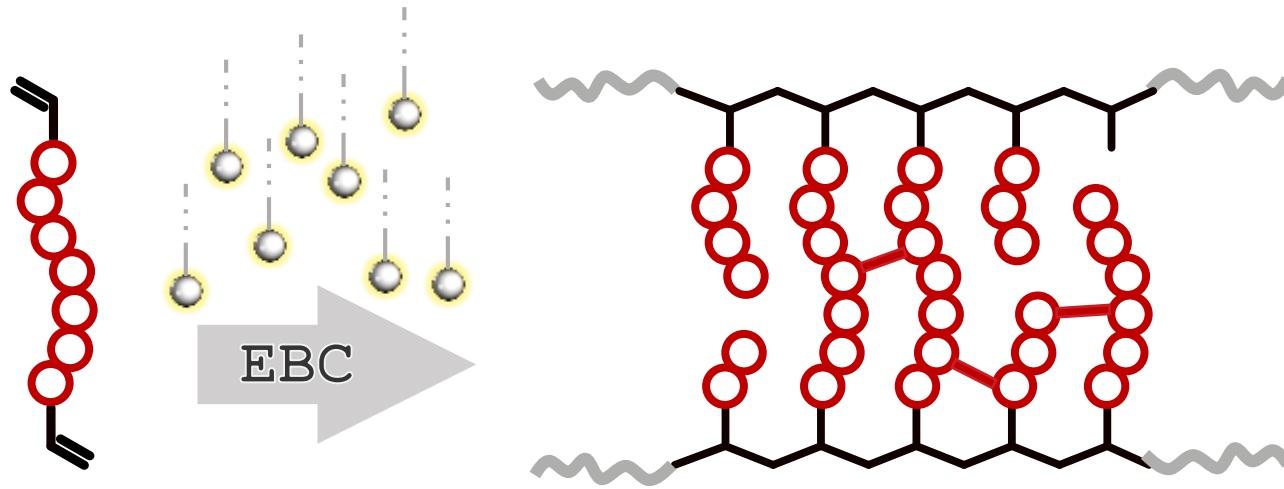


Optimal curing EB dose (rate)

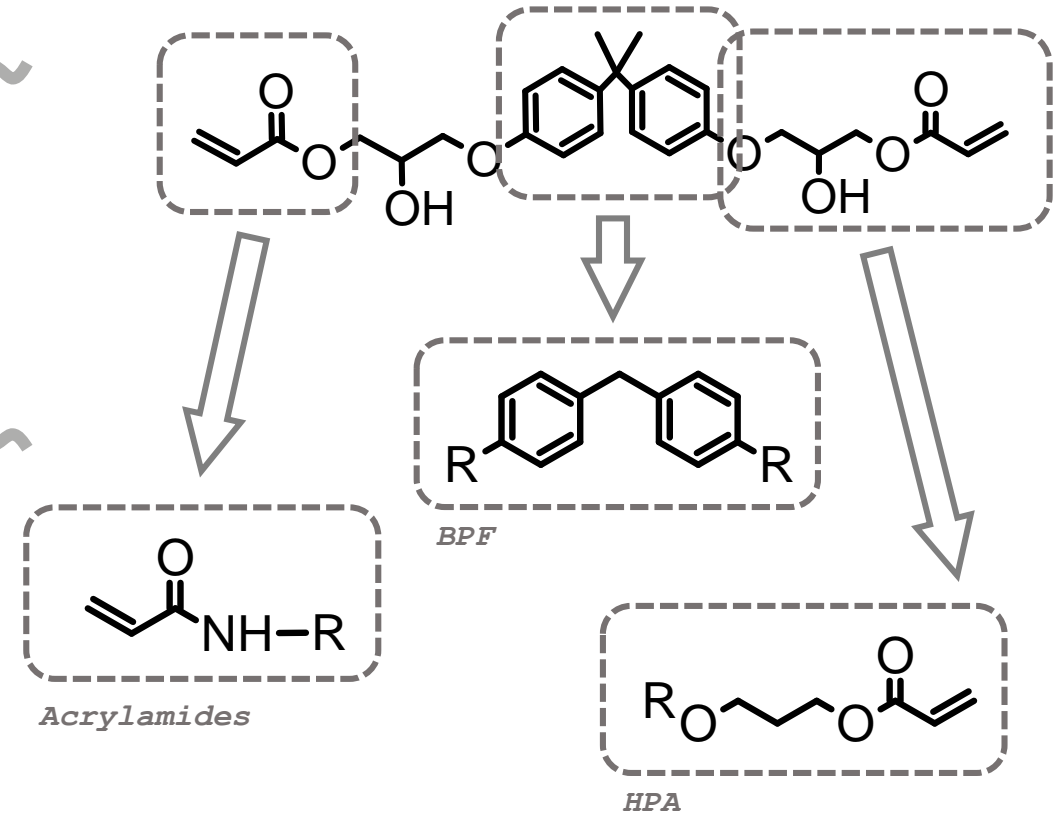


EB Acrylic Networks - Conclusions

Learnings & Implications



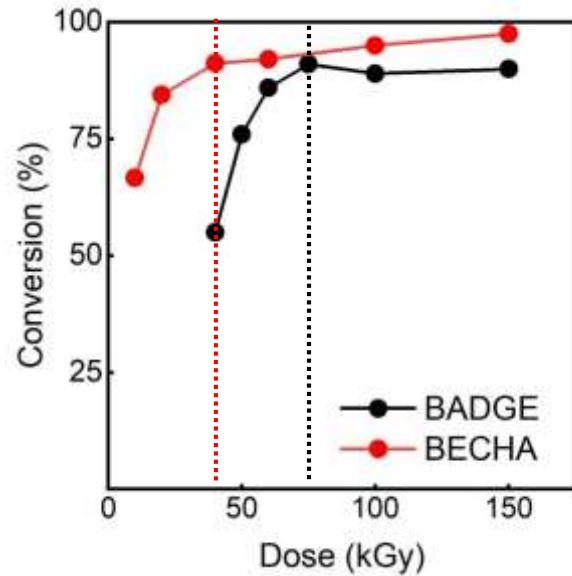
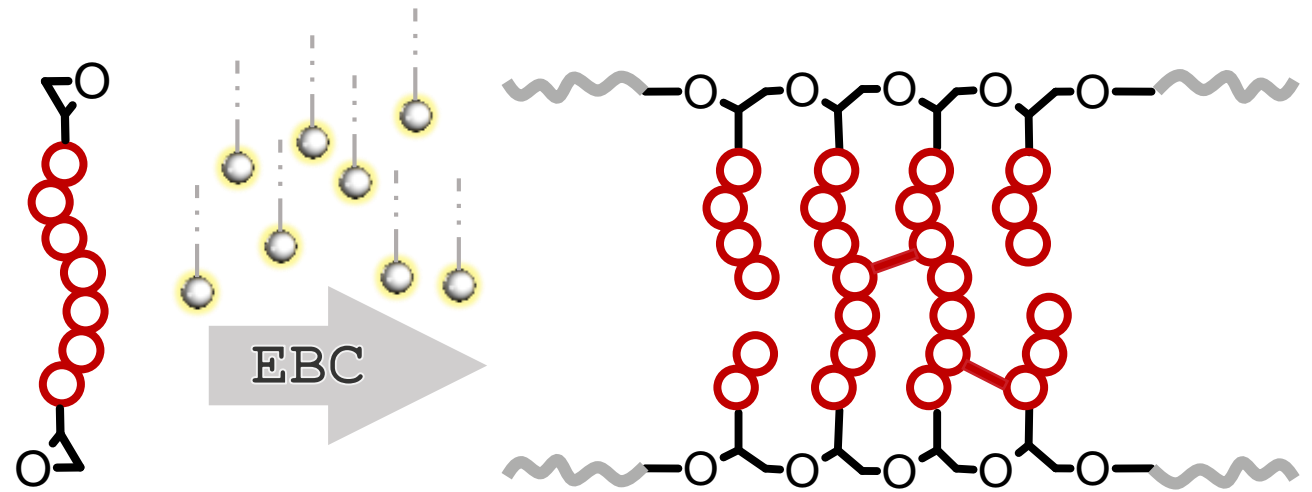
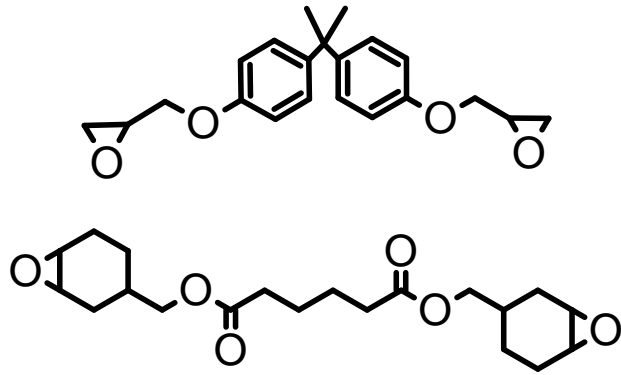
Excessive curing EB dose (rate)



- ✓ Molecular design;
- ✓ EB process optimization;
- ✓ Better understanding of interaction EB-matter and molecular manipulation.

EB Epoxy Networks - Conclusions

Learnings & Implications



- ✓ Full epoxy conversion achievable with EBC alone;
- ✓ Expanding radiation-curable coatings portfolio;

EB-Cured Polymer Networks - Conclusions

Outlook

Wanderer above the Sea of Fog, C.D. Friedrich, 1818



Network features **visualization**

(AFM, SAXS, ...).



Effective **improvement of coating properties** and performance.



Deploy **novel EB chemistries** and explore new possibilities.



Mix 'em up! **Acrylic/epoxy interpenetrating polymer networks**



(IPNs).

Acknowledgements

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SPC (Physical Chemistry) Group

Nemho Innovations BV:

Dr. Daniel Totev
Dr. Yujing Zhang
Advanced Surface Technology (AST) Team



Questions?



**Coatings Trends
& Technologies
SUMMIT**

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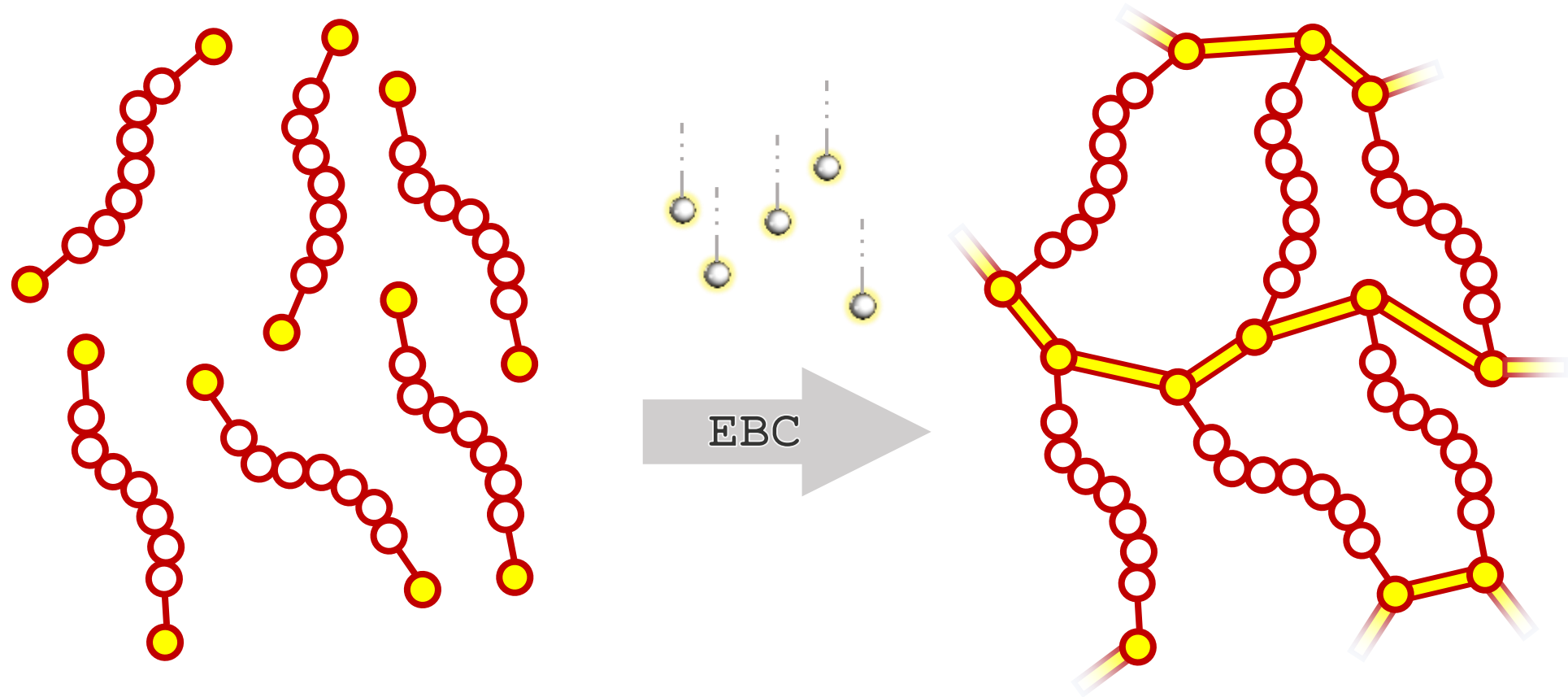
+31 (0) 6 5003 4607



Extra slides

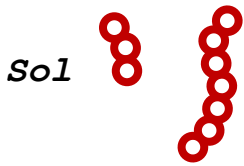
EB (UV)-Curable Coatings

Introduction



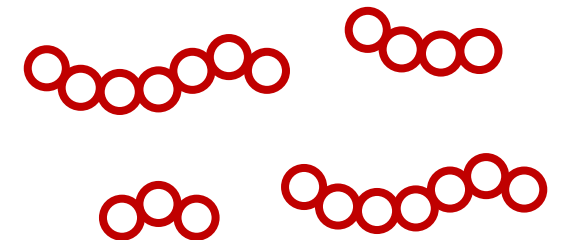
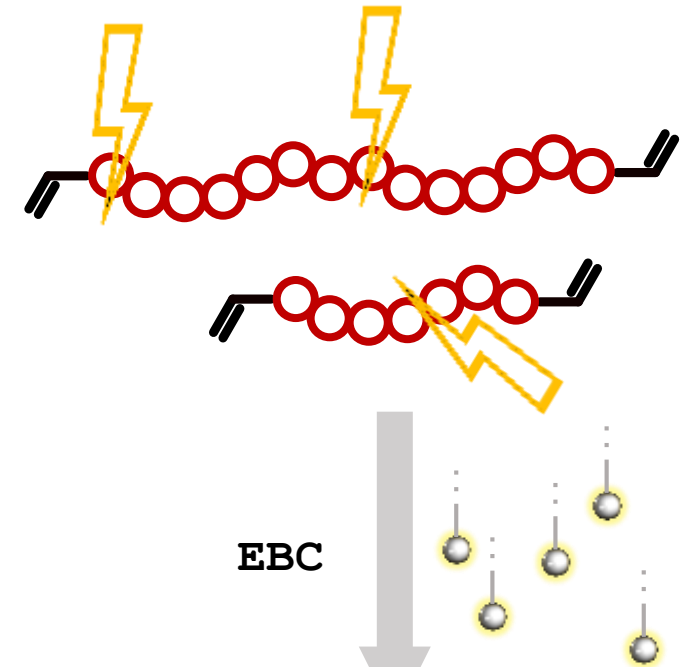
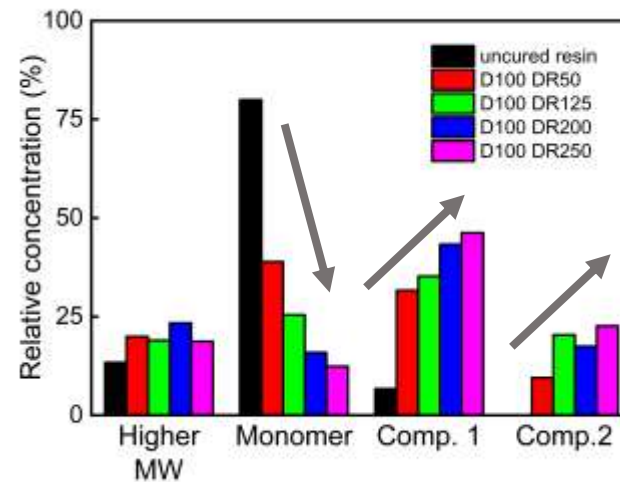
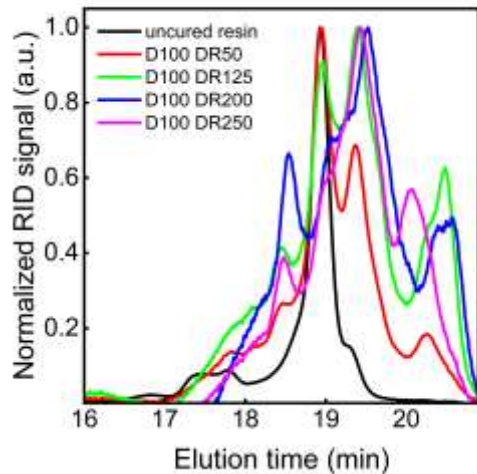
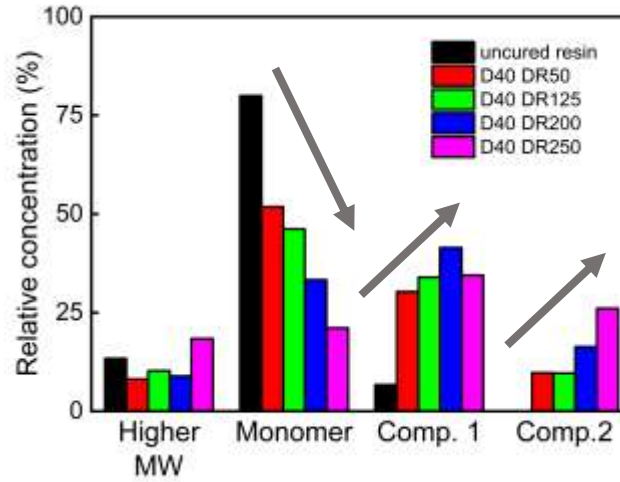
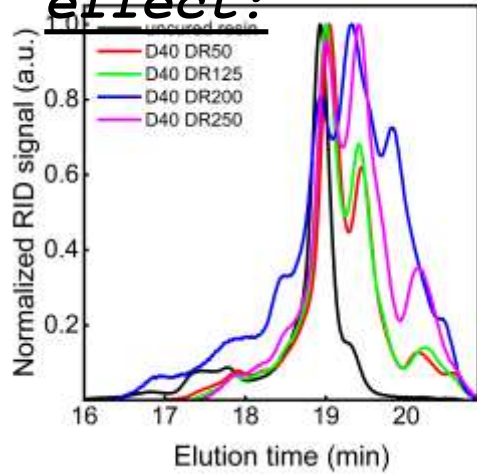
Identification of Collateral EB Reactions

SEC on Sol-Fractions



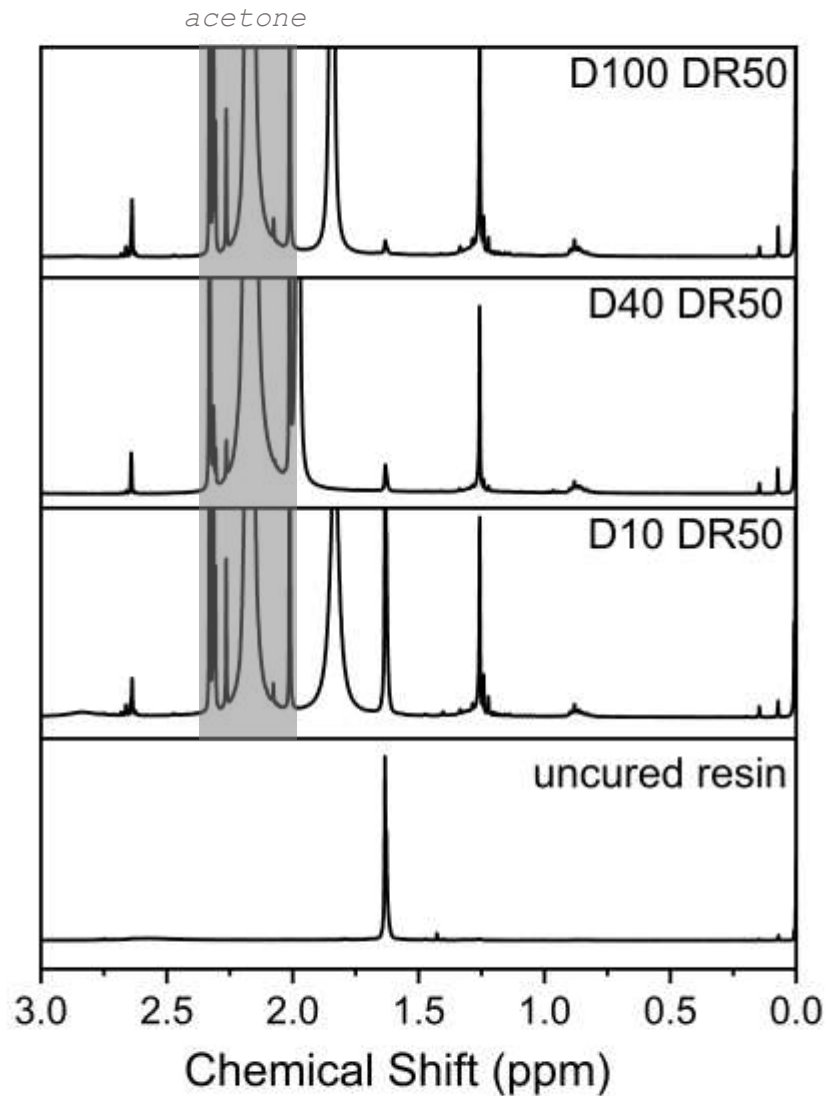
EB dose rate

effect:

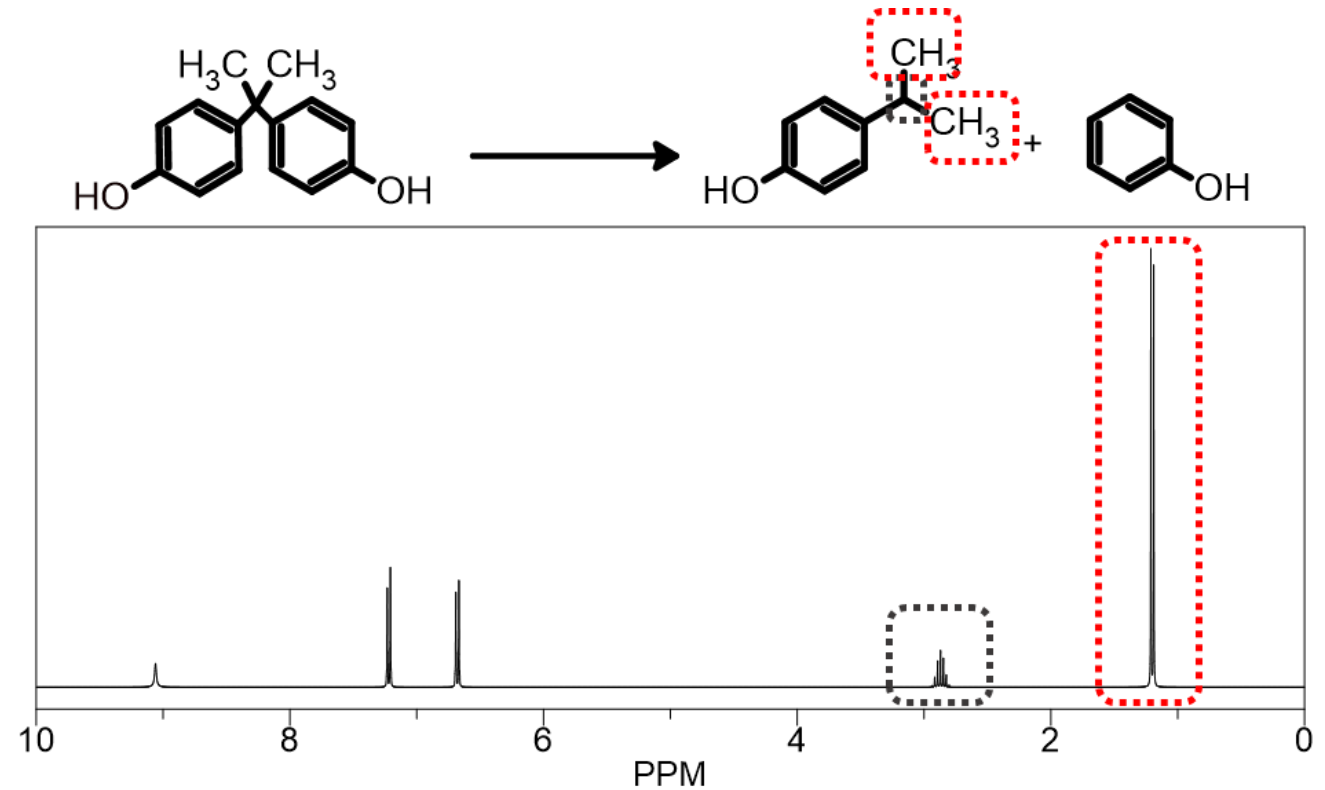


Identification of Collateral EB Reactions

NMR on Sol-Fractions

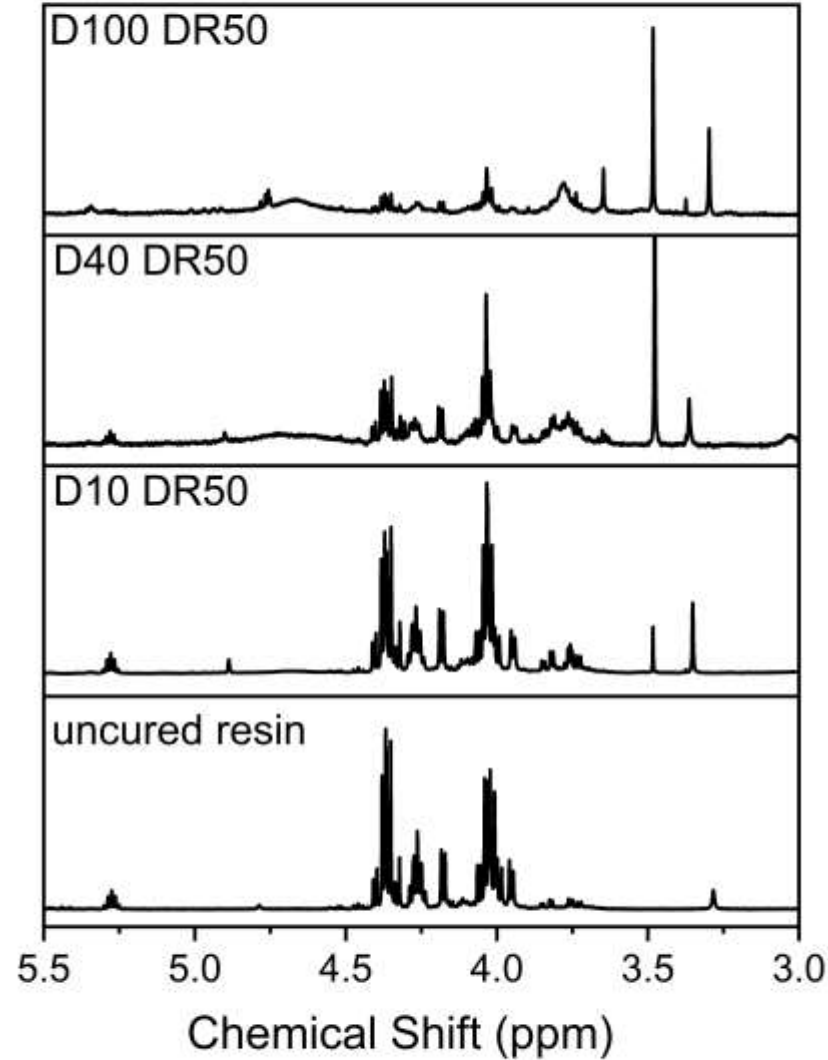


ChemDraw® simulated H-NMR spectrum:

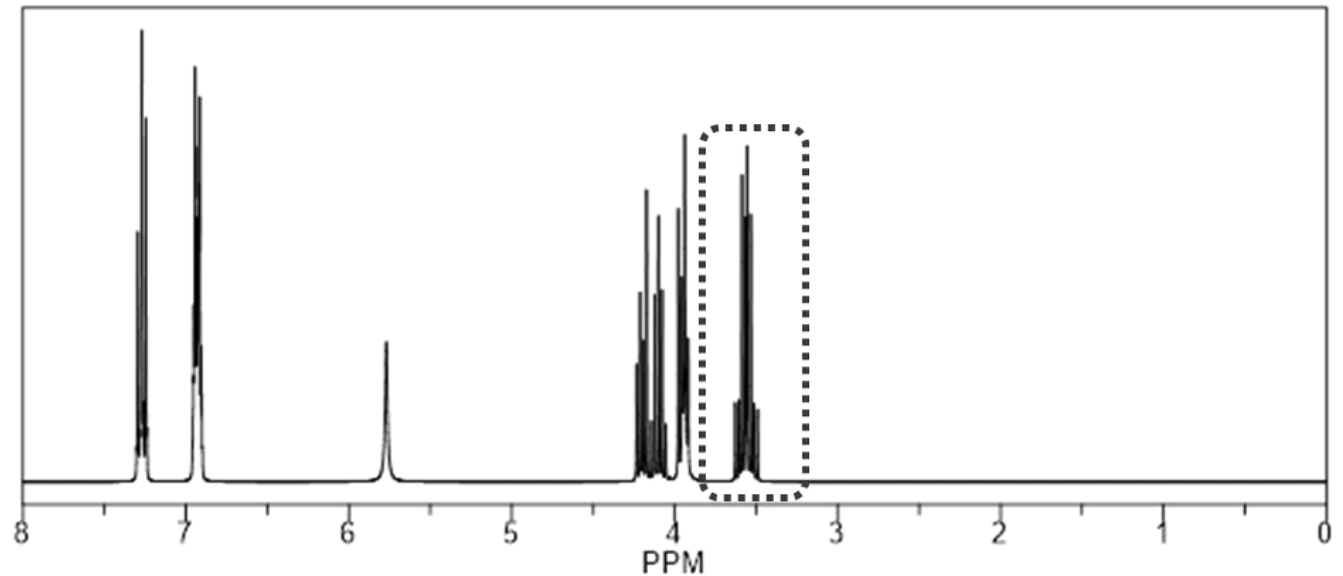
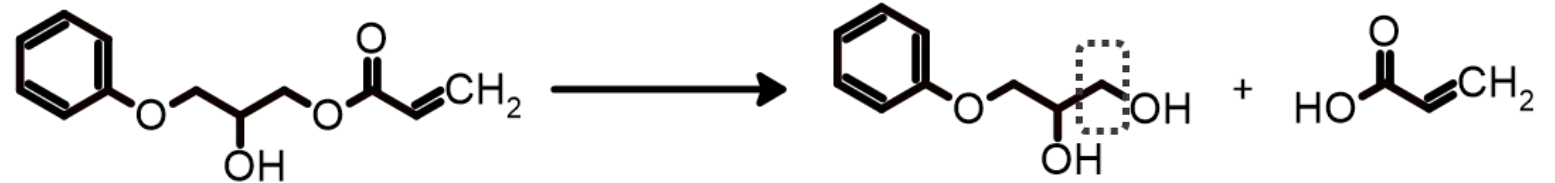


Identification of Collateral EB Reactions

NMR on Sol-Fractions

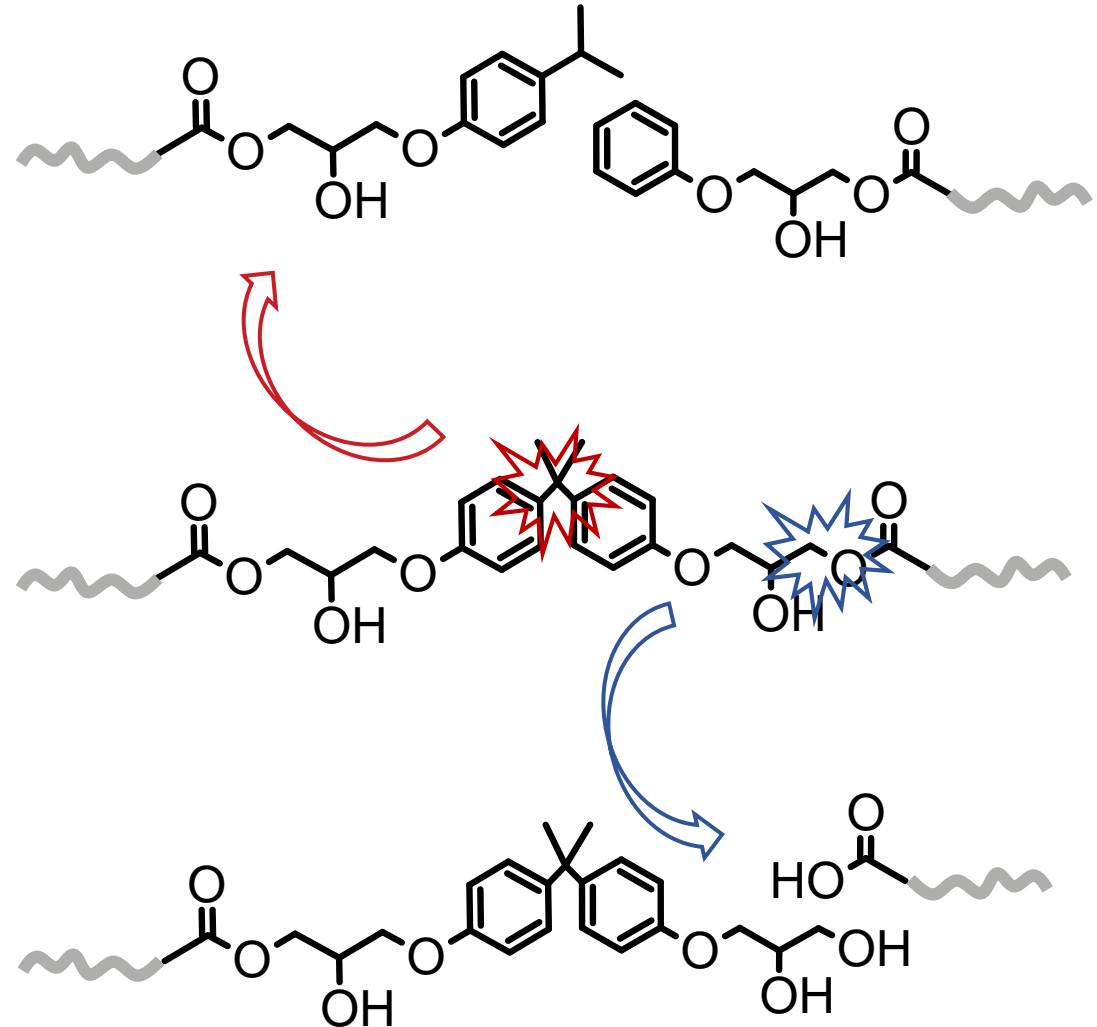
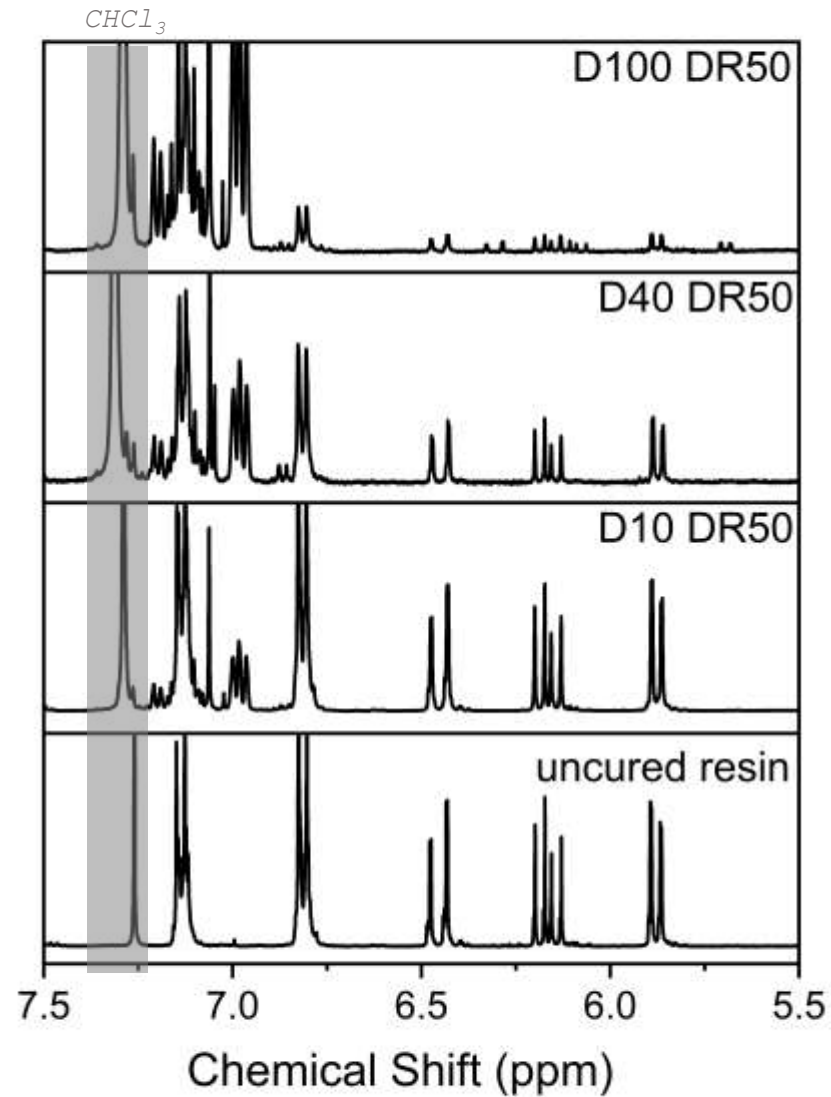


ChemDraw® simulated H-NMR spectrum:



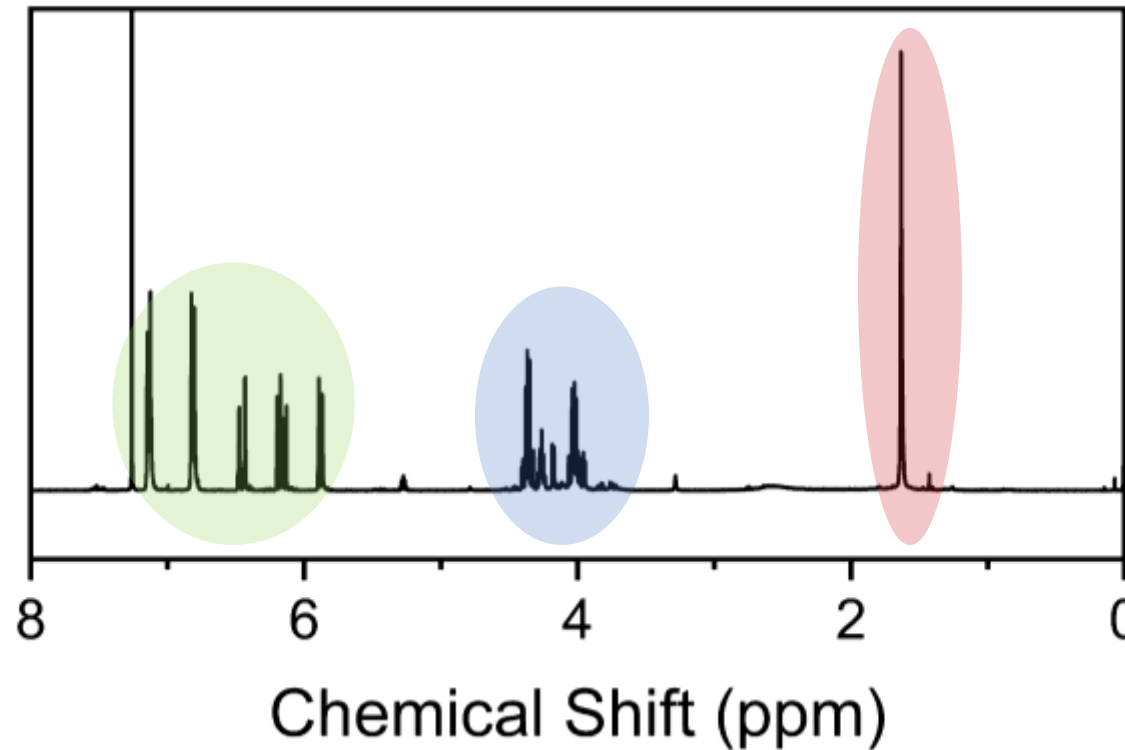
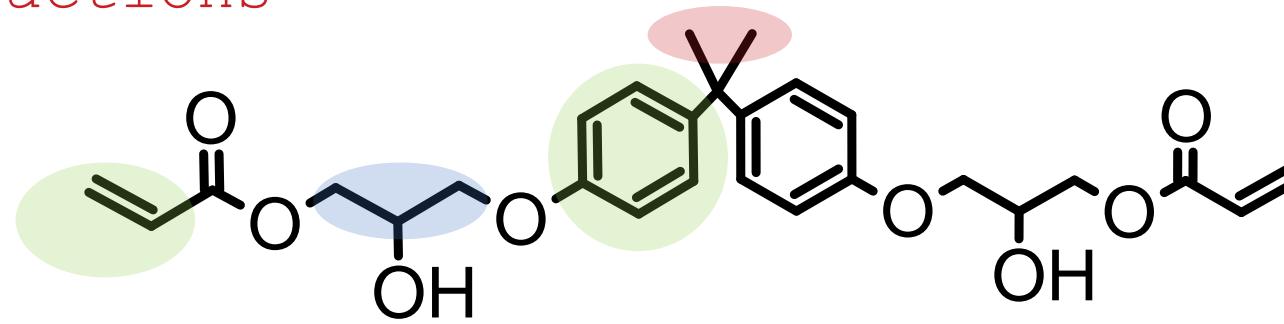
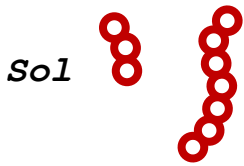
Identification of Collateral EB Reactions

NMR on Sol-Fractions



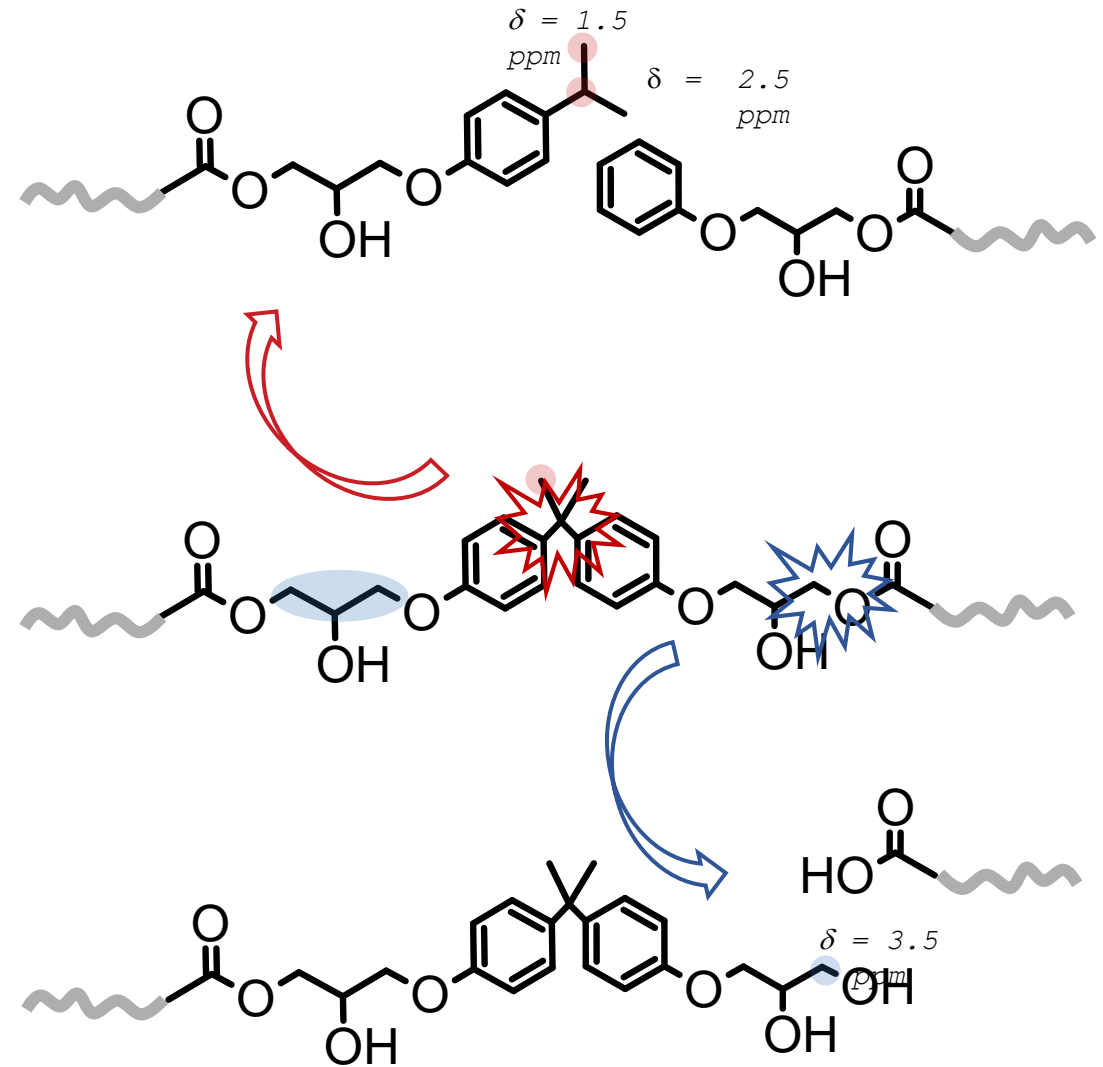
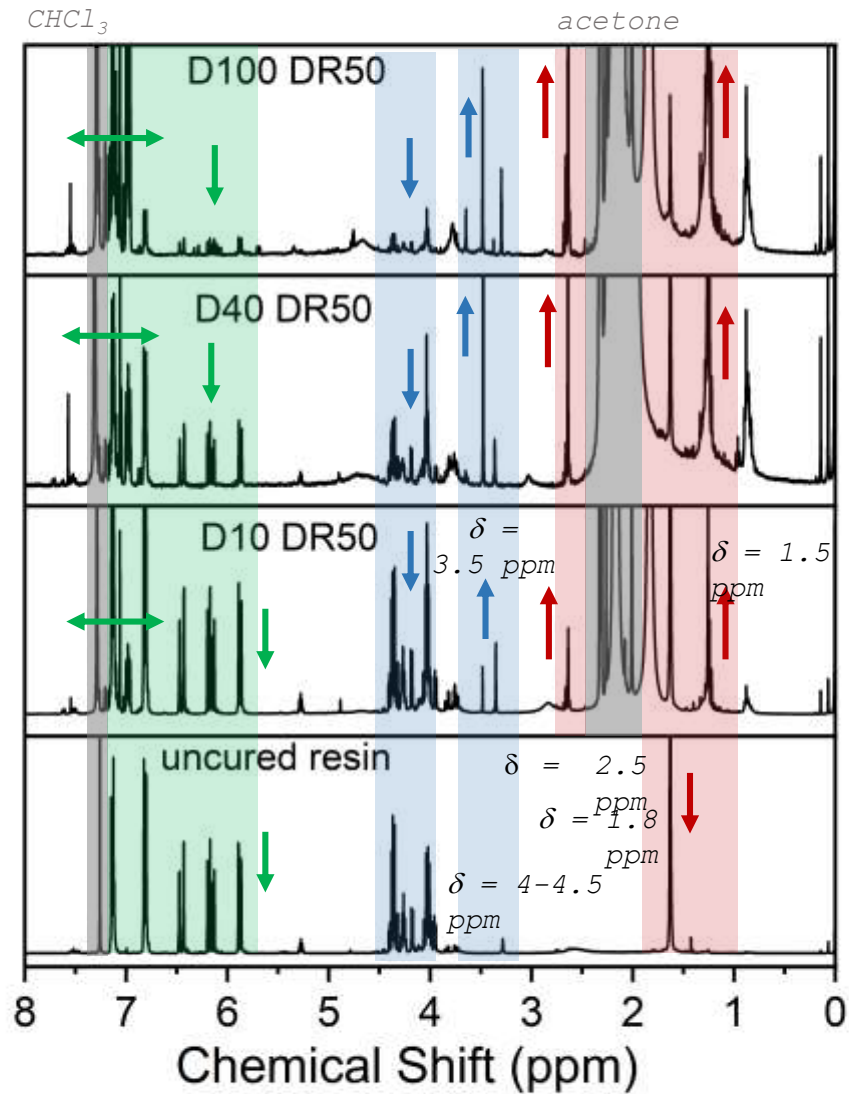
Identification of Collateral EB Reactions

NMR on Sol-Fractions

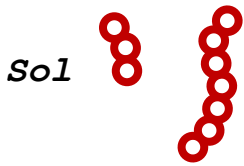


Identification of Collateral EB Reactions

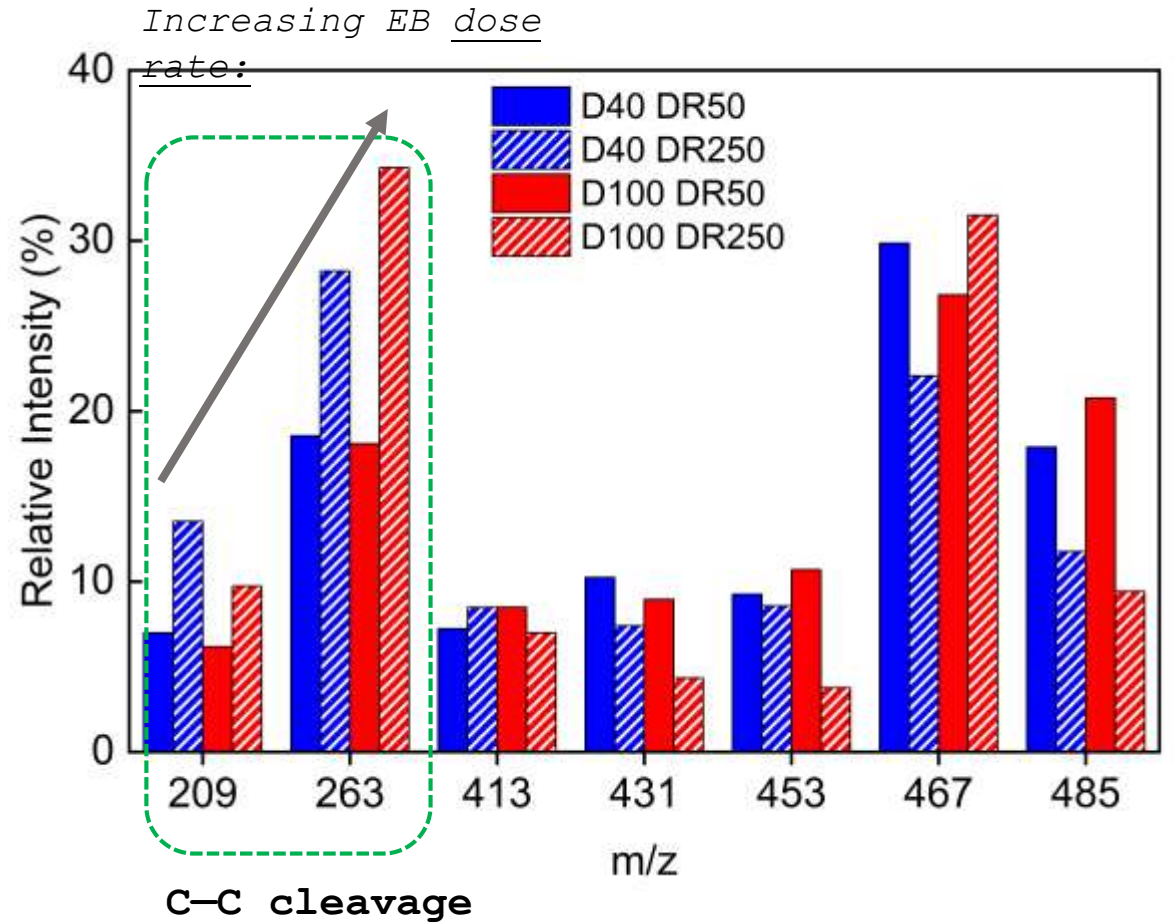
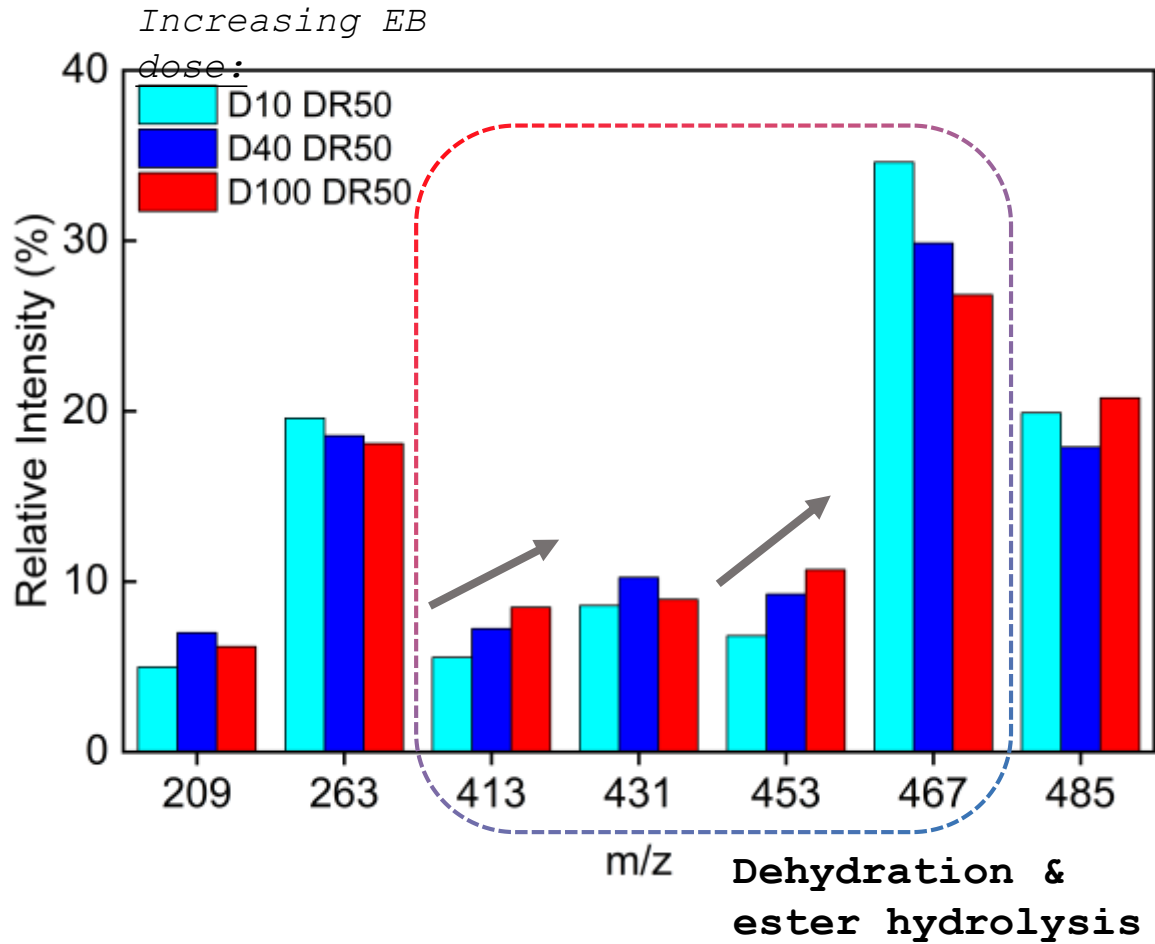
NMR on Sol-Fractions



Identification of Collateral EB Reactions

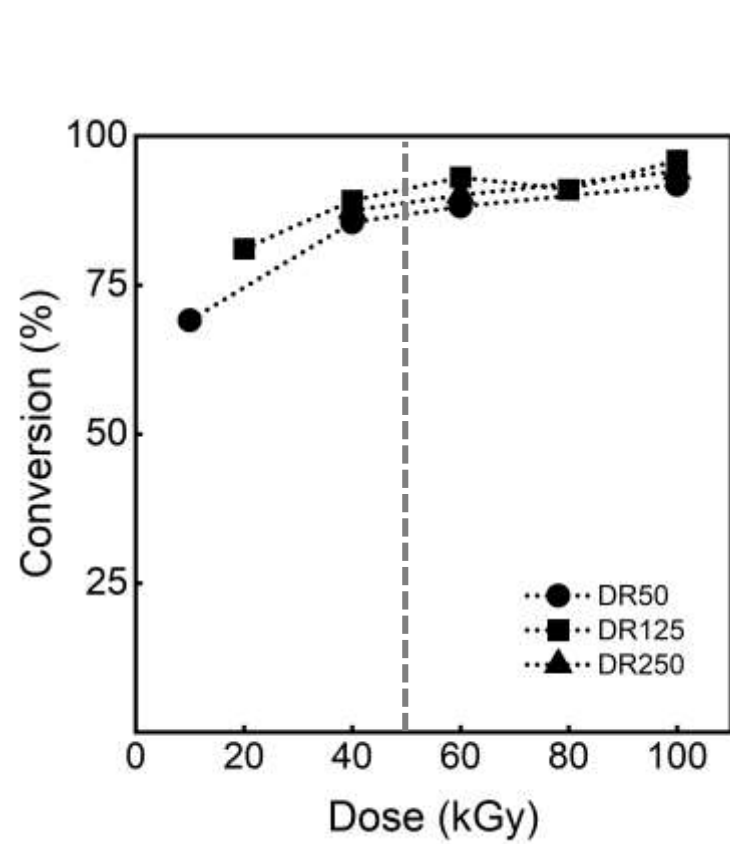
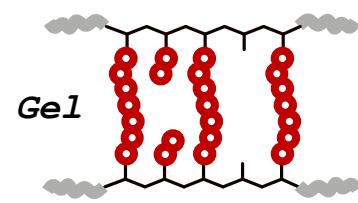


MS on Sol-Fractions

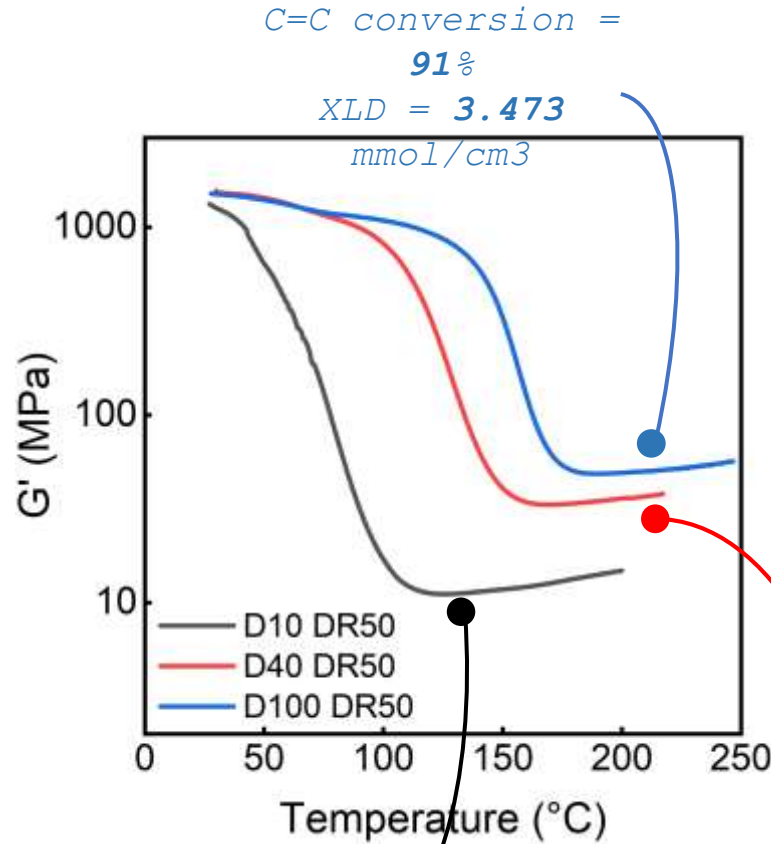


Acrylic Network Formation & Features

Attribution to EB reactions



$$\text{Crosslink density} = XLD = \frac{G'}{3 \cdot \rho \cdot R \cdot T}$$



C=C conversion = 69%
XLD = 0.929 mmol · cc

C=C conversion = 86%
XLD = 2.494 mmol/cm³

