MONOMERS AND OLIGOMERS FOR UV/EB ENERGY CURING

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The Coating Resins Company

AGENDA

Oligomers and Monomers for UV/EB Energy Curing

- UV/EB Chemistry types
- Radical UV/EB Formulations
- Oligomer Types and Performance
- Oligomer Physical Properties
- Monomer Types and Performance
- Stability
- Safety

UV/EB ENERGY CURING CHEMISTRY

Free Radical

- Polymerization through double bonds
- Acrylate functional materials most common functionality
- Methacrylate and some vinyl functional materials

Cationic

- Polymerization through epoxy groups
- Cycloaliphatic epoxies most common functionality
- Less widely used

UV FREE RADICAL CURING FORMULATION

100% Solids

- **Acrylated Resin(s)**
  basic coating properties
- **Monofunctional Monomer(s)**
  viscosity reduction, flexibility
- **Multifunctional Monomer(s)**
  viscosity reduction, crosslinking
- **Additives**
  performance fine tuning
- **Photoinitiator Package**
  radical generation

UV

CURED PRODUCT

EB FREE RADICAL CURING FORMULATION

100% Solids

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  basic coating properties
- **Monofunctional Monomer(s)**
  viscosity reduction, flexibility
- **Multifunctional Monomer(s)**
  viscosity reduction, crosslinking
- **Additives**
  performance fine tuning

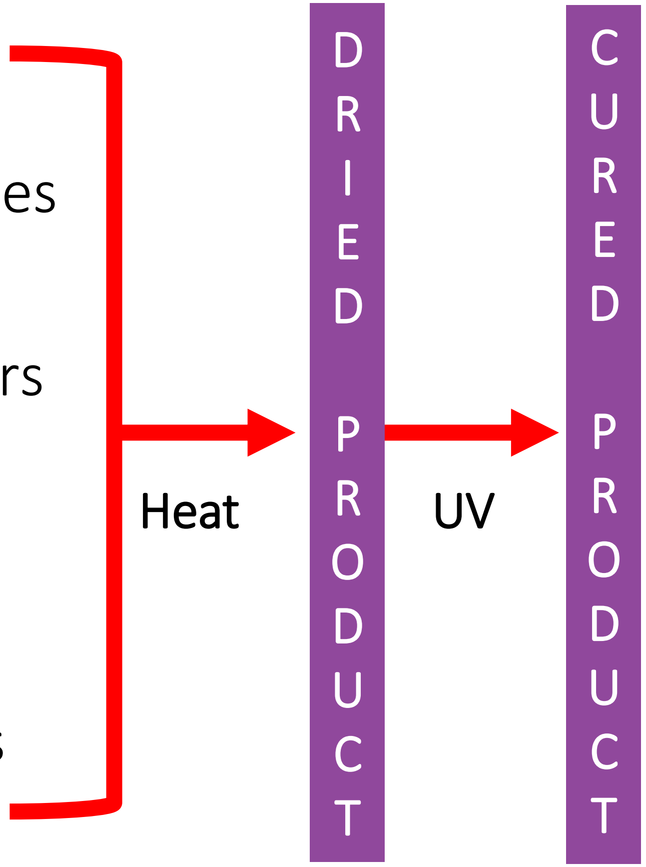
Electrons

CURED PRODUCT

UV FREE RADICAL CURING FORMULATION

Water-borne UV

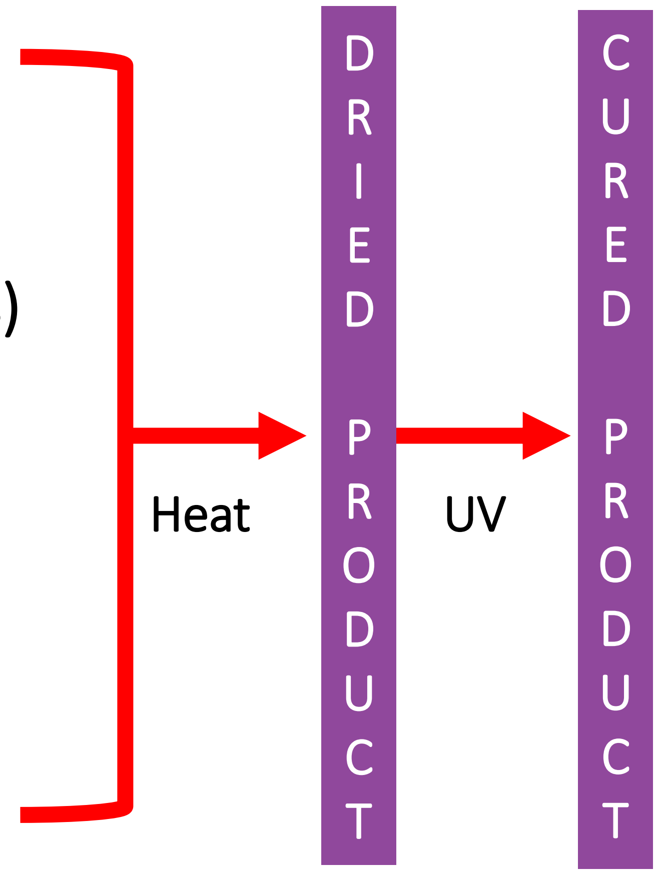
- **Acrylated Waterborne Resin(s)**
  UV PUD - basic coating properties
- **Additives**
  waxes, flatting agents, thickeners
- **Photoinitiator Package**
  radical generation
- **Water (optional)**
  viscosity reduction, lower solids



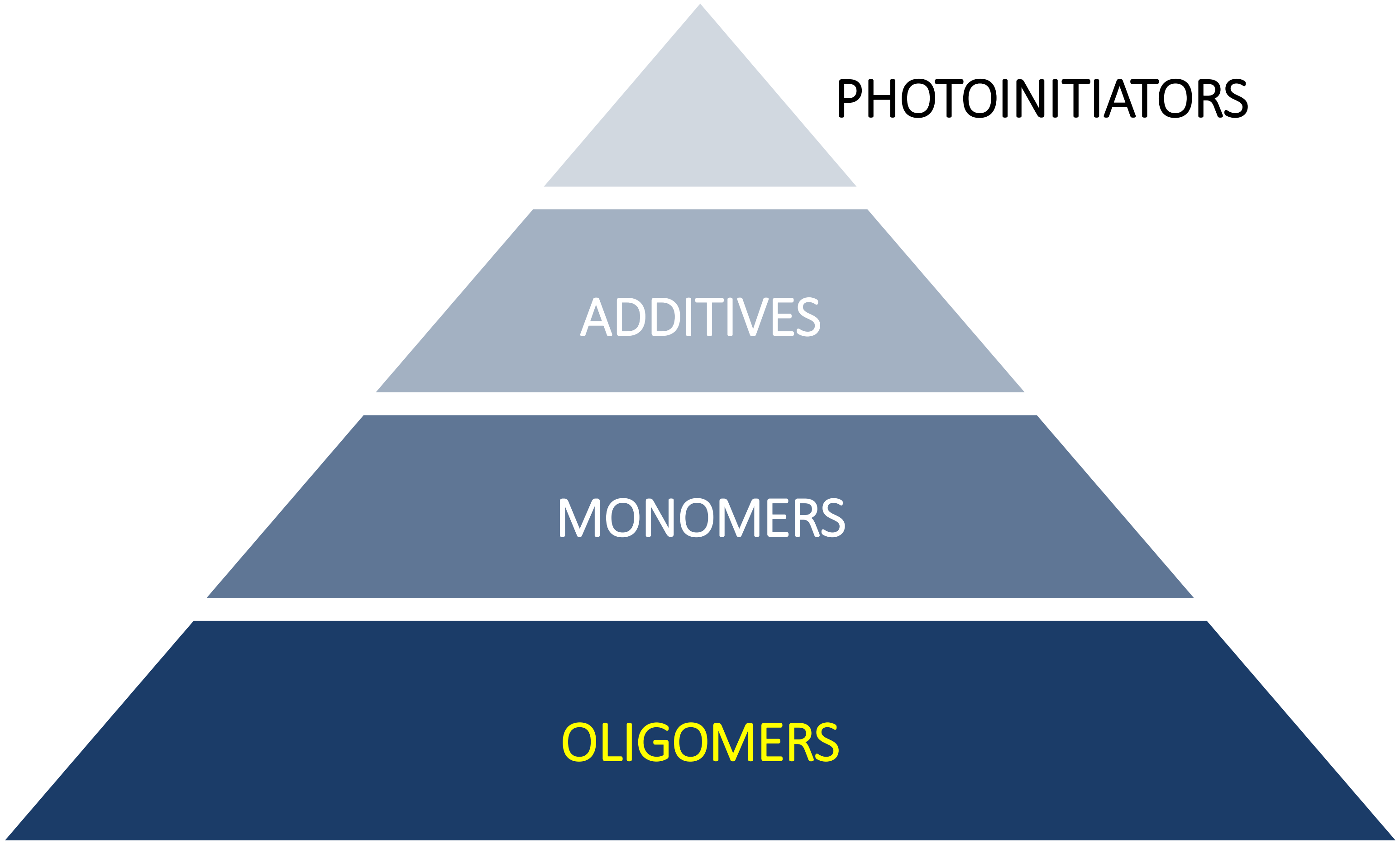
UV FREE RADICAL CURING FORMULATION

Solvent-borne UV

- **Acrylated Resin(s)**
  basic coating properties
- **Solvent (ketones, acetates, alcohols)**
  viscosity reduction
- **Photoinitiator Package**
  radical generation
- **Monomer (optional)**
  flow, adhesion



UV FREE RADICAL CURING FORMULATION



ACRYLATED OLIGOMERS (PREPOLYMERS, RESINS)

High viscosity

- Usually require dilution

High molecular weight

- 500 - 5,000

Provide much of the overall performance of cured film or ink

Functionality ranges from 2 – 10+

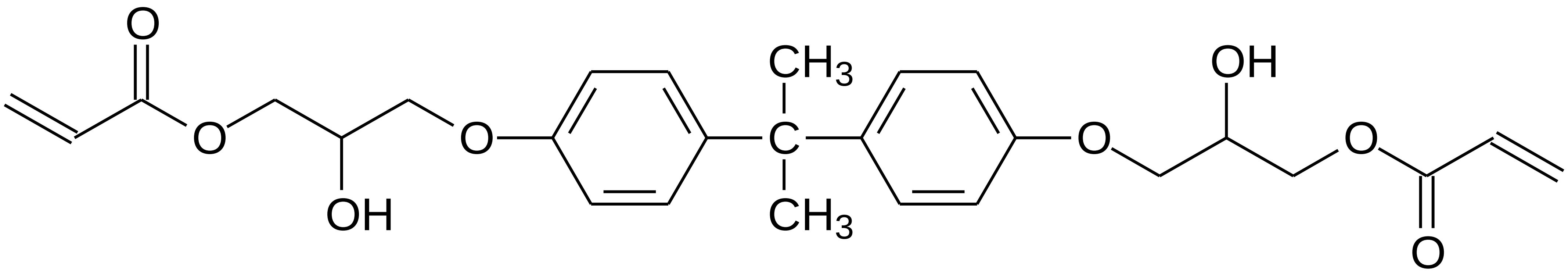
Oligomer additives/residuals can affect performance and/or labeling:

- Inhibitors, catalysts

OLIGOMERS TYPES

(Meth)Acrylated	Characteristics
Epoxies	Economical, fast curing, hard, solvent resistance; BPA issue
Aliphatic Urethanes	Flexible, tough, non-yellowing, best weathering properties
Aromatic Urethanes	Flexible, tough, lower cost than aliphatic urethanes
Polyesters	Good pigment wetting properties, lower viscosities, good printing properties
Polyethers	Amine modified, increased reactivity; low viscosities
Specialty Polyesters	Good adhesion, special applications
Amines	Faster cure speed; mitigate oxygen inhibition
Acrylics	Good weathering; low shrinkage
Waterborne	Primarily polyurethane dispersions; eliminates need for monomers; physical drying required before UV/EB energy curing

ACRYLATED EPOXY OLIGOMER



Bisphenol A Diglycidyl Ether Diacrylate

diglycidyl ether + acrylate functional organic acid

BPA derived; Issue for:
Food Packaging, IKEA, others

ACRYLATED EPOXY OLIGOMER

Basic BPA Epoxy Acrylate

- Economical
- Very fast cure response
- Poor pigment wetting
- Good hardness
- Excellent solvent and chemical resistance
- High tensile strength, low elongation
- Moderate shrinkage
- High viscosity
- Low oxygen inhibition
- OH groups available for additional reactions
- BPA derived

Fatty Acid Modified Epoxy Acrylates

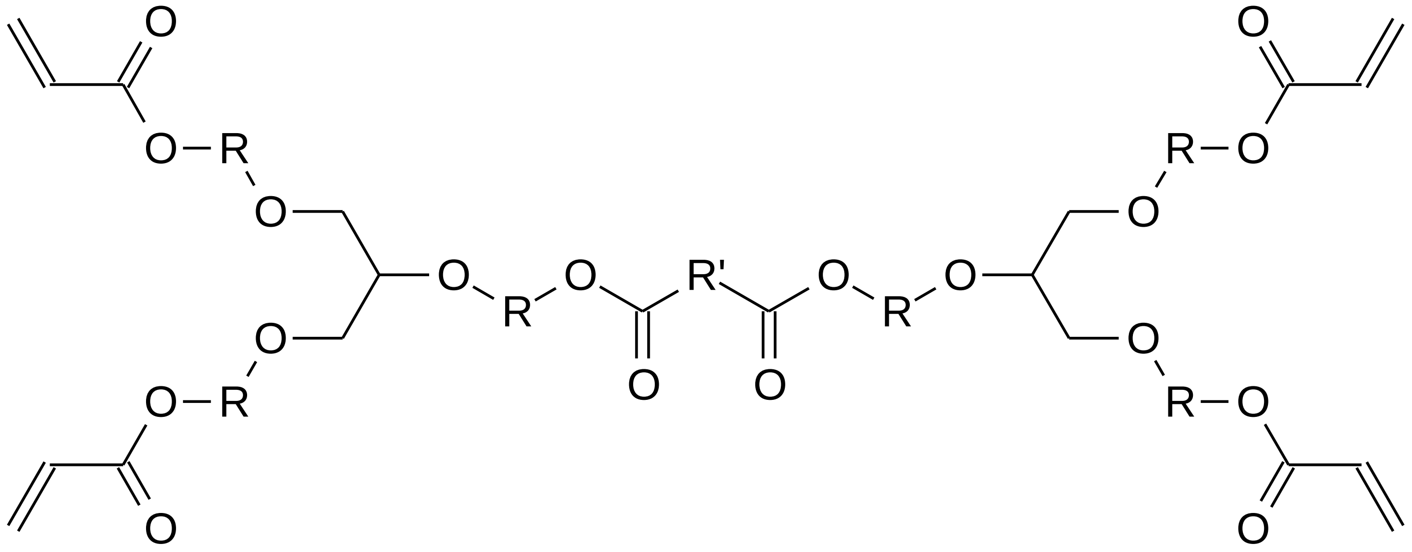
- Improved Pigment Wetting
- Slower Cure Speed
- Less Solvent Resistance
- Higher Cost
- BPA derived

Other Epoxy Acrylates

Epoxidized Oils: soya, linseed, castor

- Relatively low viscosity
- Good flow and wetting properties
- Improved flexibility
- Slower cure
- Decreased hardness, chemical resistance
- No BPA impurities

ACRYLATED POLYESTER OLIGOMER



Polyester Tetra-acrylate

Reaction product of polyol and polyfunctional organic acids

- Polyols include: ethylene glycol, diethylene glycol, glycerol, NPG, TMP and others
- Organic acids include: Phthalic, isophthalic, adipic, and fatty

Can be designed for food packaging compliance

ACRYLATED POLYESTER OLIGOMER

General Characteristics

- Some designed for general coatings applications
- Some engineered for pigment wetting and good litho performance (fatty acid modification)
- Can also be designed for food packaging compliance
- Viscosity range: 100’s - 100,000’s cP
- Moderate to high shrinkage
- Moderate to very fast cure response
- 2 - 6 functional
- 300 - 3000 MW

(ACRYLATED) POLYESTER OLIGOMERS

Acrylated

- Most popular and useful
- 2 - 6 functional
- Moderately hard and low elongation after cure
- For inks, must balance low viscosity with pigment wetting and flow

Non-acrylated

- Adhesion promoters
- Formulation extenders

(ACRYLATED) POLYESTER OLIGOMERS

Specialty

- Low shrinkage
- Good adhesion
- Moderate to fast cure response

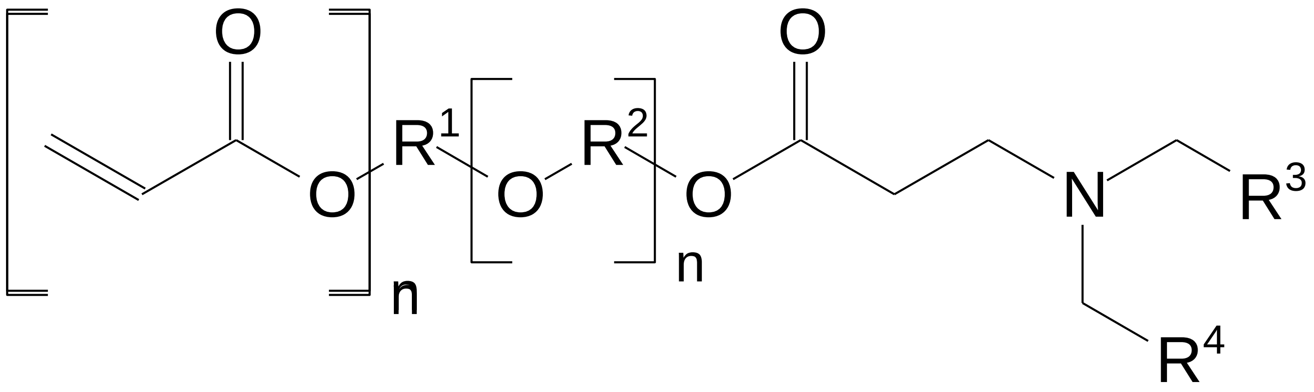
Chlorinated

- Non-acrylate functional
- Adhesion to polyolefins and metals
- Chlorine under regulatory pressure; non-chlorinated versions available

Acidic

- Non-acrylate functional
- Adhesion to polyolefins and metals

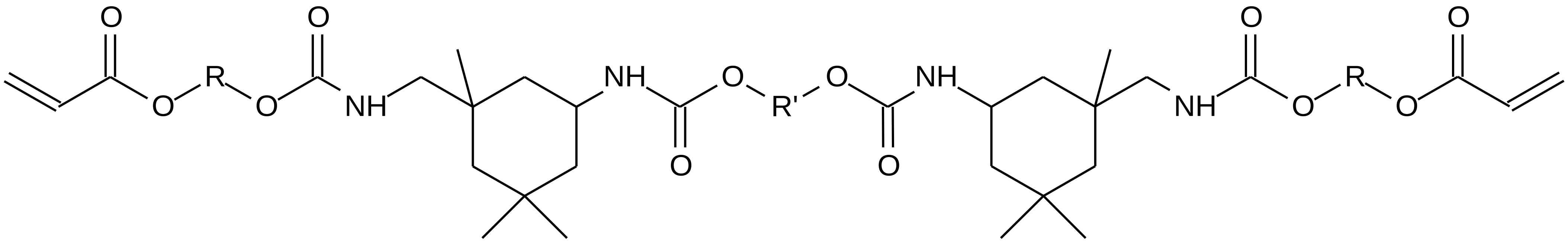
AMINE MODIFIED ACRYLATED POLYETHER OLIGOMERS



Amine Modified Polyesther Acrylate

- Amine modification increases surface cure, reduced O2 inhibition
- Relatively low viscosity
- Good hardness and chemical resistance

ACRYLATED URETHANE OLIGOMERS

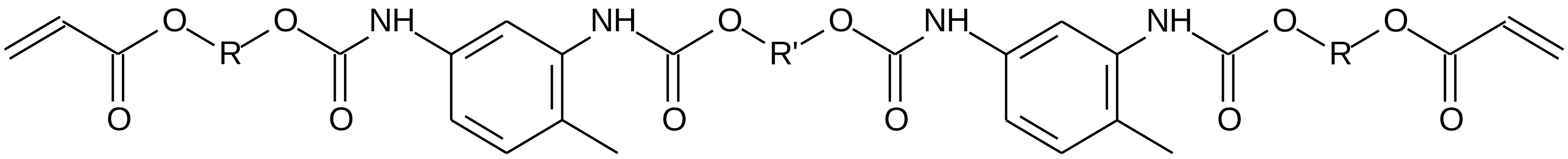


Aliphatic Urethane Diacrylate

Reaction product of isocyanate (NCO), polyol, and hydroxy-functional acrylate (HAA)

Non-yellowing
IPDI, typical diisocyanate

ACRYLATED URETHANE OLIGOMERS



<u>Aromatic Urethane Diacrylate</u>

Reaction product of isocyanate (NCO), polyol, and hydroxy-functional acrylate (HAA)

Yellowing
TDI, typical diisocyanate

ACRYLATED URETHANE OLIGOMERS

Properties of a given urethane acrylate are controlled by compositional elements

Compositional Variable

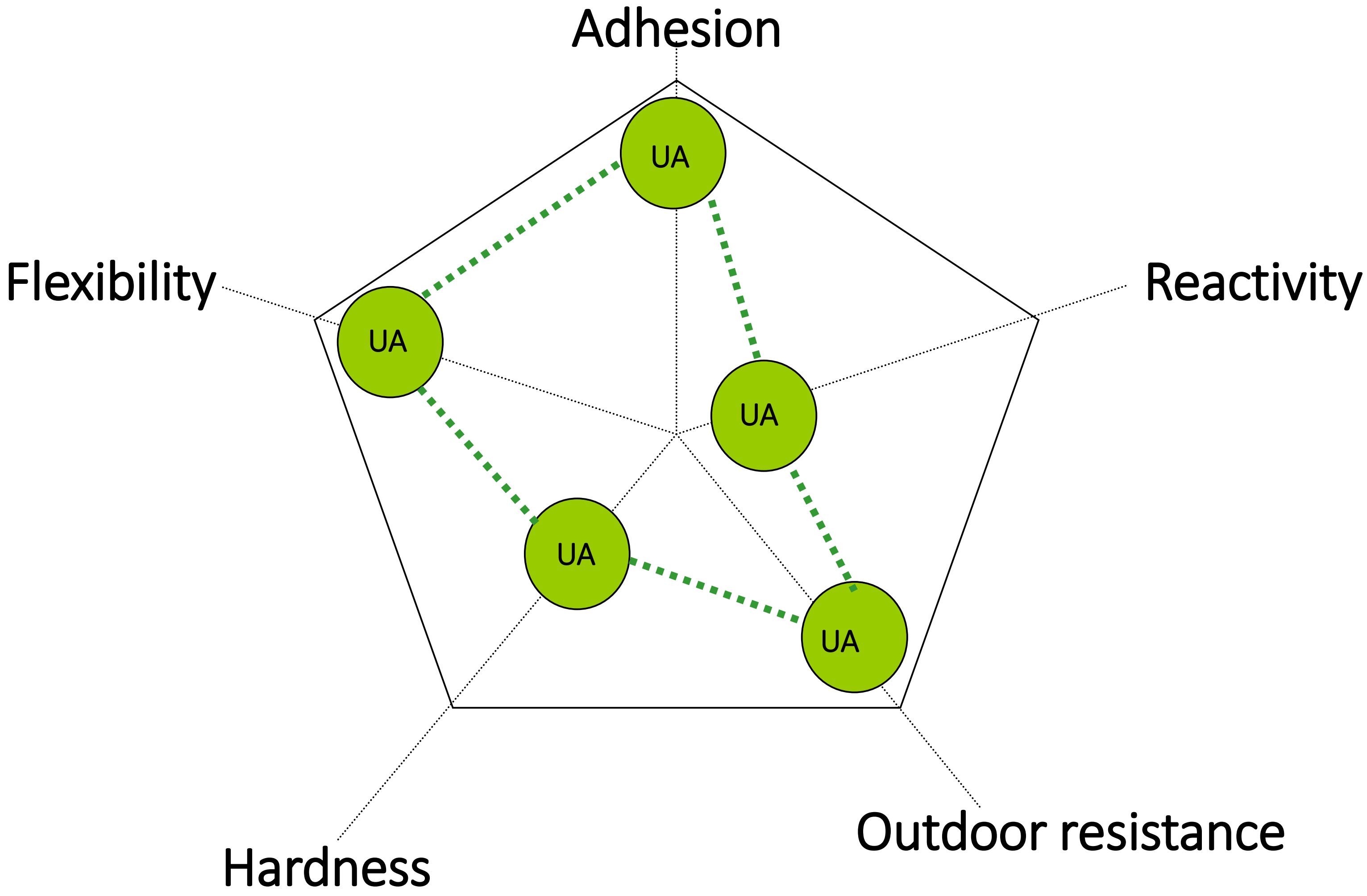
- Polyol type
- Diisocyanate type
- Functionality
- MW distribution
- Urethane content
- HAA type
- Inhibitor
- Catalyst

End Property

- Viscosity
- Cure speed
- Tensile strength
- Tensile modulus
- Elongation
- Hardness
- Adhesion
- Solvent Resistance
- Flexibility
- Weatherability

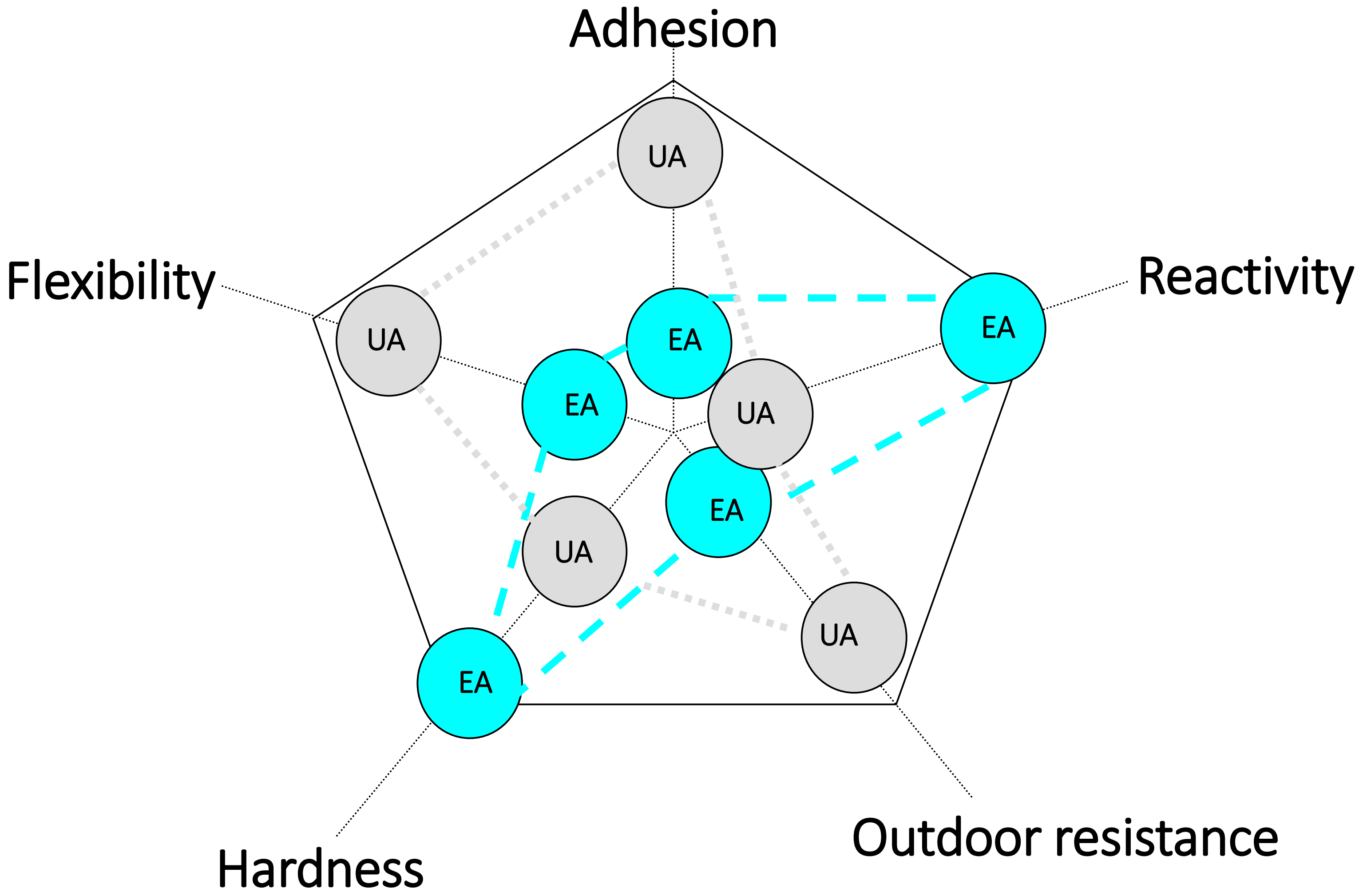
OLIGOMER PERFORMANCE PROPERTIES

Oligomer backbone chemistry: Urethane



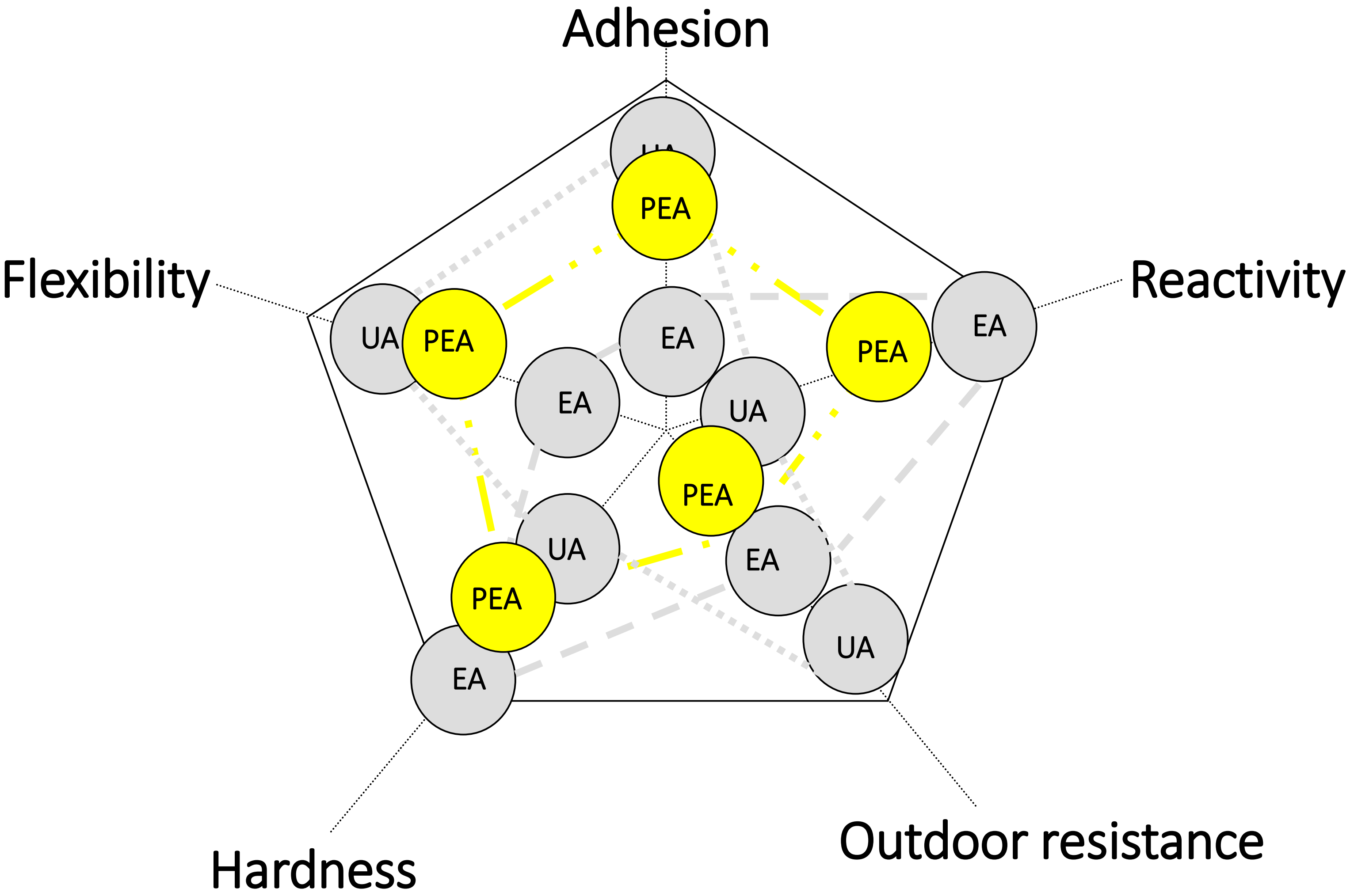
OLIGOMER PERFORMANCE PROPERTIES

Oligomer backbone chemistry: Epoxy

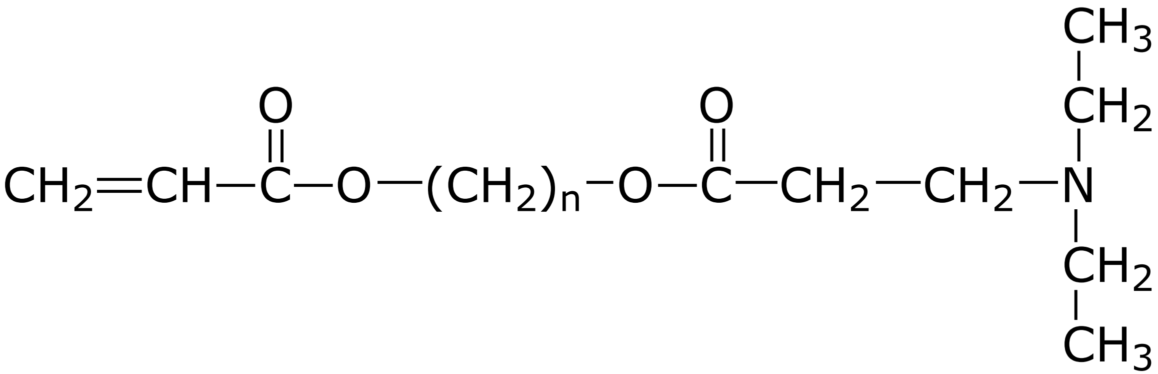


OLIGOMER PERFORMANCE PROPERTIES

Oligomer backbone chemistry: Polyester



ACRYLATED AMINE OLIGOMERS



Amine Synergists (co-initiators)

Decrease oxygen inhibition and increase cure speed

Useful in OPVs, coatings, flexo inks, etc.

Not used in litho inks because of acidic fountain solutions

ACRYLATED AMINE OLIGOMERS

Compared to non-acrylated amines:

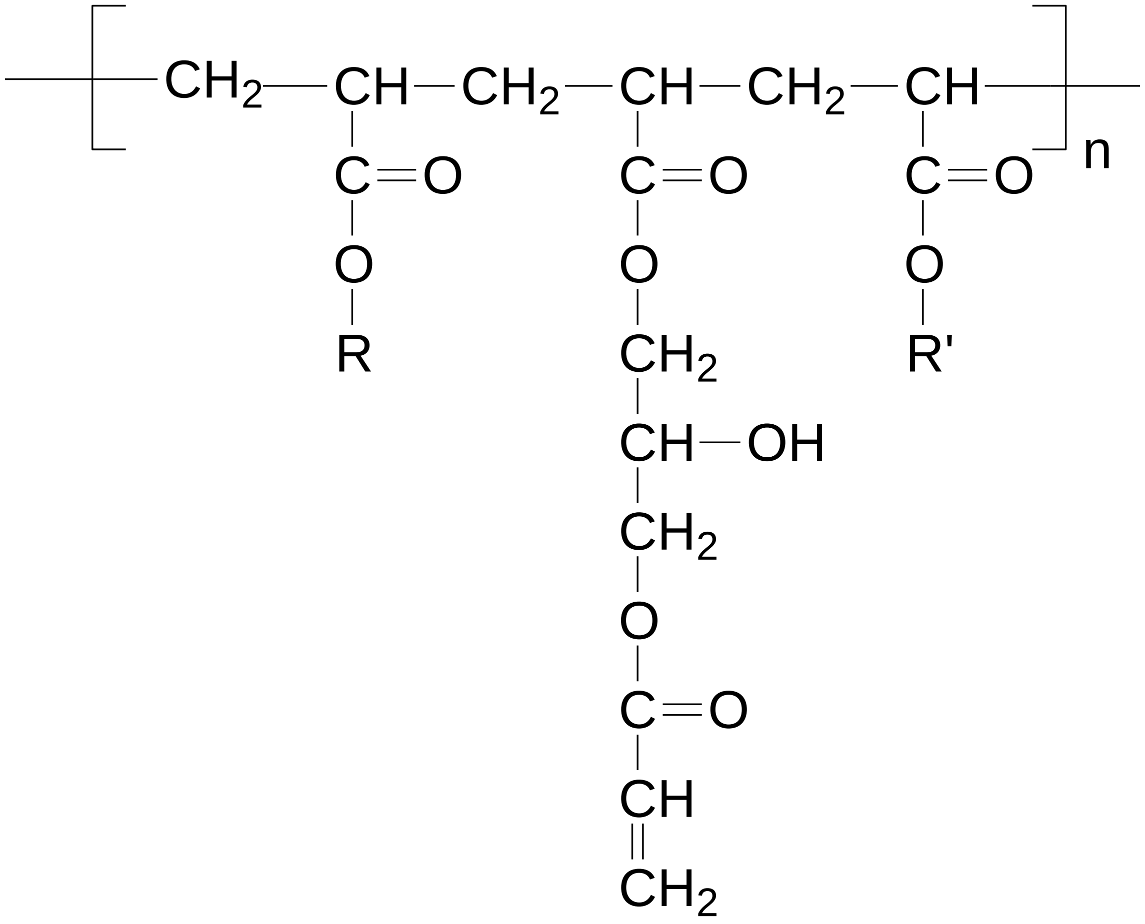
- Low odor
- Low extractables
- No blooming or discoloration
- Food packaging compliant

Not principal oligomer

- Poor mechanical properties
- High cost

Avoid use with acidic materials

(ACRYLATED) ACRYLIC OLIGOMERS



Acrylated Acrylic

(ACRYLATED) ACRYLIC OLIGOMERS

Free radical polymerization of monofunctional acrylates (BA, AA), methacrylates (MMA), and vinyls (styrene)

Broad range of physical & mechanical properties

- Tg: sub zero to >60°C
- Soft and flexible to hard and brittle
- Good to excellent weatherability

Two Types

- Acrylated
  - Improve adhesion without sacrificing cure speed
- Non-acrylated
  - Detract from cure speed
  - Improve adhesion (reduce shrinkage)

NON-ACRYLATED OLIGOMERS

Saturated Resins

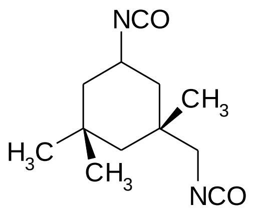
- Acrylics
- Polyesters
- Vinyls
- Hydrocarbons

Dissolve in acrylated monomers
Minimize shrinkage
Increase adhesion
Possible to meet food packaging regulations

WATERBORNE UV-PUDs

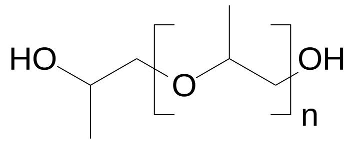
Isocyanates

- Aliphatic / aromatic
- Di, tri-functional
- Build the “hard” segment of PUD



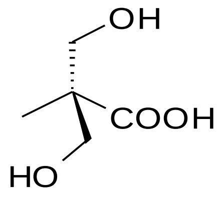
Diols

- PE, PES, PC, acrylic, hydrocarbon, silicone
- Usually di-functional
- Build the “soft” segment of PUD



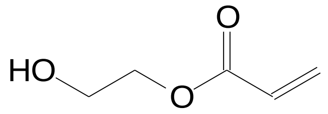
Acid

- Provides colloidal stability
- Increases adhesion
- Decreases flexibility (H-bonding)



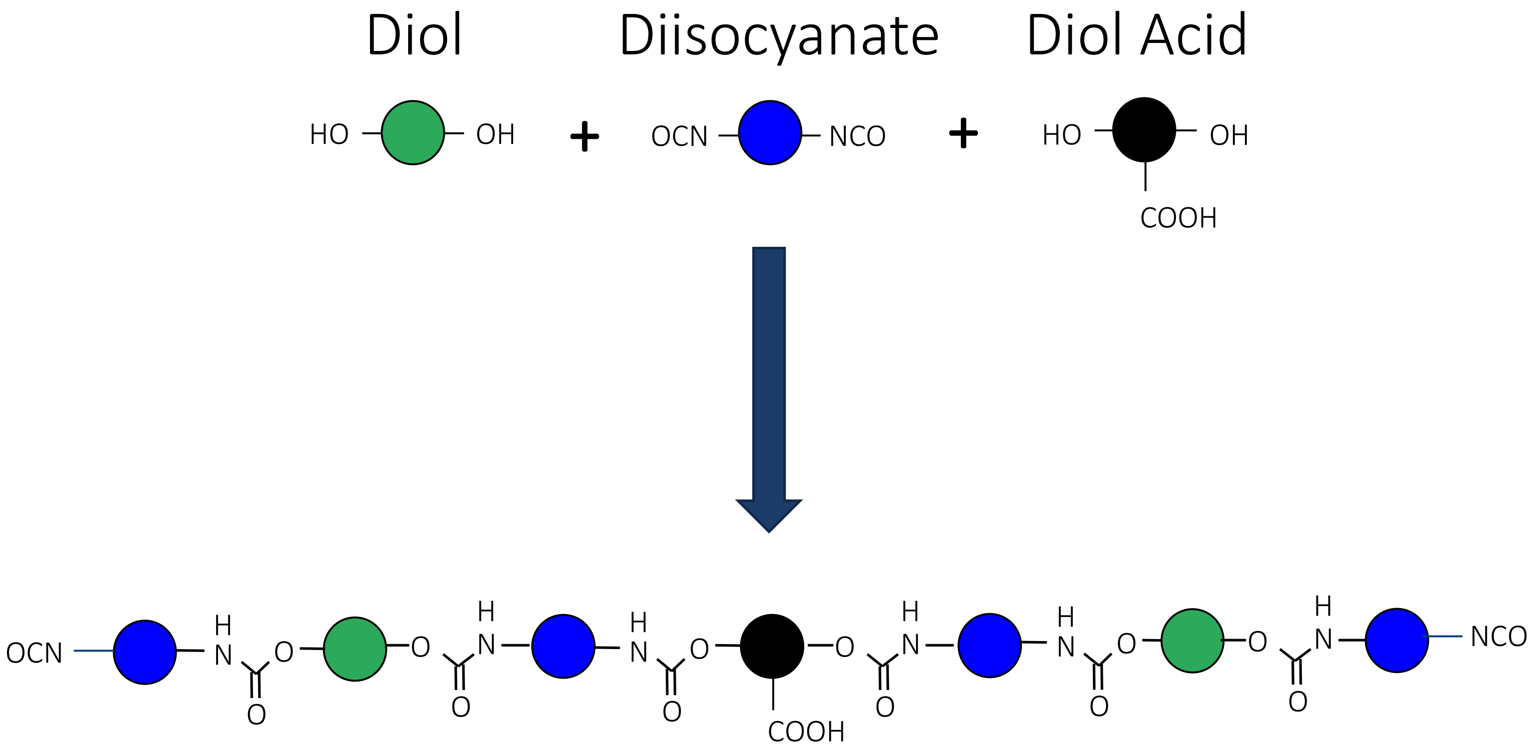
Hydroxyalkyl Acrylate

- Source of acrylate functionality
- Mono- or multifunctional (reactivity)



UV-PUD STRUCTURE

- Formation of a polyurethane pre-polymer by reaction of a diol, diisocyanate and diol acid in solvent



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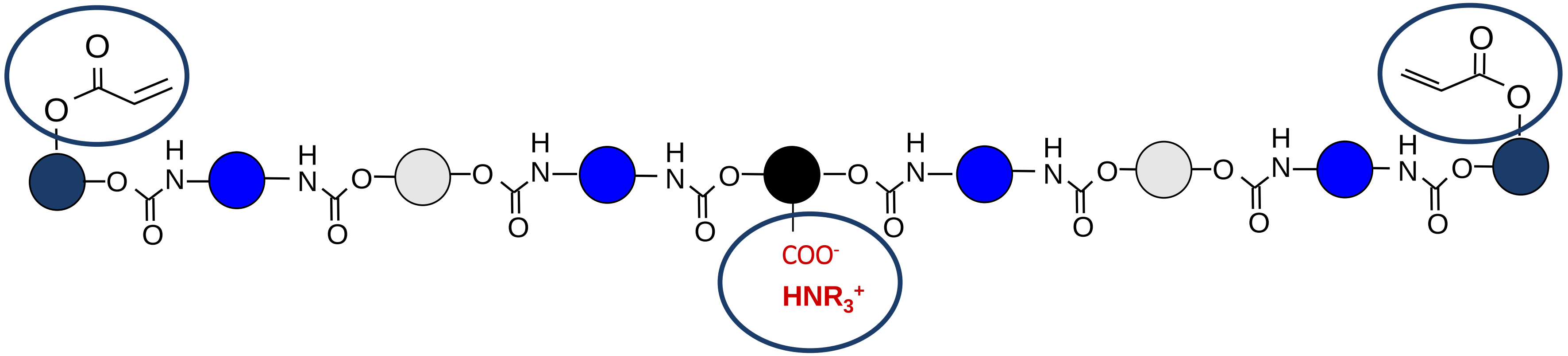
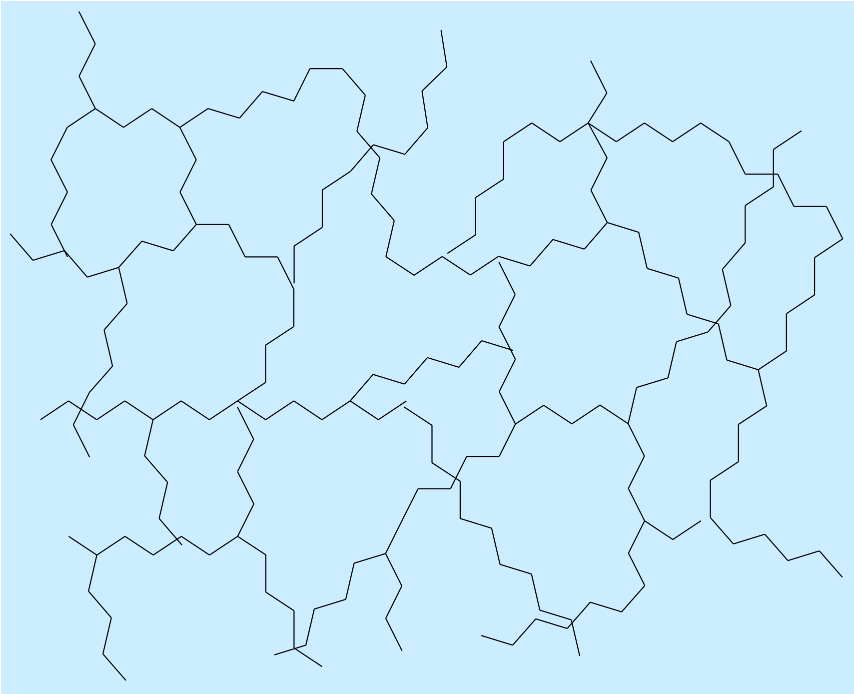
UV-PUD STRUCTURE

- Capping with hydroxyalkyl acrylate
- Neutralization and dispersion in water
- Stripping off the solvent



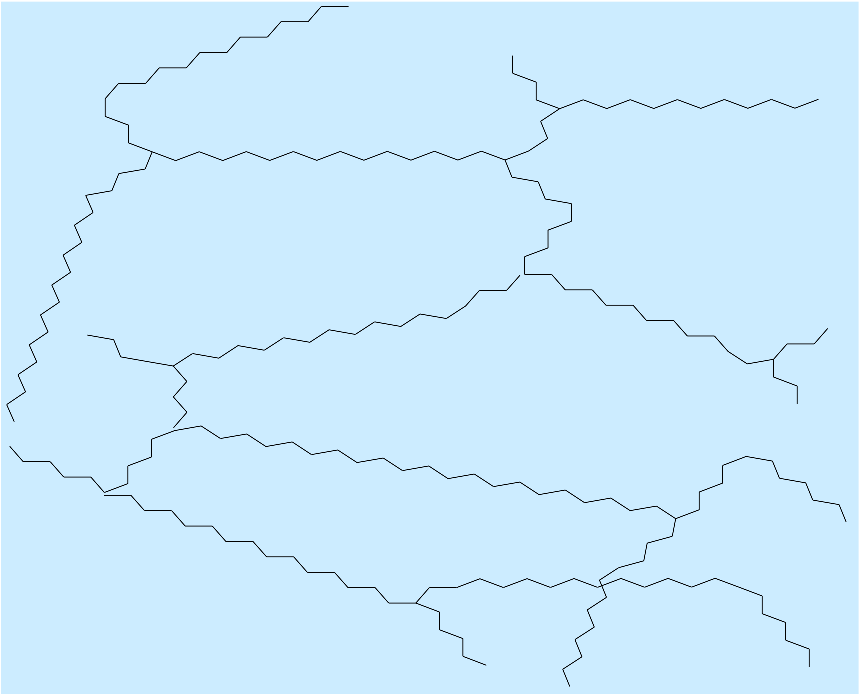
COMPARISON OF 100% SOLIDS AND UV-PUD NETWORK

100% UV



- Higher crosslinking density
- Low Mw between crosslinks
- May be brittle

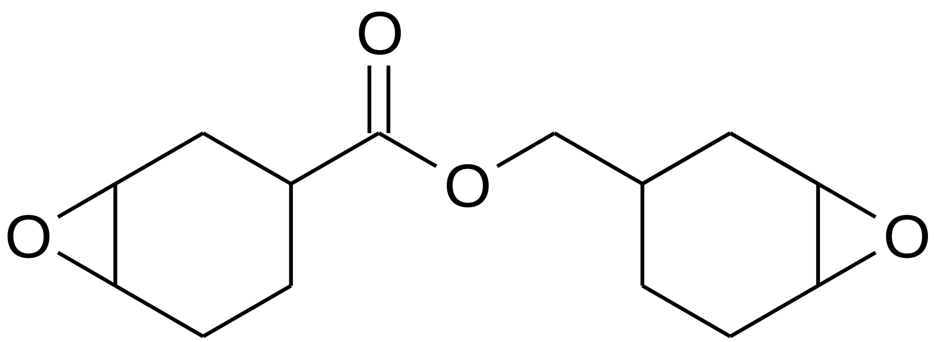
UV-PUD



- Lower crosslinking density
- High Mw between crosslinks
- Urethane hard segments
- Hard but flexible (tougher)

OLIGOMER FOR CATIONIC CURING

Cycloaliphatic Diepoxide



Major Component of Most Formulations

Used in combination with

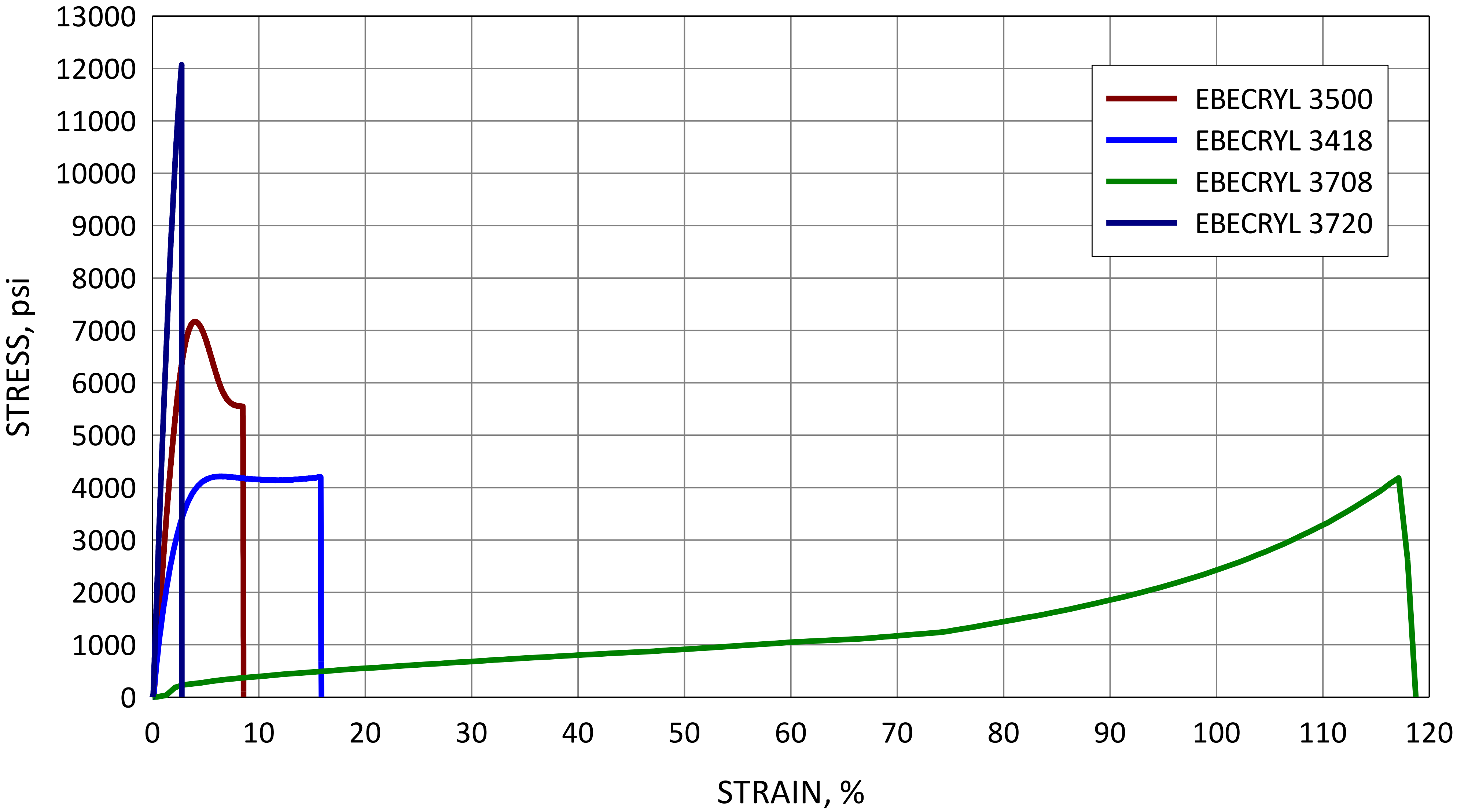
- Other cycloaliphatic epoxides
- Polyols
- Oxetanes
- Glycidyl ether epoxies
- Acrylates – hybrid cationic/radical cure systems

OLIGOMER PHYSICAL PROPERTIES

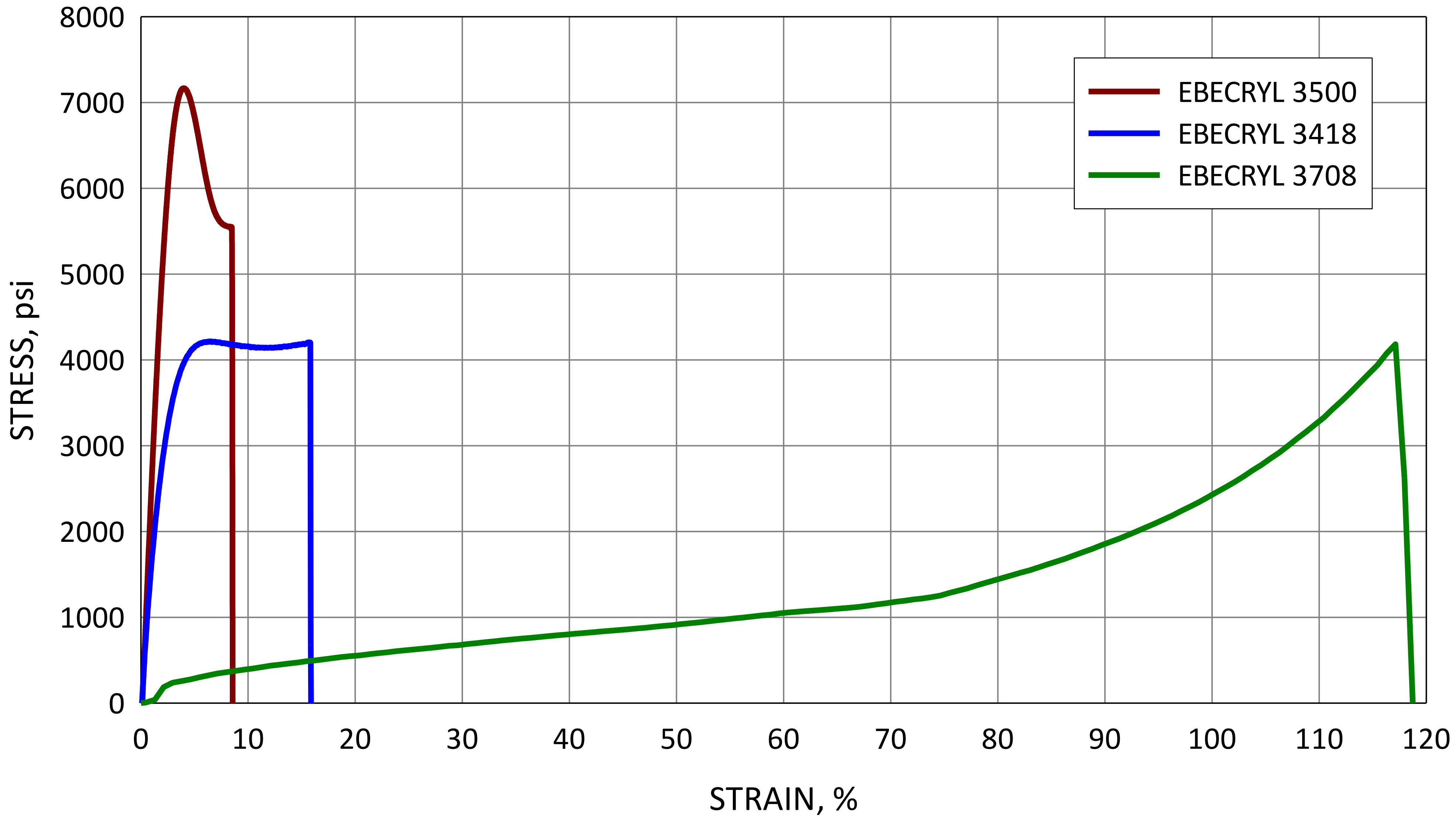
Stress/Strain Testing With Tensiometer

- UV or EB cured free films
  - Tensile strength
  - % Elongation
  - Modulus

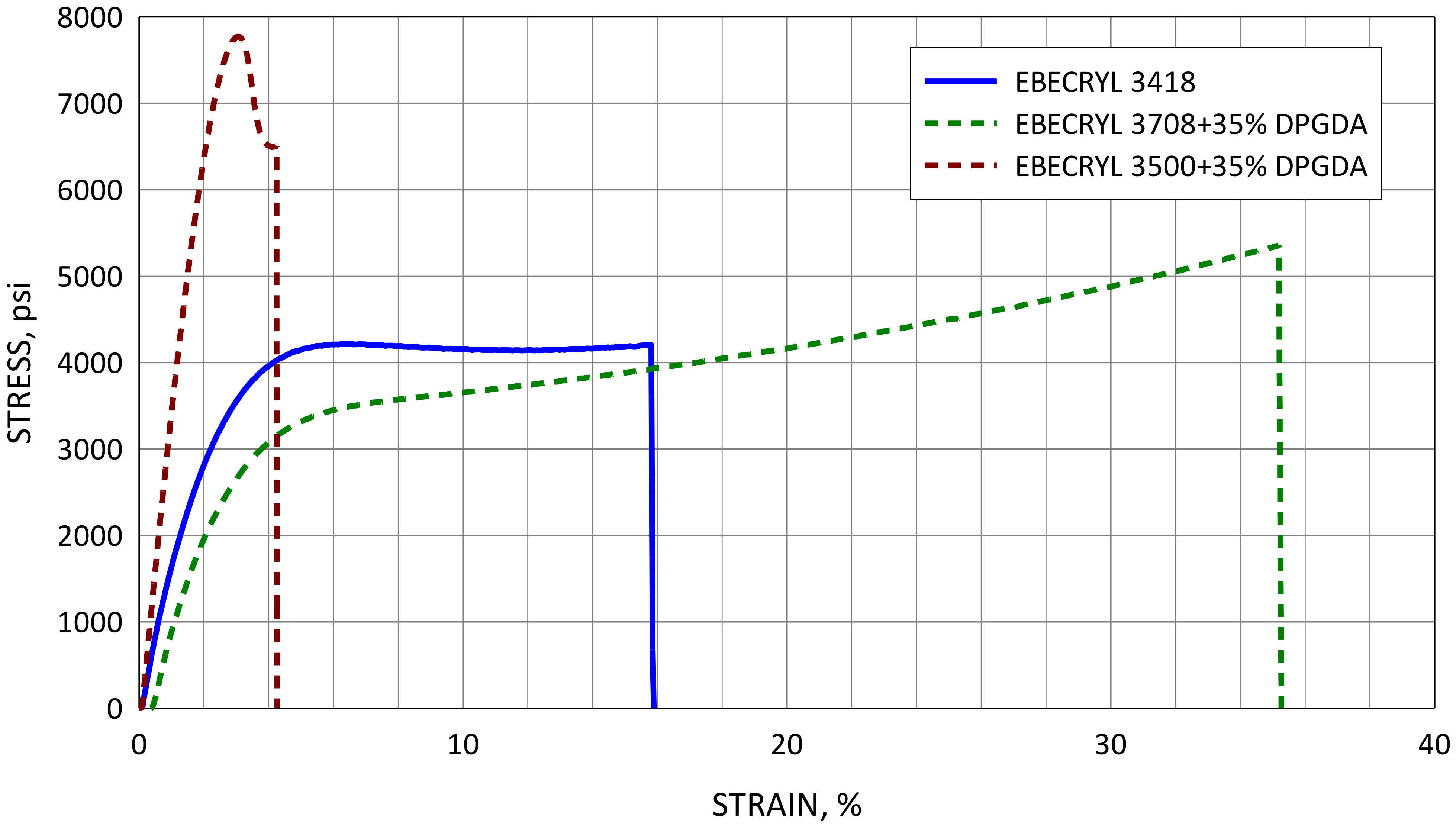
OLIGOMER PHYSICAL PROPERTIES – EPOXY ACRYLATES



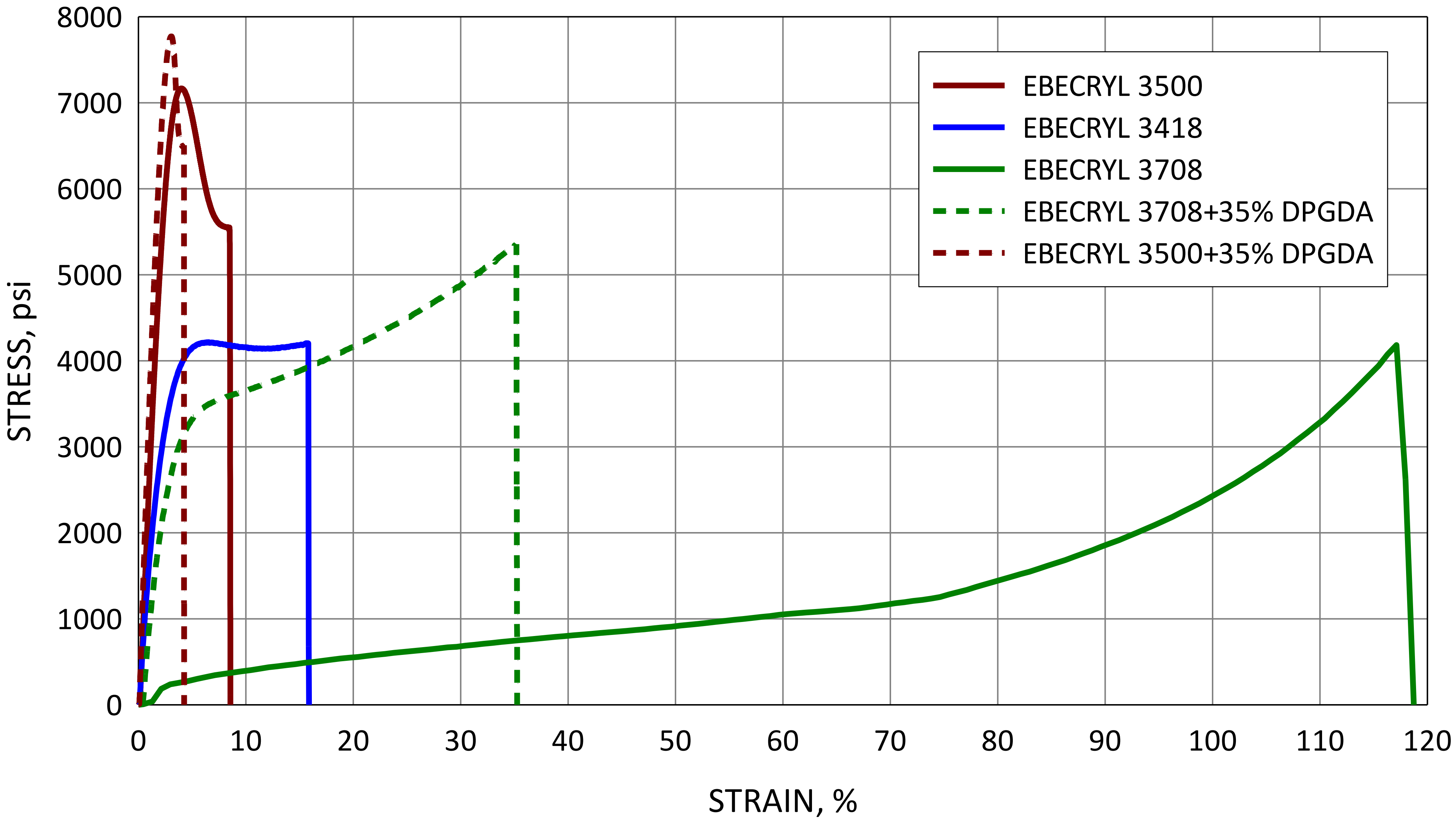
OLIGOMER PHYSICAL PROPERTIES – EPOXY ACRYLATES



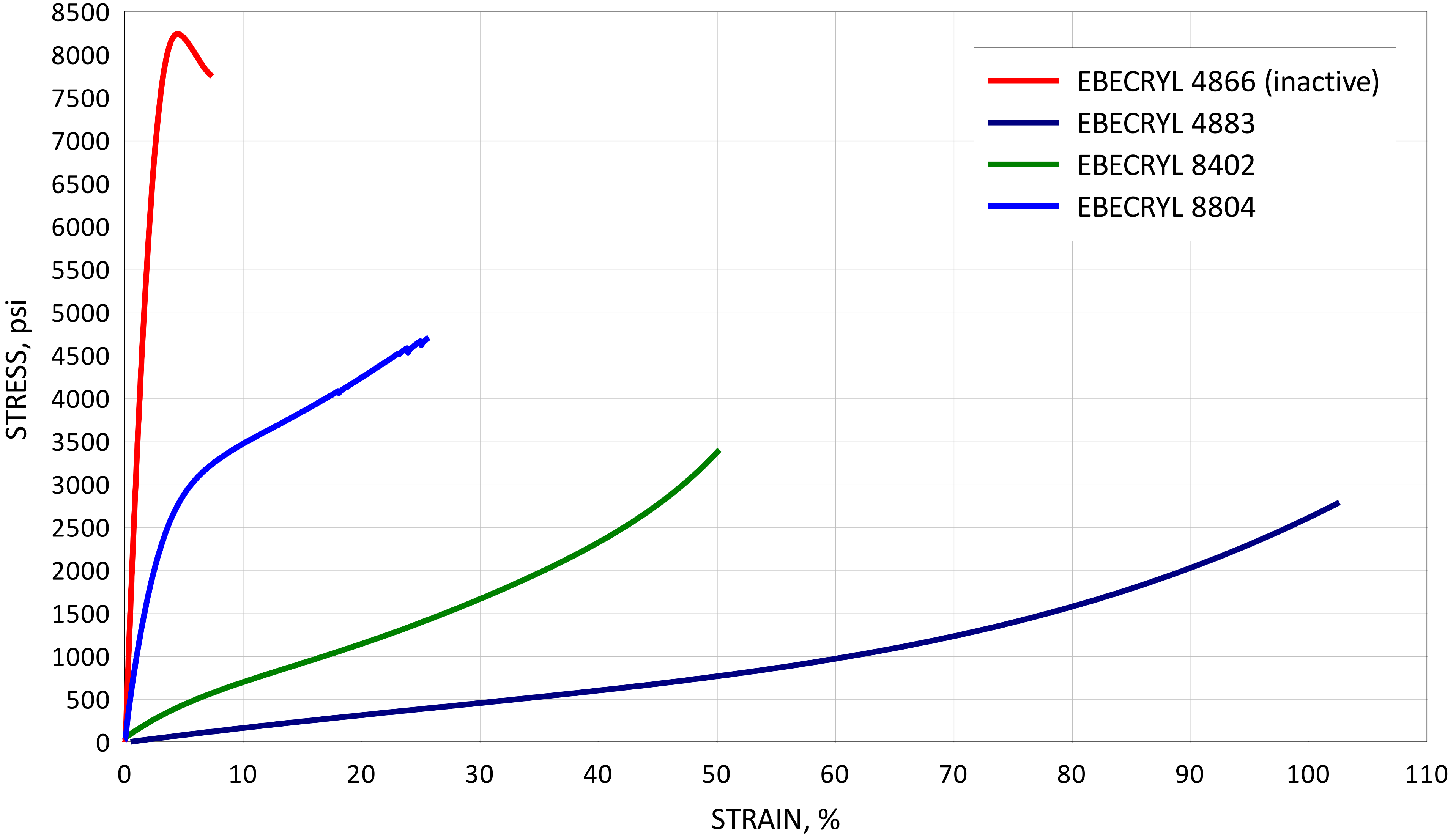
OLIGOMER PHYSICAL PROPERTIES – EPOXY ACRYLATES



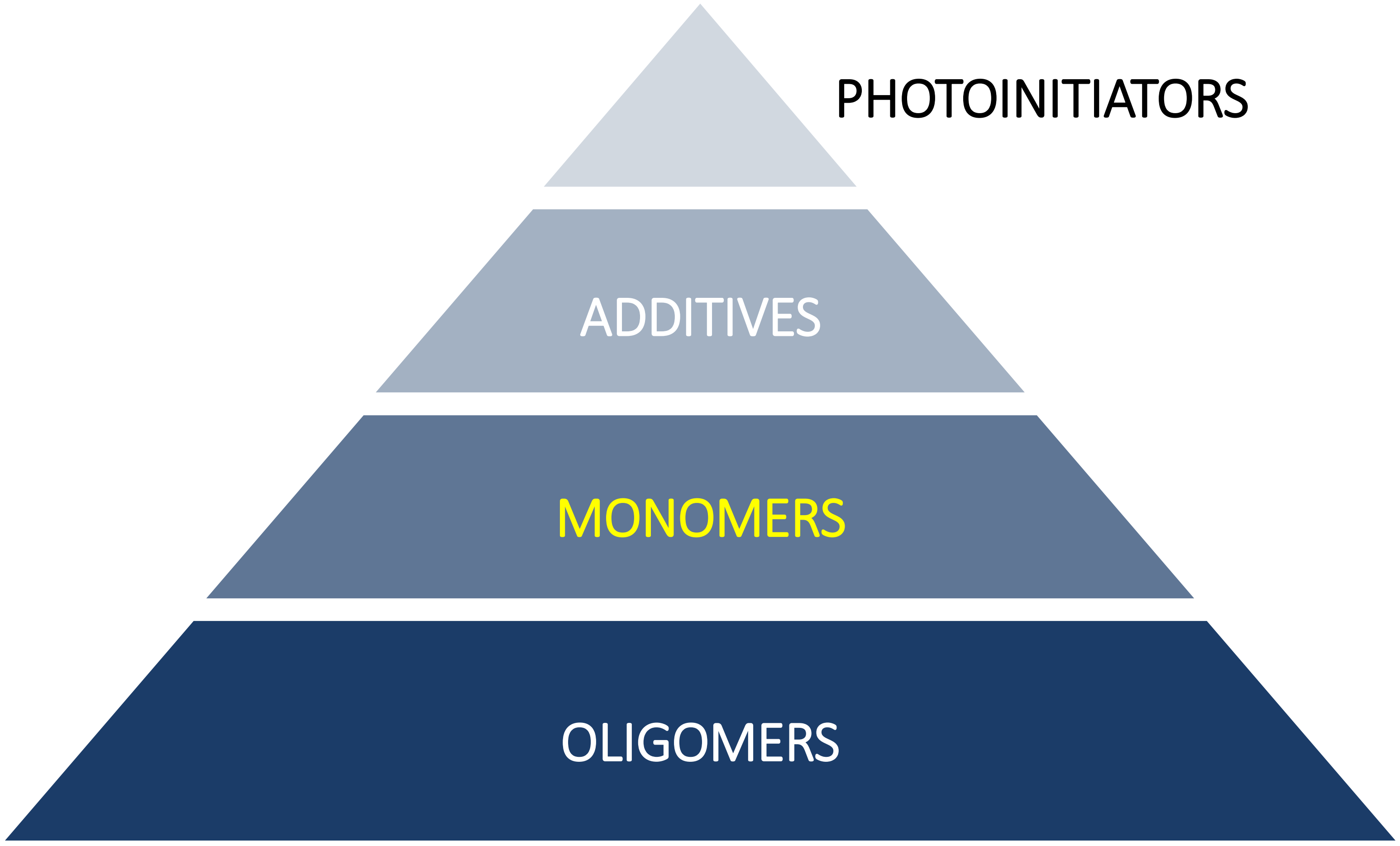
OLIGOMER PHYSICAL PROPERTIES – EPOXY ACRYLATES



OLIGOMER PHYSICAL PROPERTIES – URETHANE ACRYLATES



MONOMERS



DILUENTS

Polymerizable

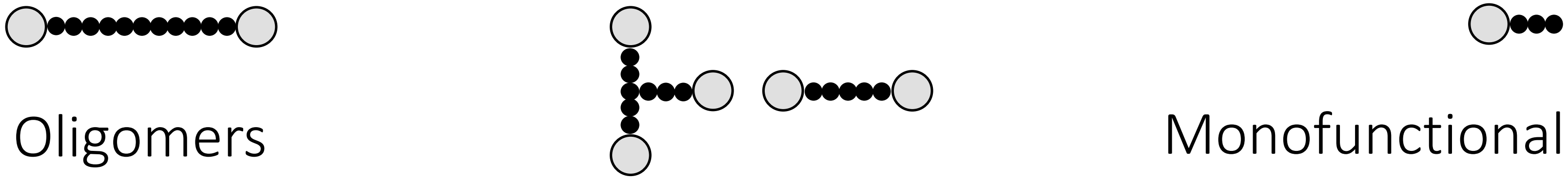
(Meth) Acrylate Monomers
(Reactive Diluents/Polyol Acrylates)

- Monofunctional
- Multifunctional (MFM'S)
- Polyol Polyacrylates
- Reactive Diluents

Non-Polymerizable

- Solvent
- Water

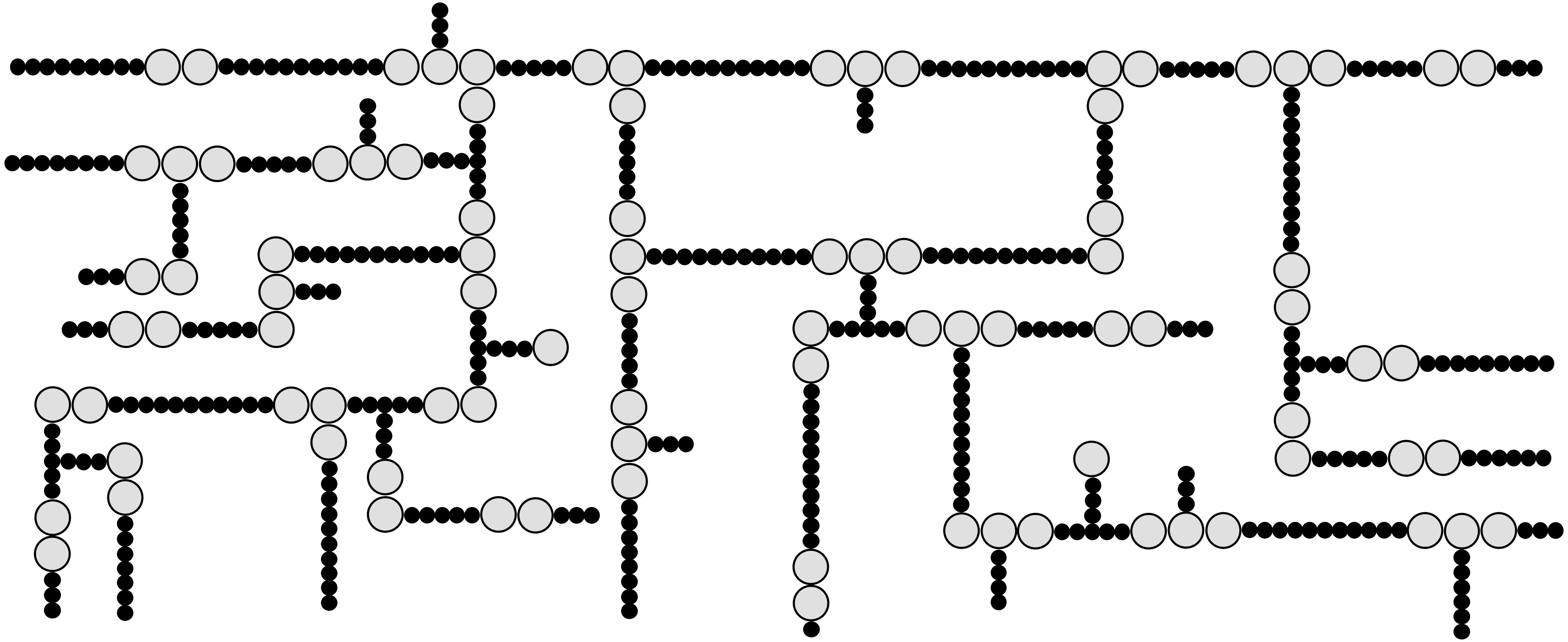
UV/EB CURED POLYMER NETWORK



Oligomers

Monofunctional Monomers

Multifunctional Monomers



Choice of Monomer Influences

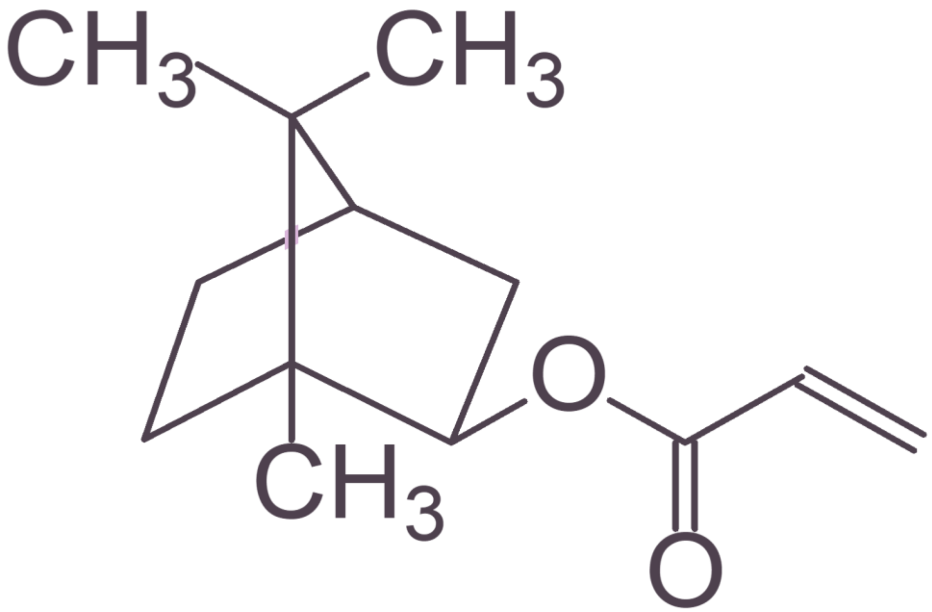
Liquid Properties

- Formulation Viscosity
- Cure Speed
- Surface Tension
- Volatility & Odor
- Stability
- Color

Cured Film Properties

- Weatherability & Color
- Flexibility
- Hardness
- Adhesion
- Resistance Properties
- Tg, Tensile Strength & Modulus, Elongation
- Shrinkage

Monofunctional Monomer



IBOA

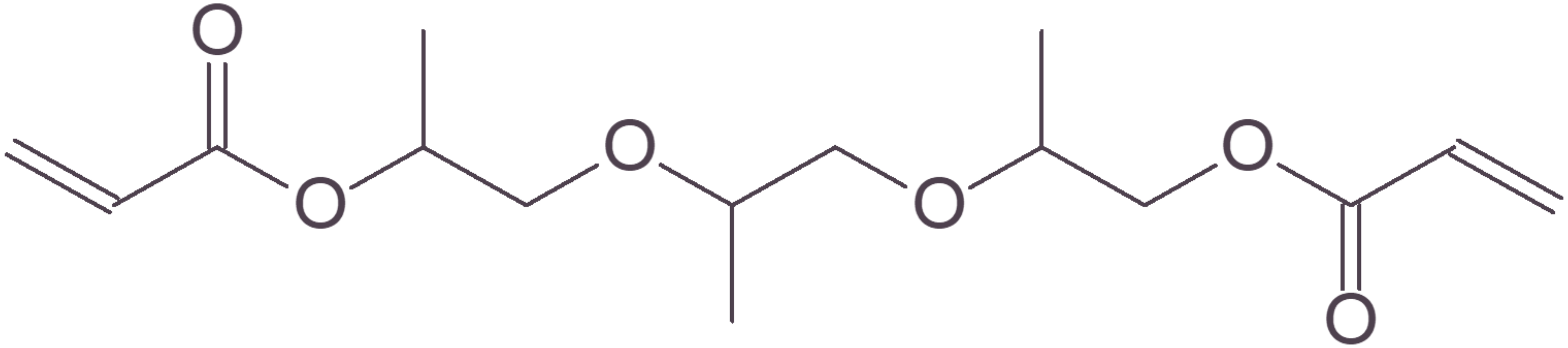
Isobornyl acrylate

MONOMER SELECTION

Monofunctional Monomers

- Lower cure speed
- Residual uncured; not for food packaging
- Impart flexibility; increase MW between x-links
- Improve adhesion
- Significantly reduce viscosity
- May cause swelling of photopolymer printing plates
- Rarely used in litho inks

Difunctional Monomer



TPGDA

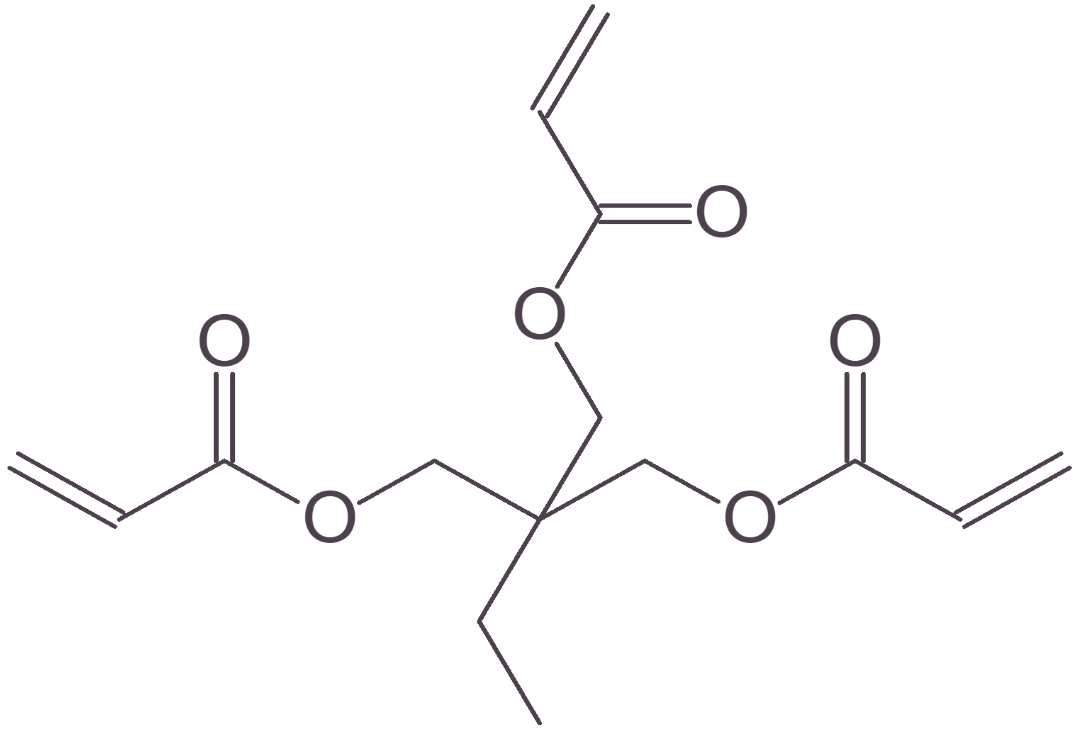
Tripropylene glycol diacrylate

MONOMER SELECTION

Difunctional Monomers

- Improve solvent resistance while maintaining flexibility
- Provide adhesion
- Reduce viscosity
- Propoxylates reduce surface tension and improve substrate wetting and increase flexibility
- Some are food packaging compliant
- Aggressive monomers may cause swelling of photopolymer plates (HDDA not used in litho)

Trifunctional and Higher Monomers



TMPTA

Trimethylolpropane triacrylate

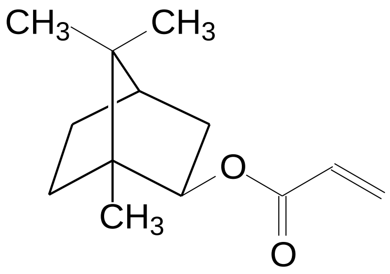
MONOMER SELECTION

Trifunctional and higher functionalities

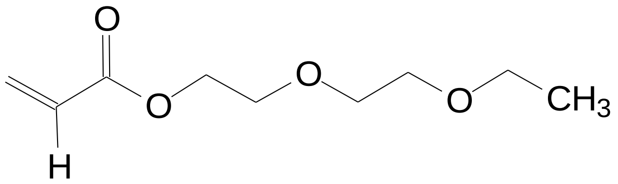
- Increase cure speed but can make material brittle
- Typically higher in viscosity and not as effective at reducing viscosity
- Propoxylated glycerol triacrylate (GPTA or OTA-480) is best pigment wetter
- Ethoxylates improve flow
- Easier to meet food packaging regulations

ACRYLATED MONOMERS

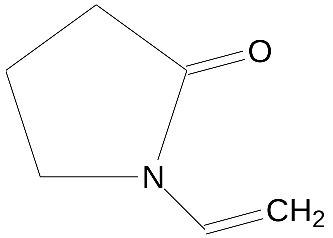
Monofunctional Monomers



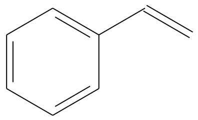
IBOA
Isobornyl acrylate



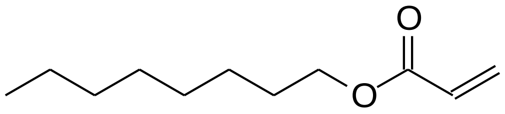
EOEOEA
2(2-Ethoxyethoxy) ethyl acrylate



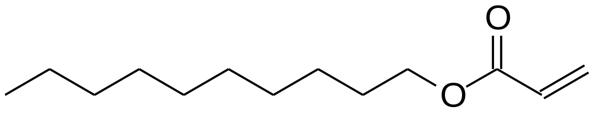
NVP
N-vinyl-2-pyrrolidone



Styrene

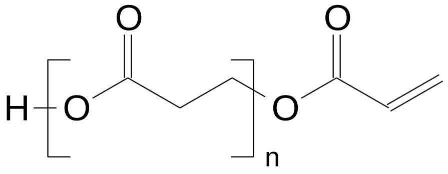


Octyl acrylate



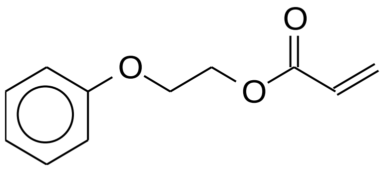
Decyl acrylate

ODA
Octyl/Decyl acrylate



average n = 1

β-CEA
β-Carboxyethyl acrylate



2-PEA
2-Phenoxyethyl acrylate

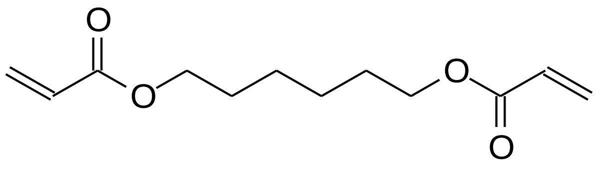
MONOFUNCTIONAL MONOMER EFFECTS

	VISCOSITY (cP, 25°C)	CURE SPEED[1] (fpm)
Styrene	1000	12
Octyl/Decyl acrylate	1200	60
N-vinyl-2-pyrrolidone	1750	>200
2(2-Ethoxyethoxy) ethyl acrylate	1800	100
2-Phenoxyethyl acrylate	5000	110
Isobornyl acrylate	13000	75
β-Carboxyethyl acrylate	22000	150

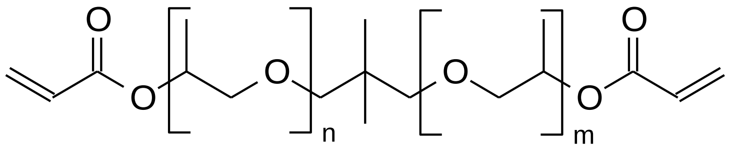
30% monomer in 70% epoxy diacrylate oligomer; 4 pbw photoinitiator

(1) Cured with 2 Fusion 300 watt/inch electrodeless type H lamps.

Difunctional Monomers

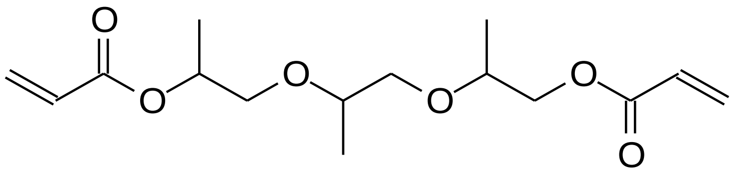


HDDA
1,6-Hexanediol diacrylate

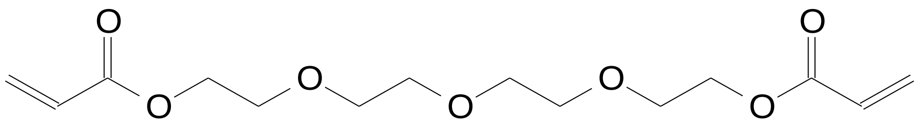


n + m ~ 2

$NPG(PO)_2DA$
Neopentyl glycol propoxy diacrylate



TPGDA
Tripropylene glycol diacrylate



TTEGDA
Tetraethylene glycol diacrylate

DIFUNCTIONAL MONOMER EFFECTS

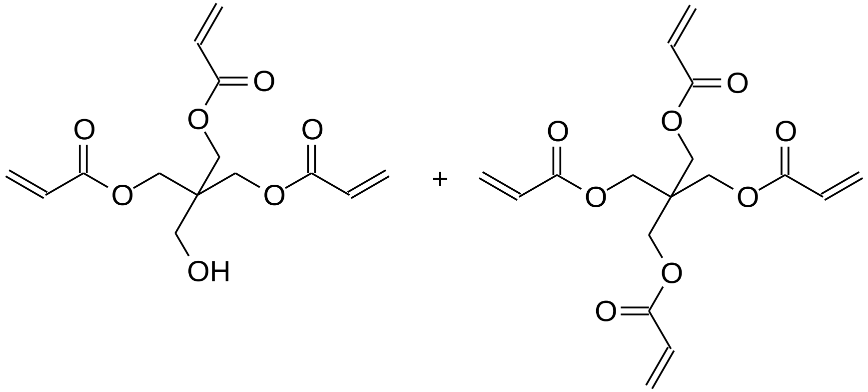
	VISCOSITY (cP, 25°C)	CURE SPEED(1) (fpm)
1,6-Hexanediol diacrylate	2100	200
Tetraethylene glycol diacrylate	4100	125
Tripropylene glycol diacrylate	7550	100
Neopentyl glycol propoxy diacrylate	9560	100

30% monomer in 70% epoxy diacrylate oligomer; 4 pbw photoinitiator

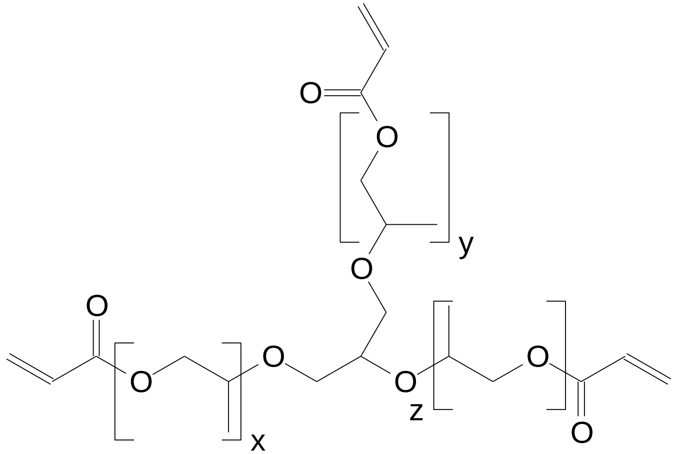
(1) Cured with 2 Fusion 300 watt/inch electrodeless type H lamps.

ACRYLATED MONOMERS

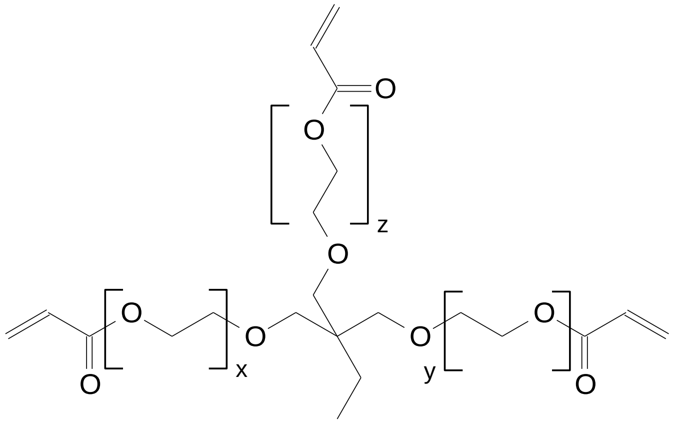
Trifunctional and Higher Monomers



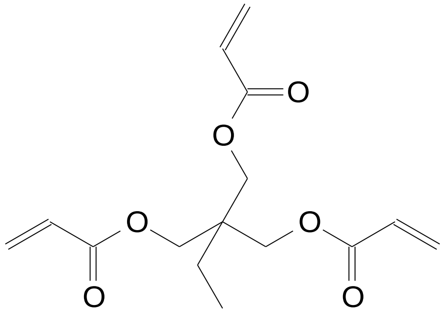
PETA
Pentaerythritol tri/tetraacrylate



GPTA
Glycerol propoxy triacrylate



TMPEOTA
Trimethylolpropane ethoxy(3) triacrylate



TMPTA
Trimethylolpropane triacrylate

TRIFUNCTIONAL MONOMER EFFECTS

	VISCOSITY (cP, 25°C)	CURE SPEED[1] (fpm)
Trimethylolpropane trimethacrylate	10400	15
Trimethylolpropane ethoxy(3) triacrylate	13000	200
Pentaerythritol tri/tetraacrylate	25000	110
Trimethylolpropane triacrylate	25400	200
Glycerol propoxy triacrylate	46250	125

30% monomer in 70% epoxy diacrylate oligomer; 4 pbw photoinitiator

(1) Cured with 2 Fusion 300 watt/inch electrodeless type H lamps.

MONOMER STRUCTURE-PROPERTY SUMMARY

Property	Monomer Functionality			
	Mono	Di	Tri	Tetra & >
Reactivity	⟶			
Flexibility	⟵			
Hardness	⟶			
Solvent Resistance	⟶			
Tensile Strength	⟶			
Elongation	⟵			
Shrinkage	⟶			
Adhesion	⟵			

Polymerization Inhibitors

200-1000 ppm of a radical scavenger

- Quinones
- Usually HQ for oligomers
- HQMME for monomers

Oxygenated systems

Generally no effect on cure speed

May impact labeling

- New GHS regulations

(METH)ACRYLATES in general:

Non-toxic

May be irritants
- Skin
- Eye

Low vapor pressure, non-flammable

Good industrial/lab hygiene
- Review SDS's
- Wear appropriate PPE
  - Safety glasses
  - Gloves
  - Lab coats

THANK YOU FOR YOUR ATTENTION!

Questions?

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