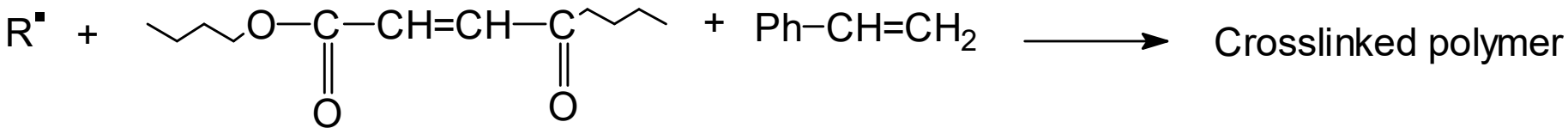
MONOMERS

RADICAL PHOTOCURABLE MONOMERS

- Unsaturated polyester resins
- Acrylates and Methacrylates
- Thiol-ene systems

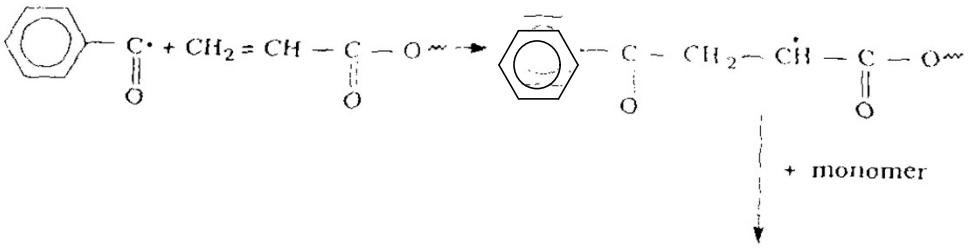
UNSATURATED POLYESTER RESINS



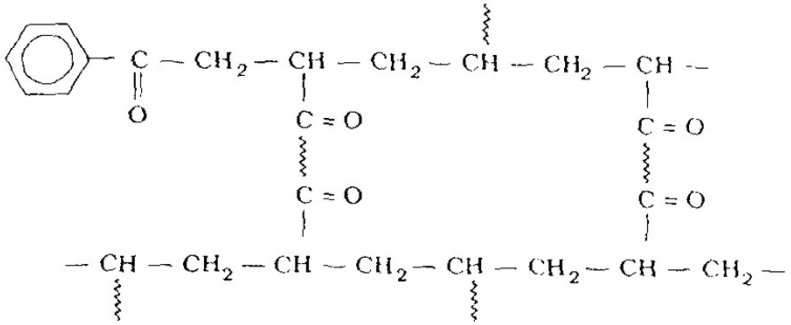
Photopolymerizable resins consisting of an unsaturated polyester dissolved in styrene were among the first to be used in large scale UV-curing applications. Here the radical initiated crosslinking occurs by direct addition copolymerization of the vinyl monomer with the unsaturations (usually maleic or fumaric structures) located on the polyester backbone.

ACRYLATED AND METHACRYLATED RESINS

Initiation



Propagation

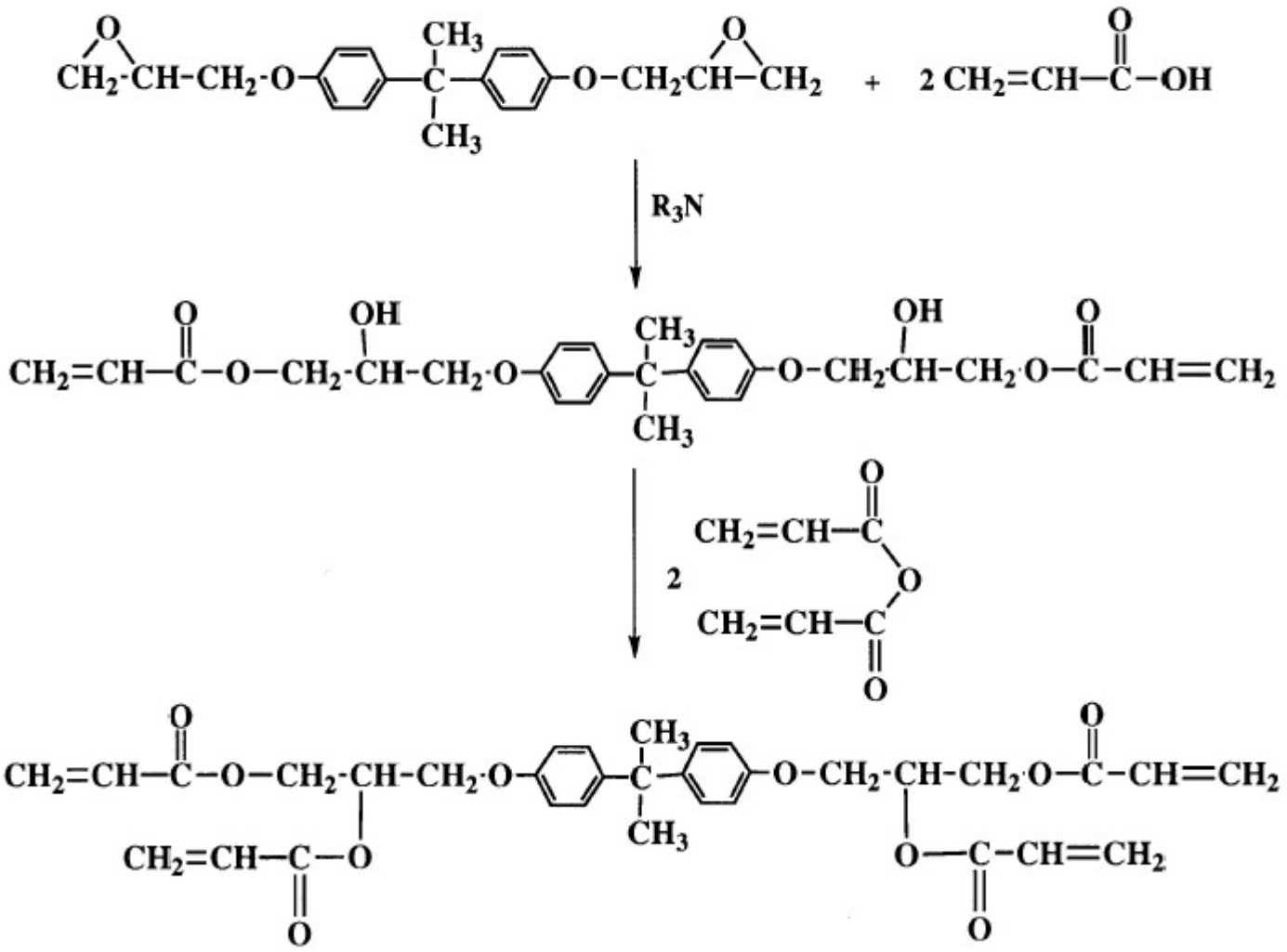


Termination

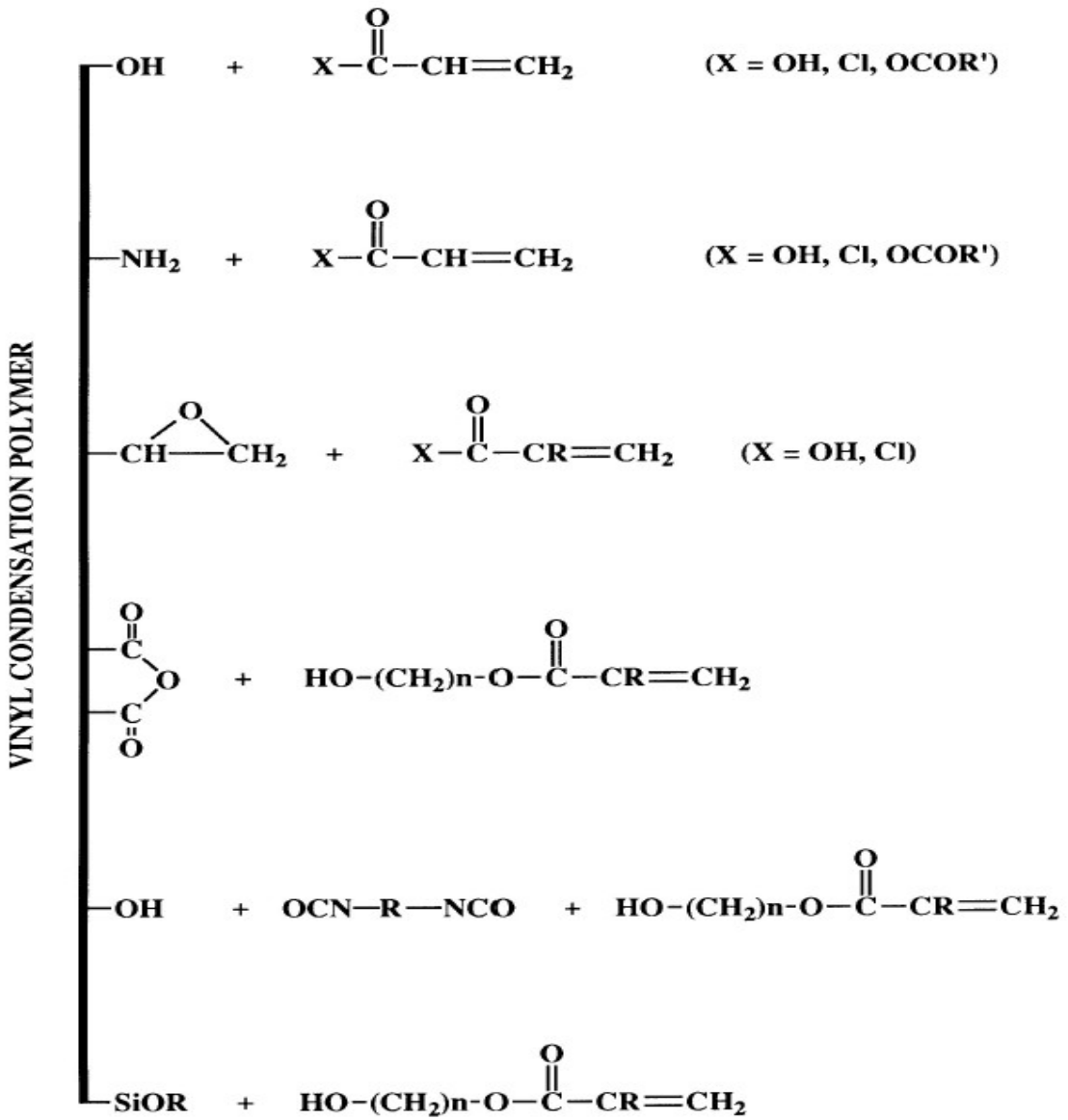
$P_n^{\bullet} + P_m^{\bullet} \longrightarrow P_n P_m$

$P_n^{\bullet} \longrightarrow$ Occlusion

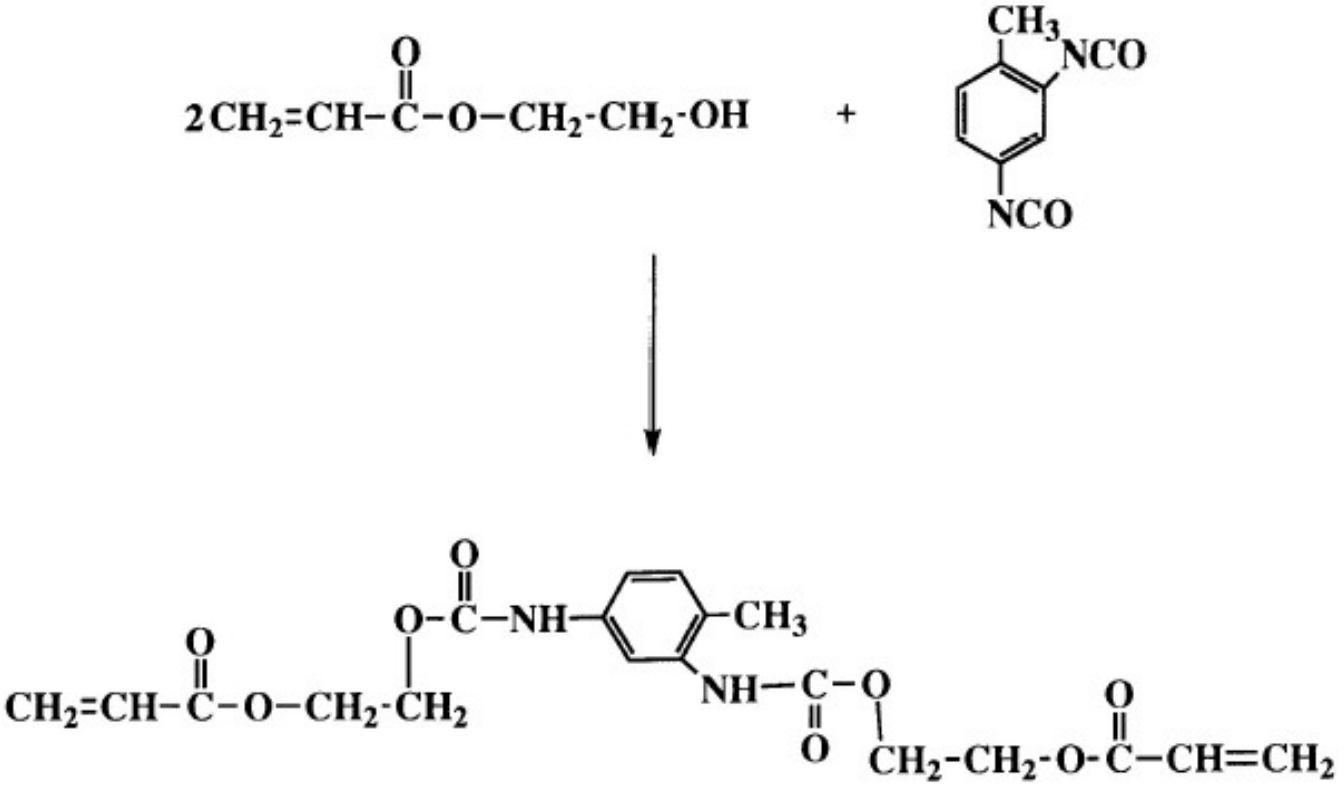
EPOXYACRYLATES



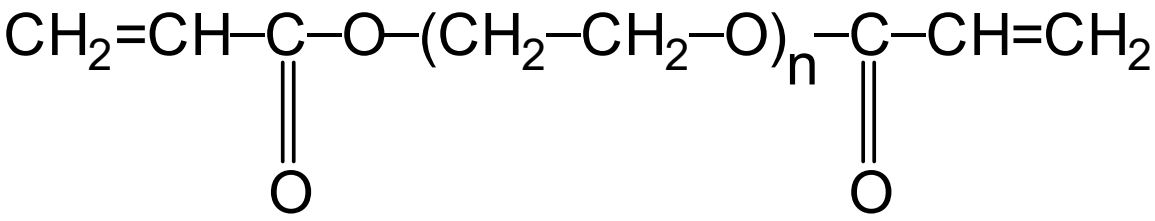
ACRYLATE MODIFIED PREPOLYMERS

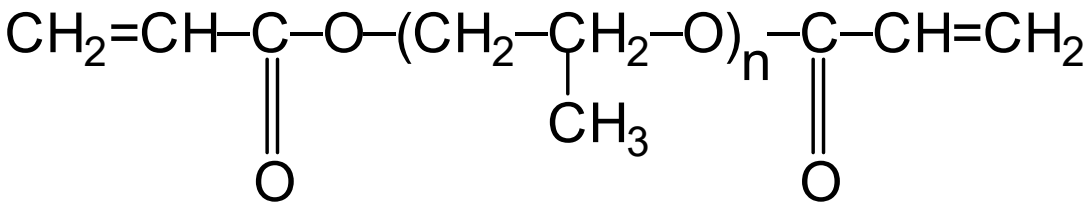


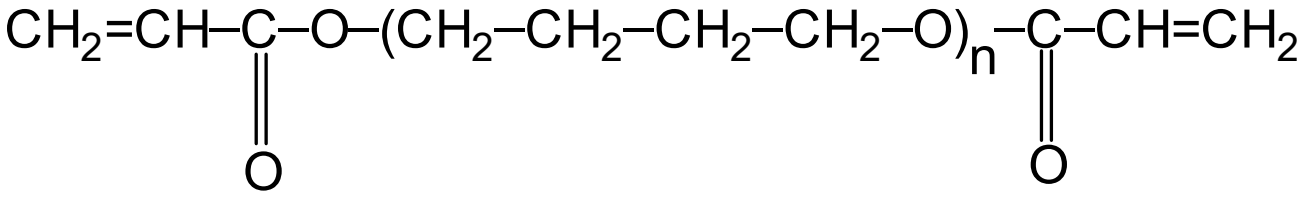
URETHANE-ACRYLATES



Polyalkylene glycol diacrylate





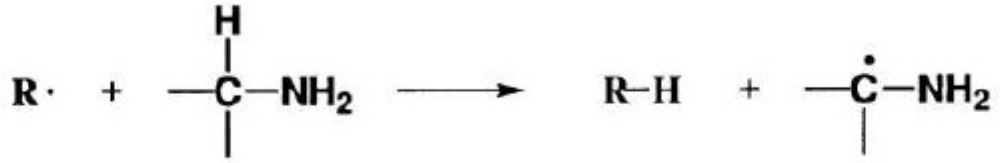


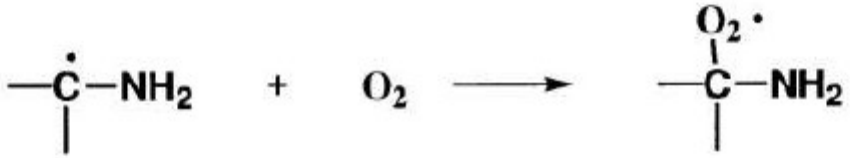
CRITERIA OF SELECTION

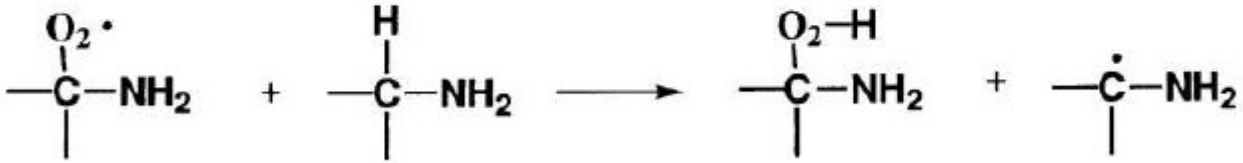
OLIGOMER	PROPERTIES
ACRYLATED EPOXIES	HARD, SOLVENT RESISTANCE, LOW COST, FAST CURE
ALIPHATIC URETHANES	FLEXIBLE, TOUGH, NON-YELLOWING
AROMATIC URETHANES	FLEXIBLE, LOW VISCOSITY
ACRYLICS	GOOD WEATHERING, LOW T_g
POLYESTERS	LOW VISCOSITY, FLEXIBLE

METHODS OF REDUCING OXYGEN INHIBITION

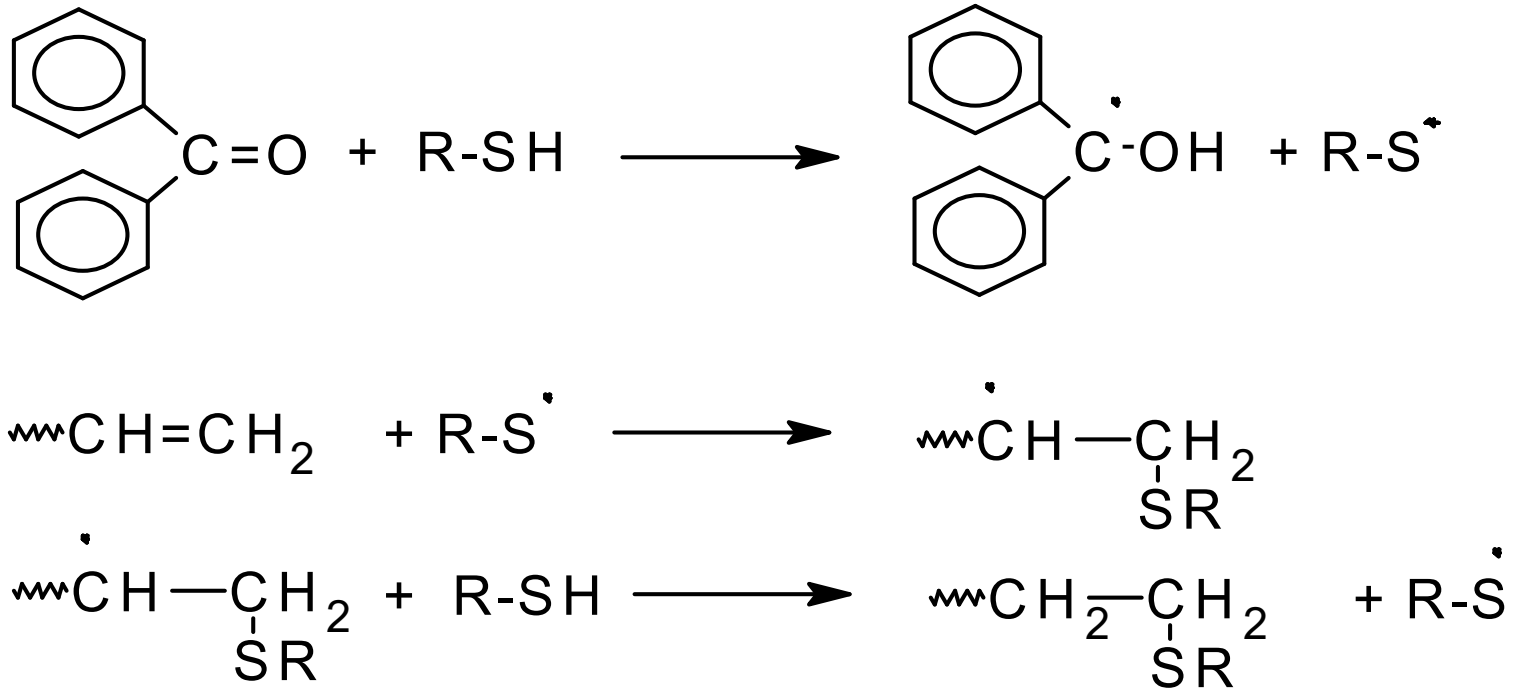
- NITROGEN BLANKETING
- USE OF OXYGEN-INSENSITIVE MONOMERS
- WAX
- AMINE ADDITIVES
- USE OF COVER SHEETS
- LARGE AMOUNTS OF PHOTOINITIATORS


R·
H
NH2
R–H
NH2


NH2
O2
O2
NH2

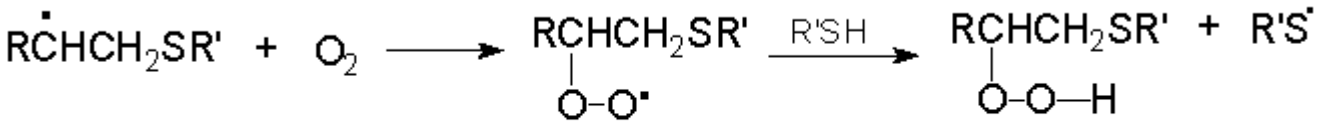

O2
NH2
H
NH2
O2–H
NH2
NH2

THIOL-ENE SYSTEMS

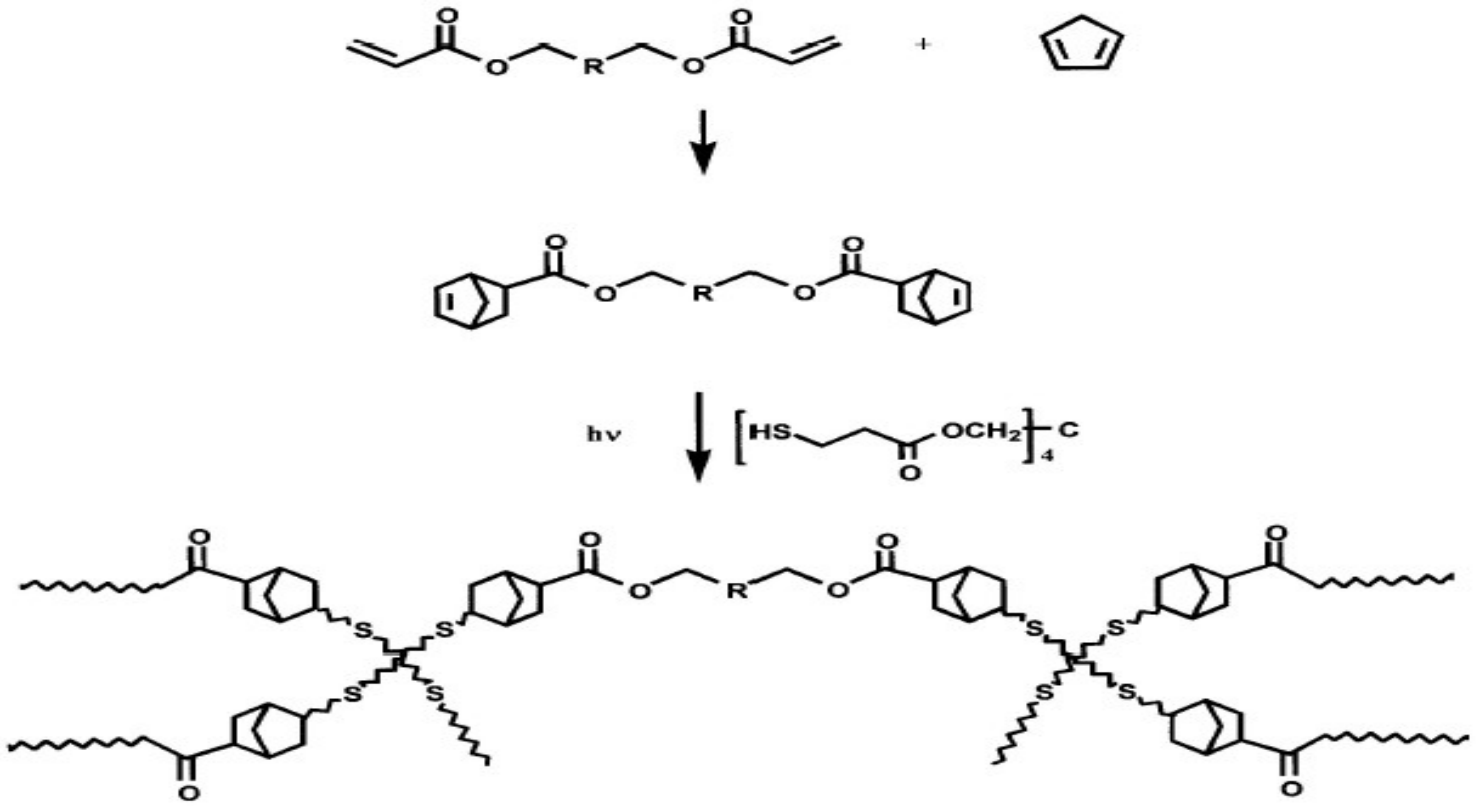


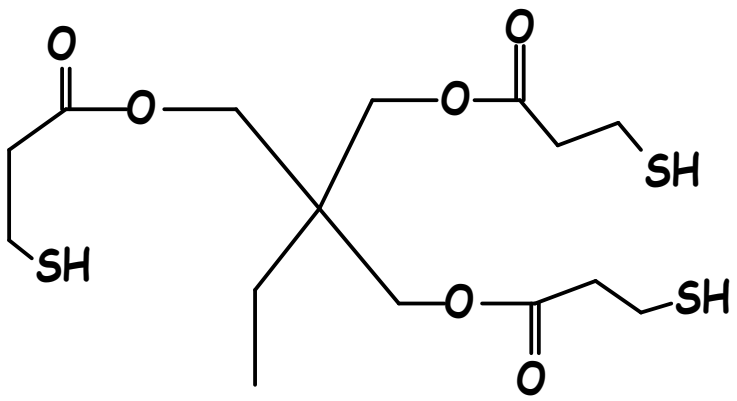
The thiol-ene process proceeds via a chain-growth reaction involving a stoichiometric addition of the thiyl radical to the ene group giving rise to an alternating structure.

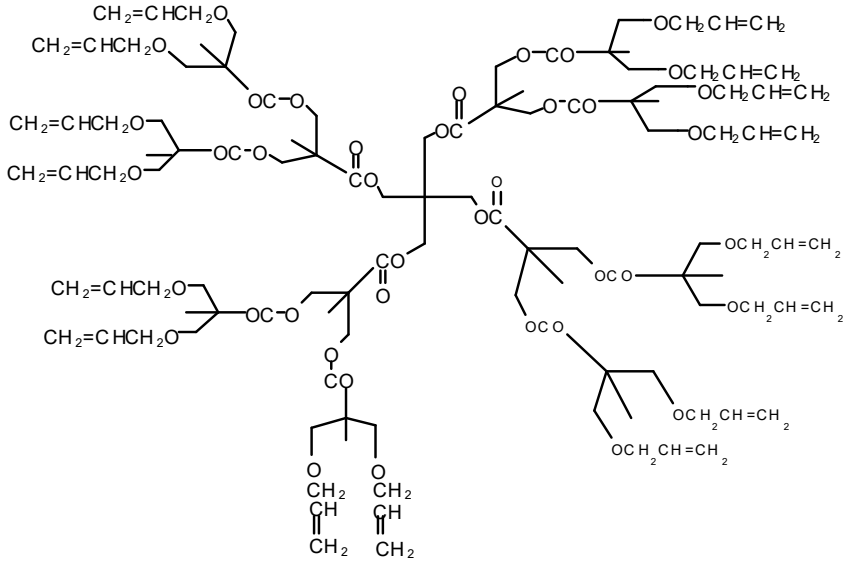
- No oxygen inhibition



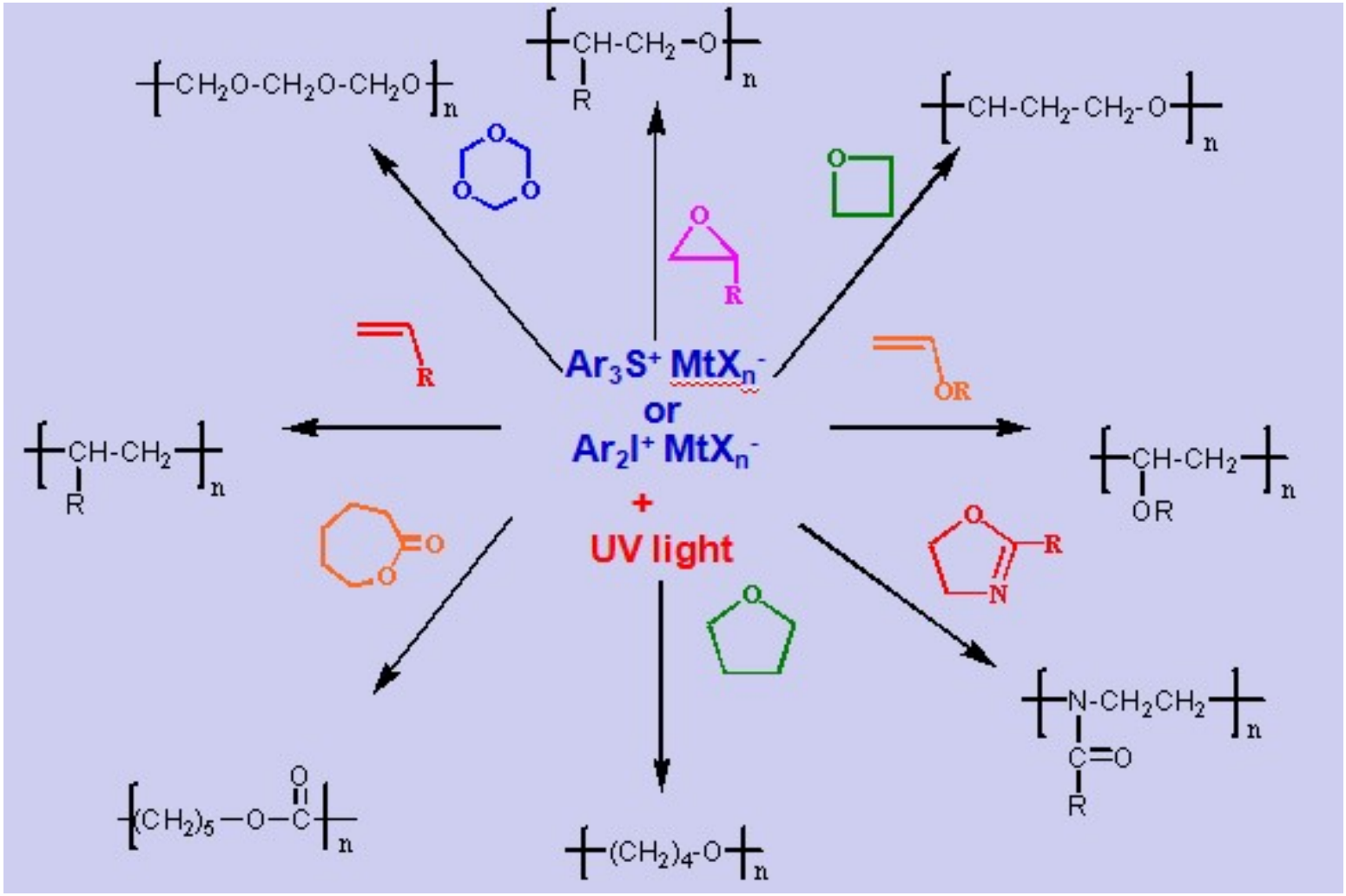
- delaying the onset of gelation
- reactivity also in the absence of photoinitiator-
- reduced shrinkage
- Safer alternative to acrylic monomers


O
O
R
O
O
+
O
O
R
O
O
hν
HS
OCH2
4
C
O
S
S
S
S
O
O
R
O
O
S
S
S
S
O
O

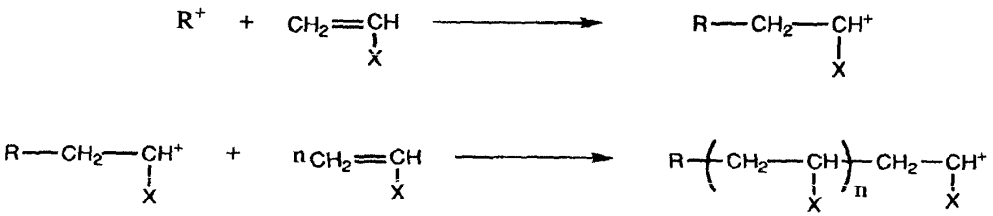




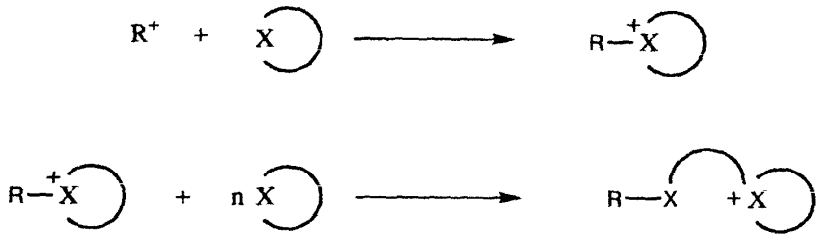
CATIONIC PHOTOCURABLE MONOMERS



Vinyl Monomers

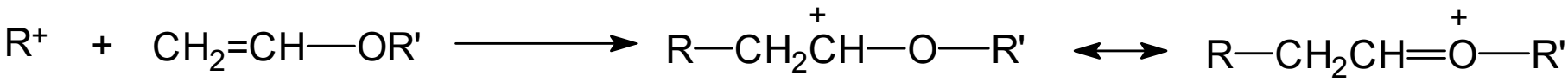


Heterocyclic Monomers



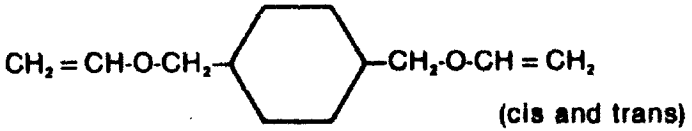
R^+ = H^+, Carbenium ions, Lewis Acids, etc.

VINYL ETHERS

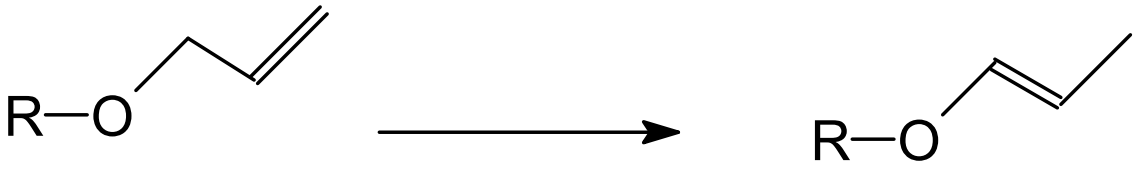


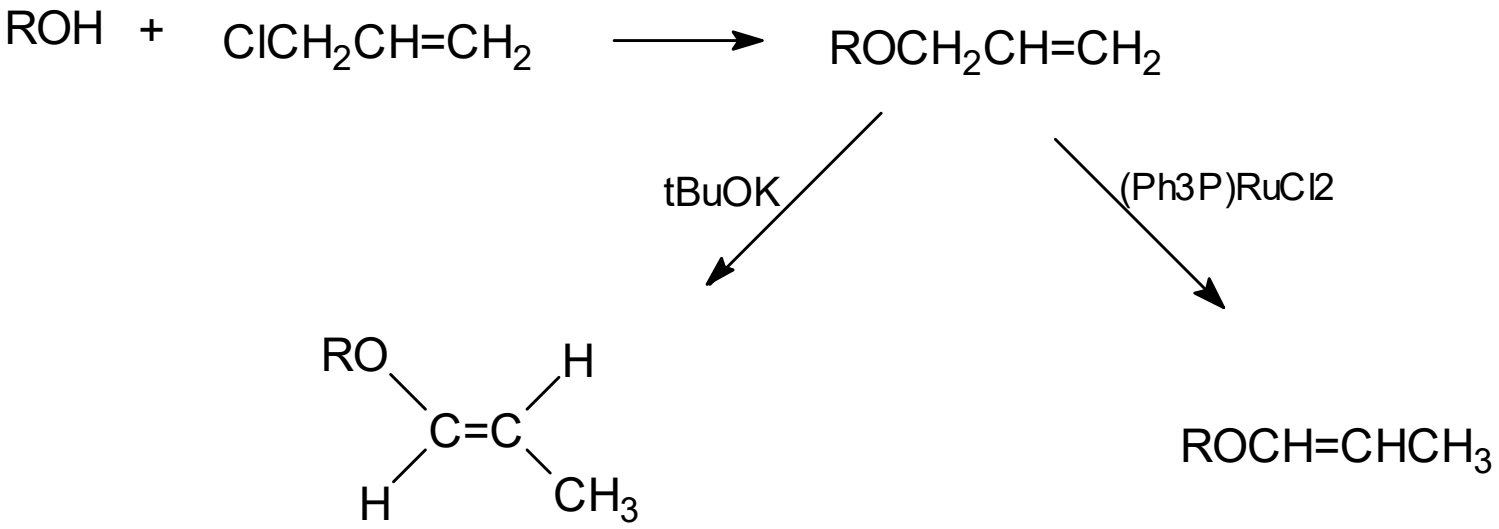
Vinyl ether monomers have appeared to be an attractive alternative to acrylates because they possess low toxicity and low odor as well as high reactivity. Vinyl ether exhibit a higher curing rate than epoxides under UV-irradiation and their reactivity is sometimes comparable to the acrylates. The high reactivity of vinyl ethers in cationic polymerization is a consequence of the electron-rich nature of the carbon-carbon double bond. Resonance structures may be drawn which illustrate the stabilization of the resulting carbocation.

PROPERTIES OF VARIOUS MULTIFUNCTIONAL VINYL ETHER MONOMERS

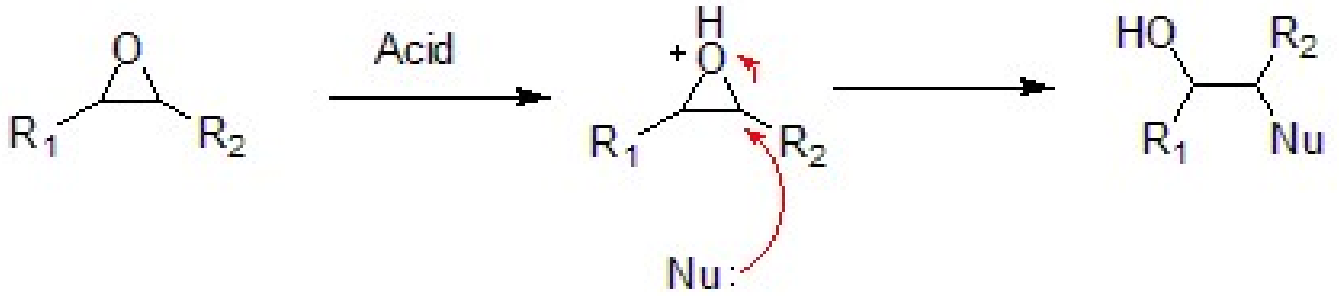
Structure	Properties	References
$CH_2=CH\text{-}O\text{-}(CH_2)_2\text{-}O\text{-}CH=CH_2$	bp = 126 °C η_D^{20} = 1.4338	C.A. 38,330 (1944)
$CH_2=CH\text{-}O\text{-}(CH_2)_3\text{-}O\text{-}CH=CH_2$	bp = 35 °C (50mm)	
$CH_2=CH\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH(CH_3)\text{-}O\text{-}CH=CH_2$	bp = 75 °C (60 mm)	
$CH_2=CH\text{-}O\text{-}(CH_2)_6\text{-}O\text{-}CH=CH_2$	bp = 100 °C (15 mm)	
$CH_2=CH\text{-}(O\text{-}CH_2\text{-}CH_2)_2\text{-}O\text{-}CH=CH_2$	bp = 110 °C (18 mm)	U.S. 1,959,927; PB 87, 917
$CH_2=CH\text{-}(O\text{-}CH_2\text{-}CH_2)_3\text{-}O\text{-}CH=CH_2$	bp = 126 °C (18 mm)	U.S. 1,956,927; PB 87,917
$CH_2=CH\text{-}O\text{-}(CH_2)_4\text{-}O\text{-}CH=CH_2$	bp = 41-42 °C (0.65 mm)	
$CH_2=CH\text{-}O\text{-}(CH_2)_2\text{-}O\text{-}(CH_2)_4\text{-}O\text{-}(CH_2)_2\text{-}O\text{-}CH=CH_2$	bp = 102-104 °C (0.25 mm)	
 (cis and trans)	bp = 118 °C (5 mm)	

PROPENYL ETHERS

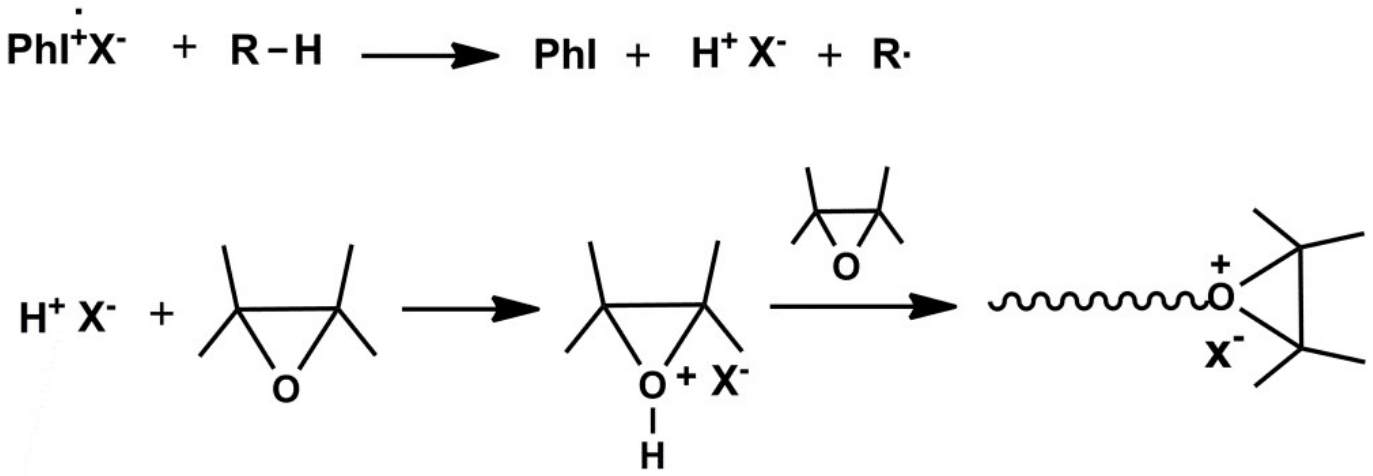




EPOXIDES



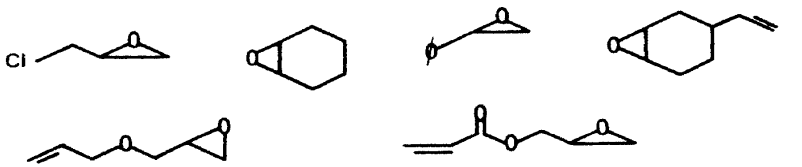
EPOXIDES



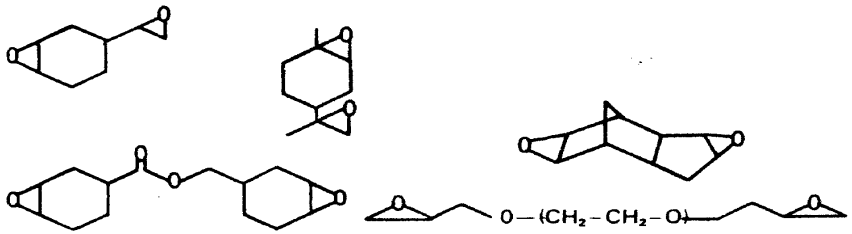
In the presence of a photogenerated protonic acid, the ring-opening polymerization of epoxides proceeds through the oxonium ion.

PHOTOPOLYMERIZABLE EPOXY RESINS

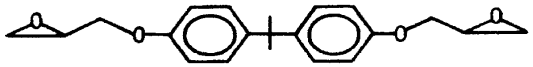
Monofunctional Epoxies



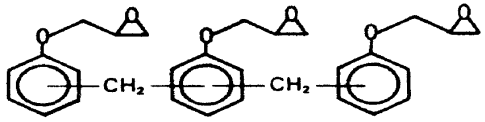
Difunctional Epoxies

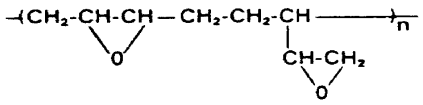


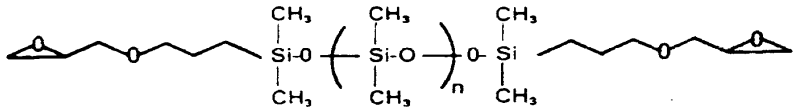
Epoxy Prepolymers



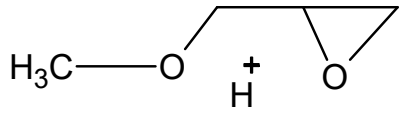
and Higher Oligomers





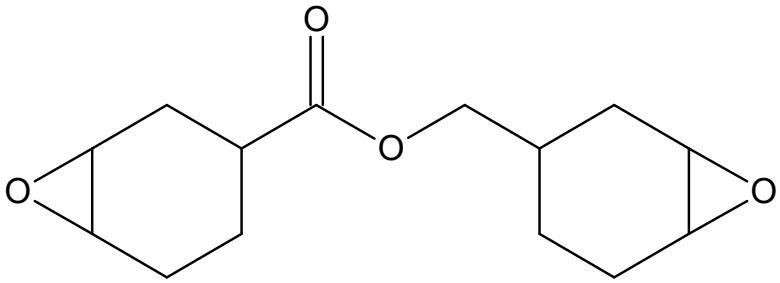


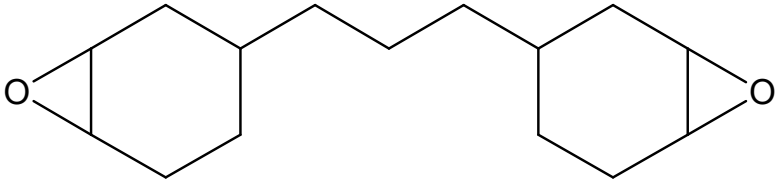
Stabilisation of oxonium ion through hydrogen bonding



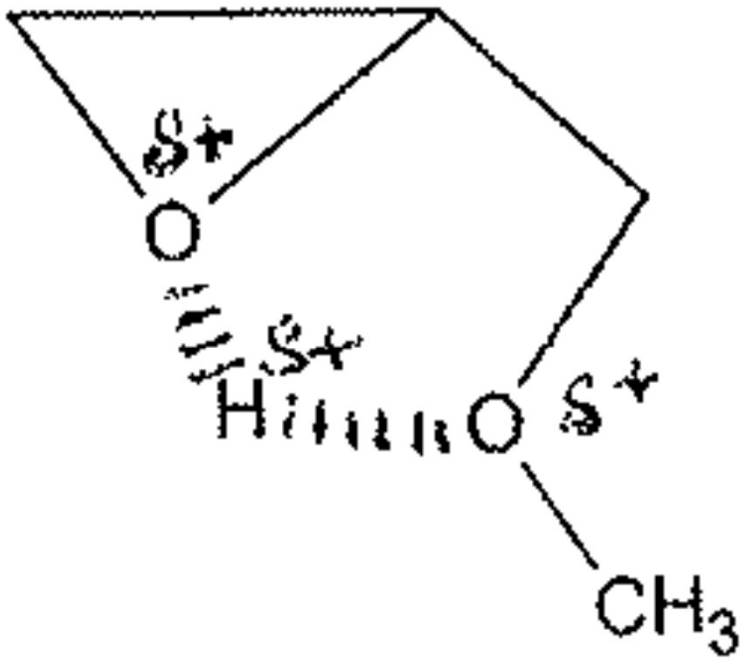
See: J V Crivello, Polymer Preprints, 2007, *48(1)* 316-317

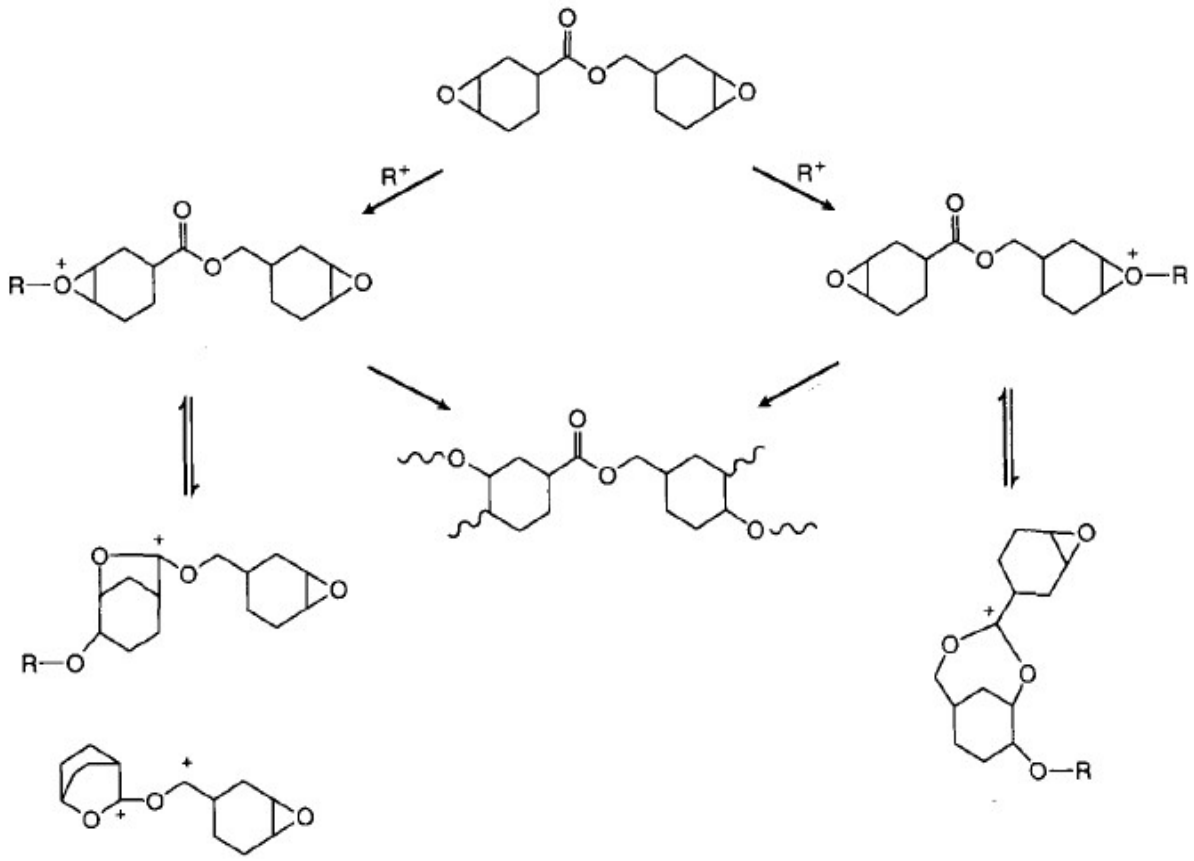
Deactivating effect of carbonyl groups





See: H Sasaki, Proceedings RadTech North America, 2004, Paper 2.4


δ+
O
δ+
δ+
O
CH3


R+
R+
R—O
O—R
R—O
O—R

Factors Affecting the Efficiency and Speed of Cationic UV Curing

Photoinitiator Structure

Structure of the cation - governs absorption characteristics

Structure of the anion - controls the strength of the acid generated
$SbF_6^- > AsF_6^- > PF_6^- > BF_4^-$

Presence of a Photosensitizer

Broadens the spectral sensitivity

Polymerizable Substrate and Composition

Reactivity - Vinyl ethers > Epoxides

Epoxides: cycloaliphatic > linear aliphatic > glycidyl ethers > glycidyl esters

Functionality - tri > di > mono

Substrate thickness

Substrate absorption characteristics

Presence of fillers/pigments

Presence of chain transfer agents and inhibitors

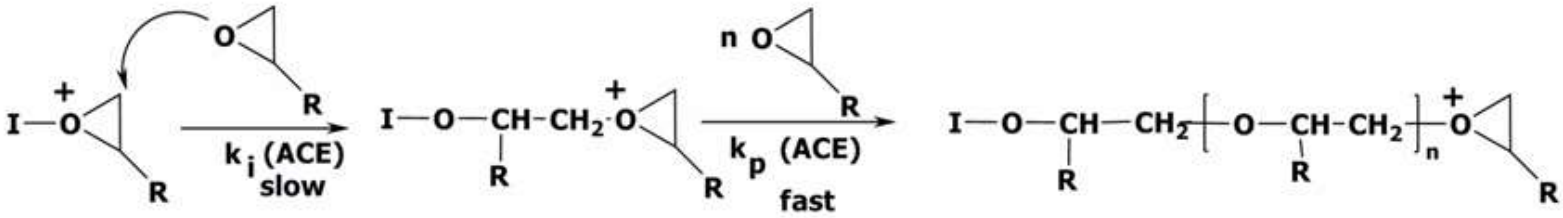
Environmental Parameters

Light intensity - determines no. of photons

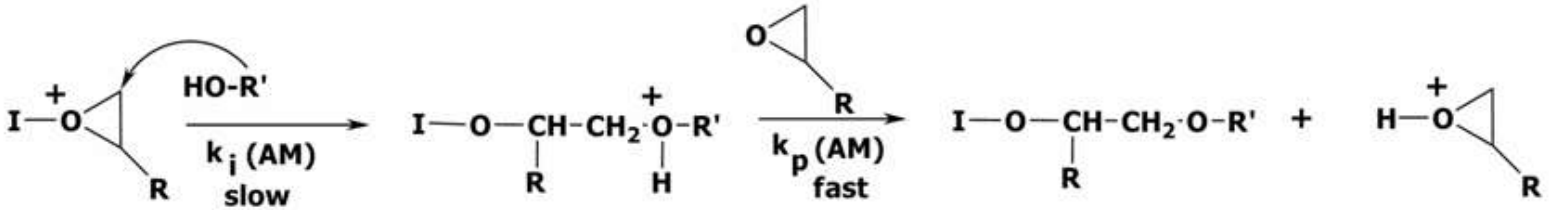
Emission wavelength - should be matched to photoinitiator

Substrate temperature - determines rate of postcure

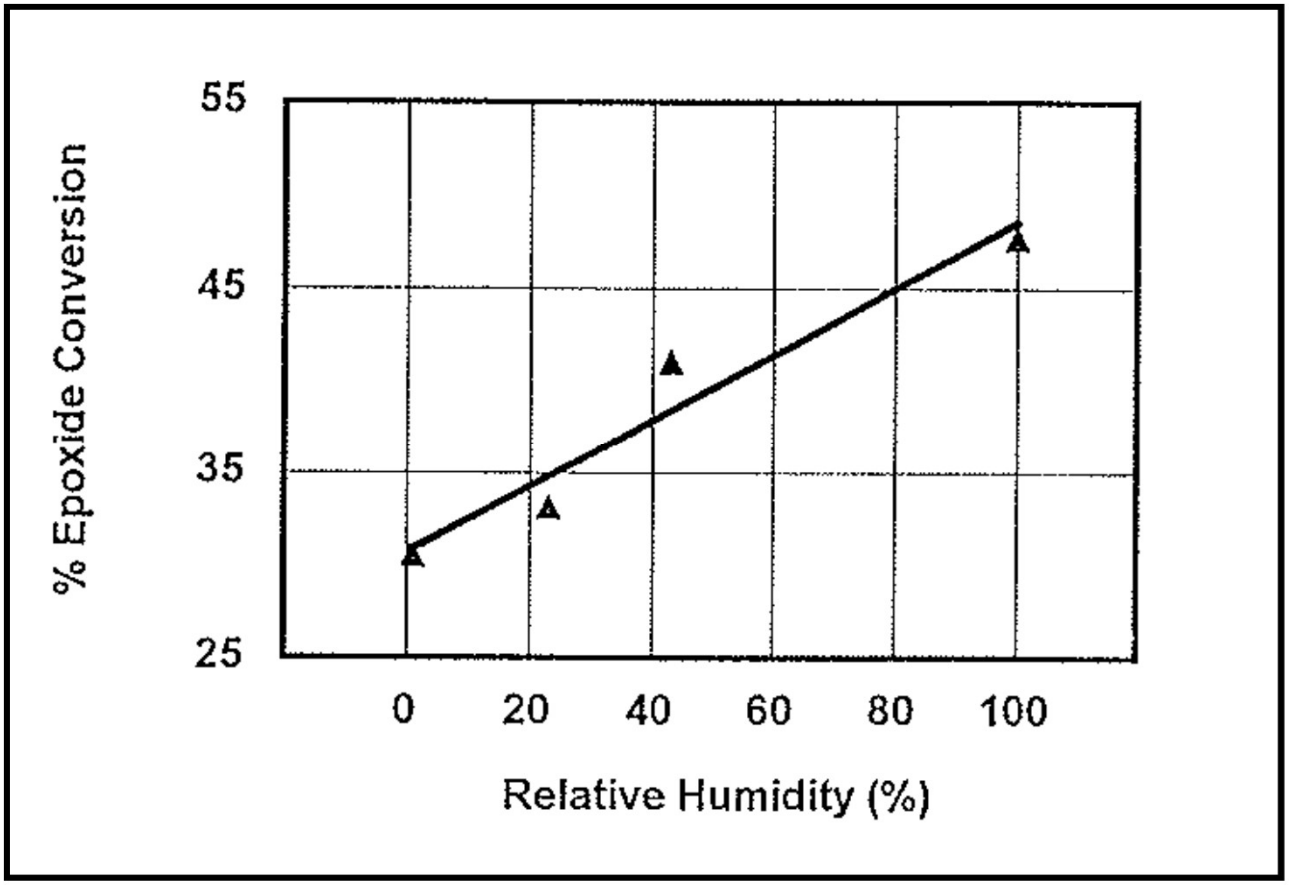
Activated chain end mechanism (ACE)

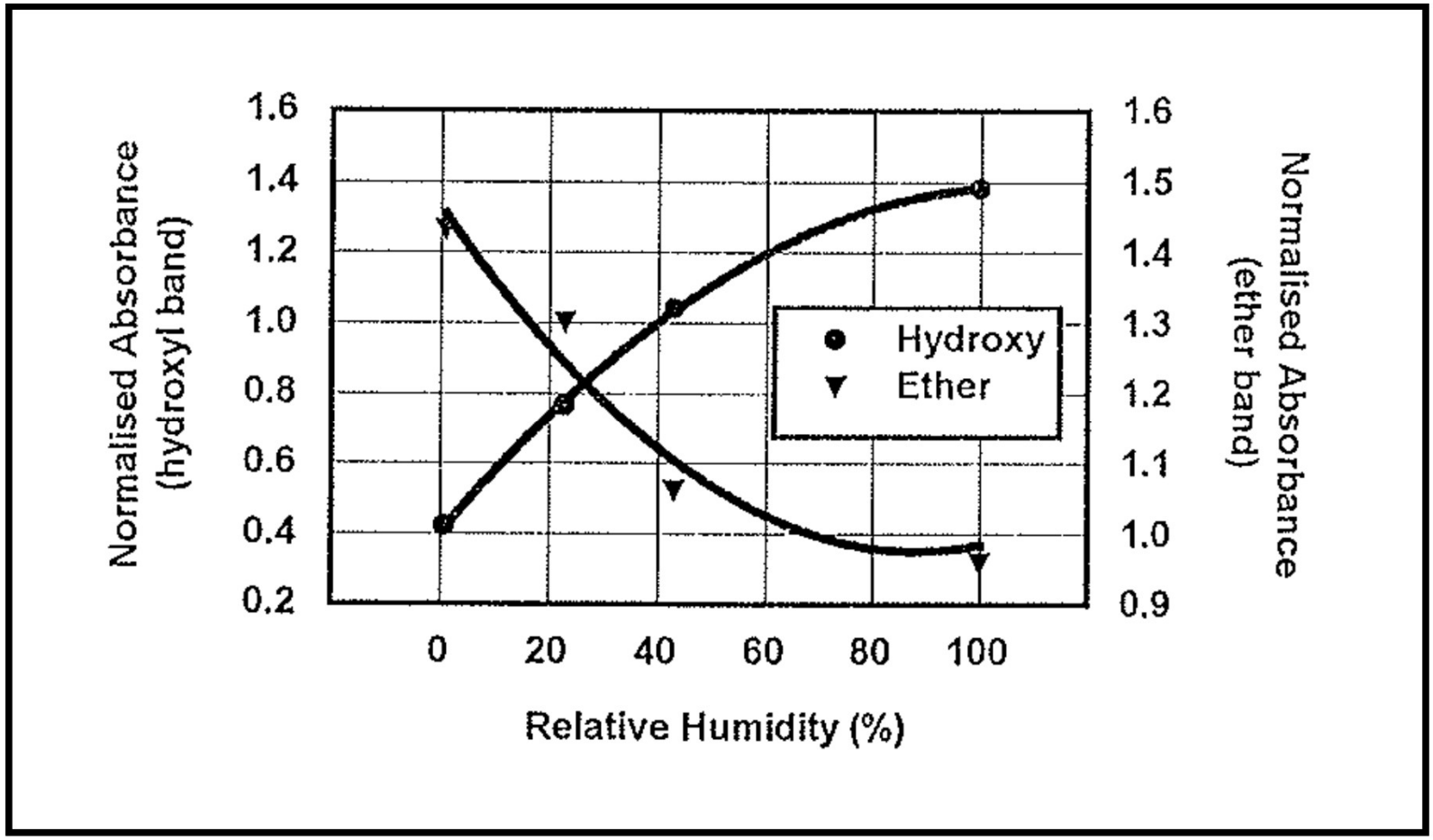


Activated monomer mechanism (AM)



Humidity effect on epoxy group conversion




Normalised Absorbance (hydroxyl band)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
20
40
60
80
100
Relative Humidity (%)
Hydroxy
Ether
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
Normalised Absorbance (ether band)