

NEW DEVELOPMENTS IN CATALYSIS

King Industries Inc.
Werner Blank
King Industries Inc.

WERNER J. BLANK
KING INDUSTRIES INC.

wblank@kingindustries.com

www.kingindustries.com

www.wernerblank.com



Phone 203-866-5551

FAX 203-855-5605

CATALYSTS FOR CROSSLINKING



MELAMINE

HIGH NH or HMMM



ISOCYANATE

FREE OR BLOCKED



EPOXY

COOH, OH,



SILOXANE

UV

FREE RADICAL

CATIONIC

OXIDATION

WHY ARE NEW CATALYSTS REQUIRED

BENEFITS OF CATALYSIS

ENVIRONMENTAL REGULATIONS

HEAVY METAL TOXICITY

NEW COATING SYSTEMS

POWDER, SLURRY, HIGH SOLIDS

NEW PERFORMANCE REQUIREMENTS

STABILITY-REACTIVITY

RESISTANCE PROPERTIES

MULTIPLE CURE MECHANISM

AVOID NEW CHEMICALS

ENERGY ISSUES

FASTER CURE, LOWER TEMPERATURE

CATALYSTS

RESIN SYNTHESIS

POLYESTER-ALKYD

ACRYLIC

POLYURETHANE

EPOXY

POLYETHER

CROSSLINKING

CATALYSTS FOR CROSSLINKING

CROSSLINKER

MELAMINE

ISOCYANATE (BL)

EPOXY

SILOXANE

UV

FREE RADICAL

CATIONIC

OXIDATION

FUNCTIONAL

HYDROXYL

WATER

CARBOXYL / ANHYDRIDE

AMINE

ACTIVE HYDROGEN

AMIDE

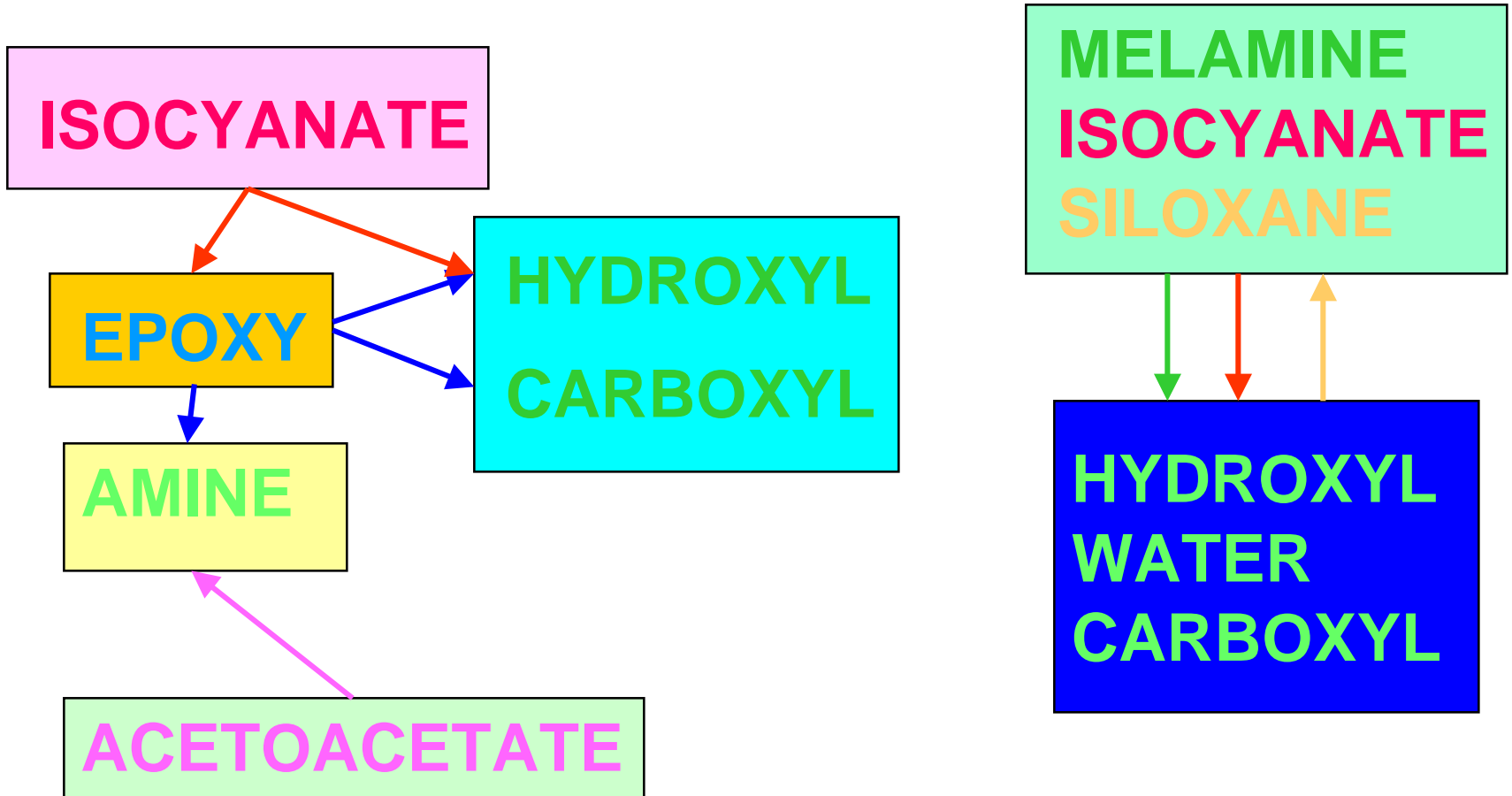
CARBAMATE

URETHANE

ACETOACETATE

UNSATURATION

COMBINATION CROSSLINKING



COATING SYSTEMS

SOLVENT BORNE

**REGULAR
HIGH SOLIDS
SOLVENT-FREE**

WATER-BORNE

**SOLUTION
EMULSIONS
APPLICATION**

POWDER

**SOLID
SLURRY**

Crosslinking Creation of networks

+

-

solvent resistance

elongation

hardness

flexibility

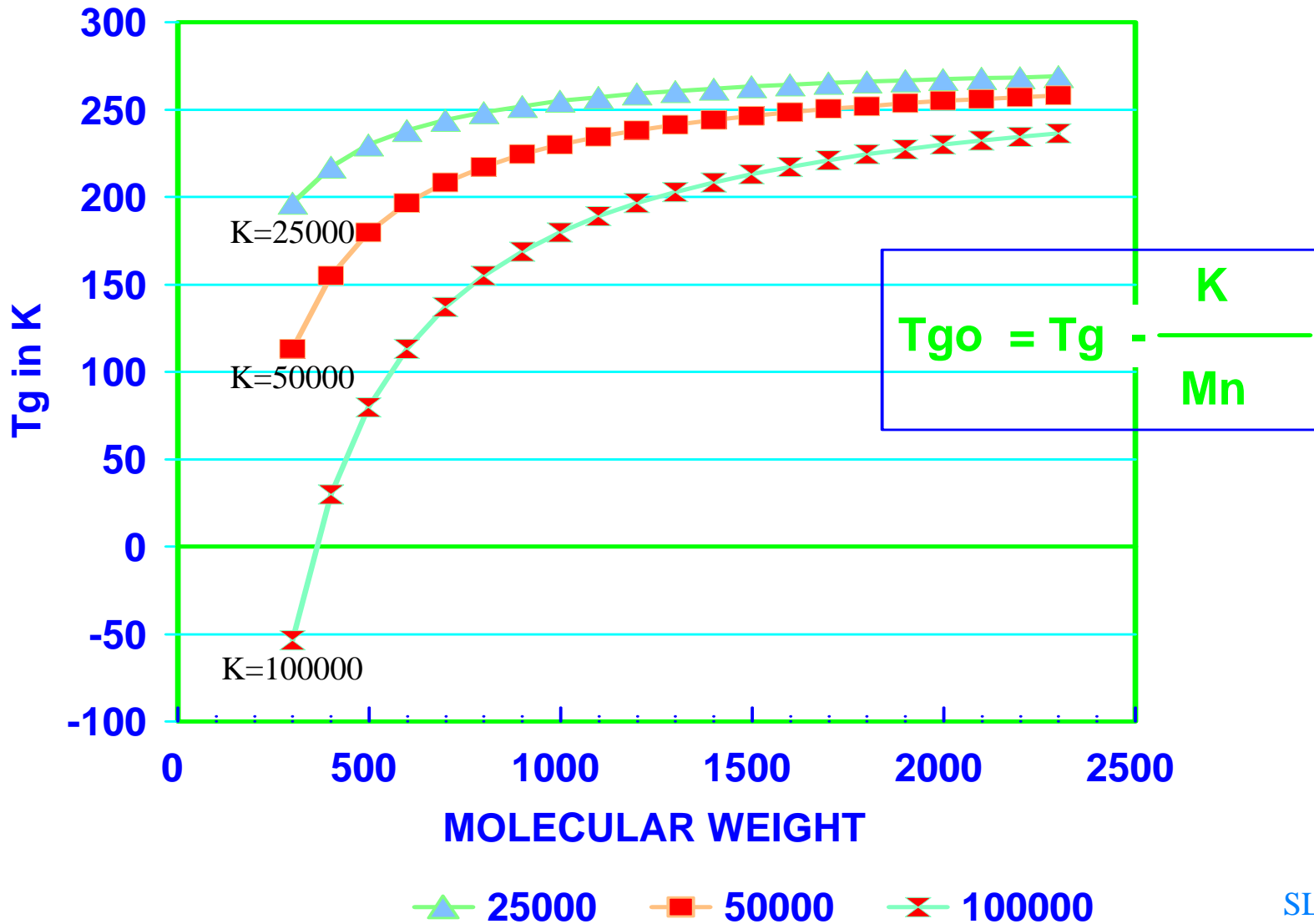
chemical resistance

durability

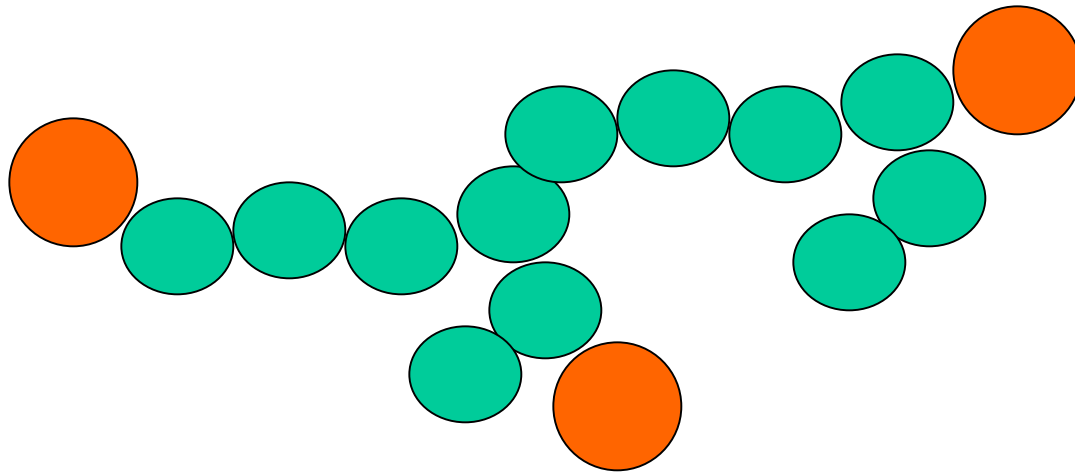
flexibility

T_g

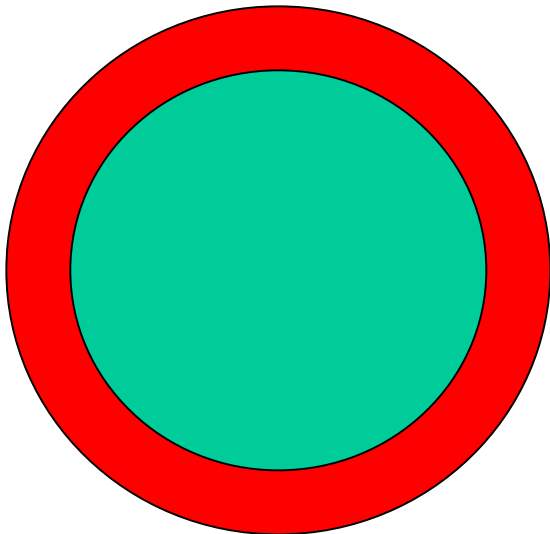
Tg vs MOLECULAR WEIGHT OF OLIGOMERS



Waterborne Coatings



Soluble



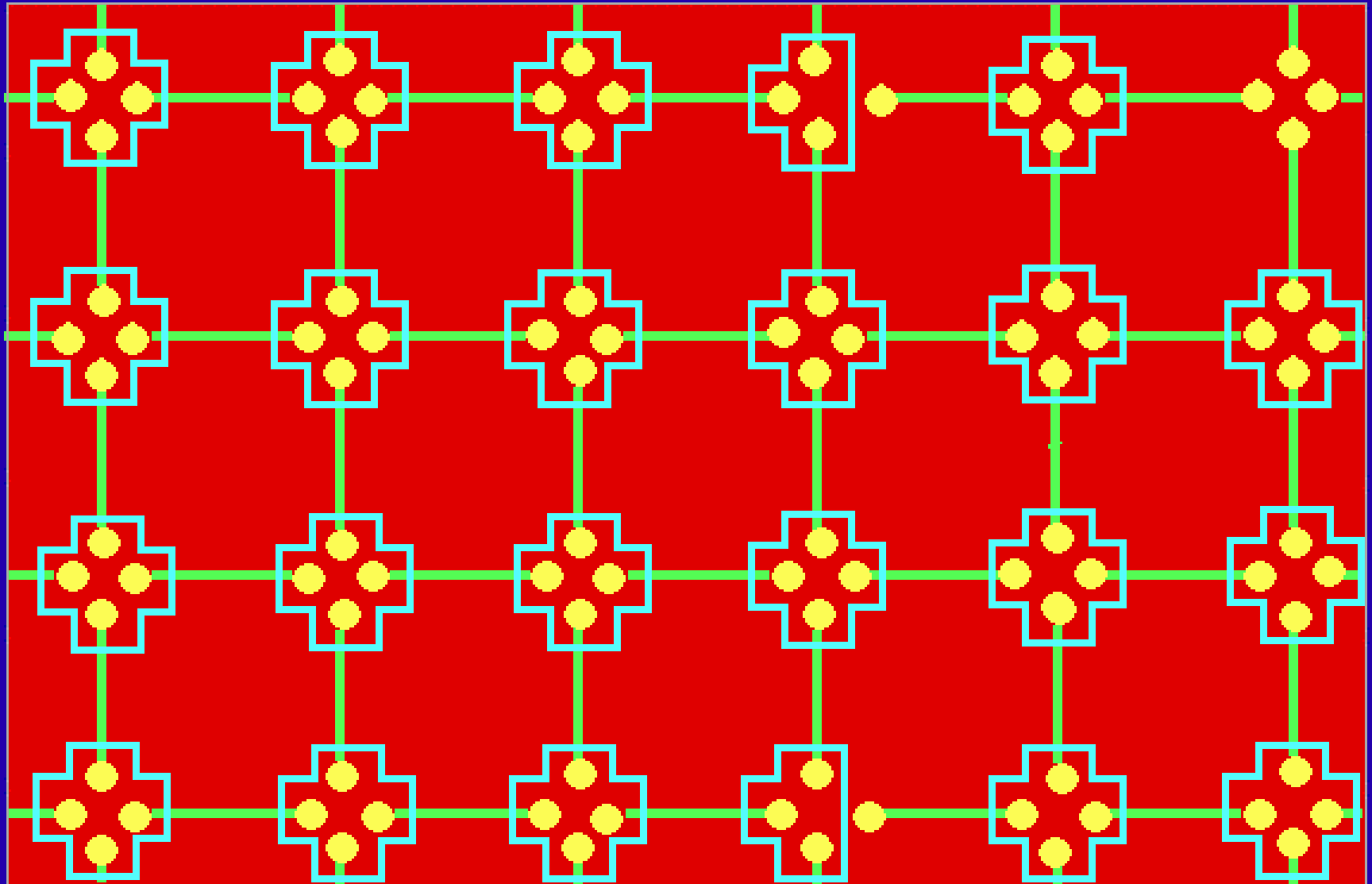
Dispersion

Waterborne coatings

	Acid number	Appearance
Soluble	50 - 200	Clear
Colloid	20 - 50	Turbid
Dispersion	0 - 20	White

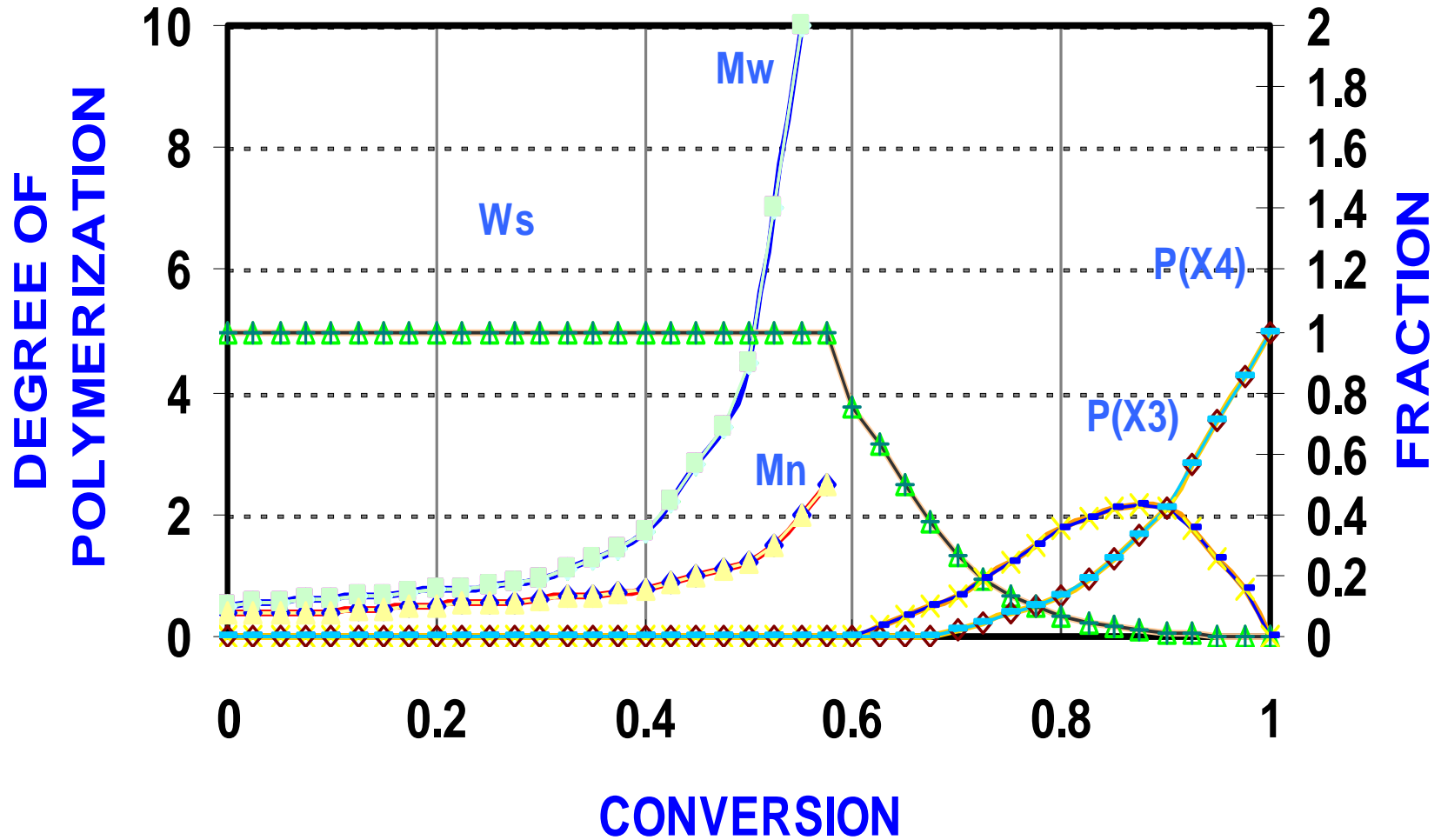
CROSSLINKED NETWORK

TETRAFUNCTIONAL CROSSLINKER

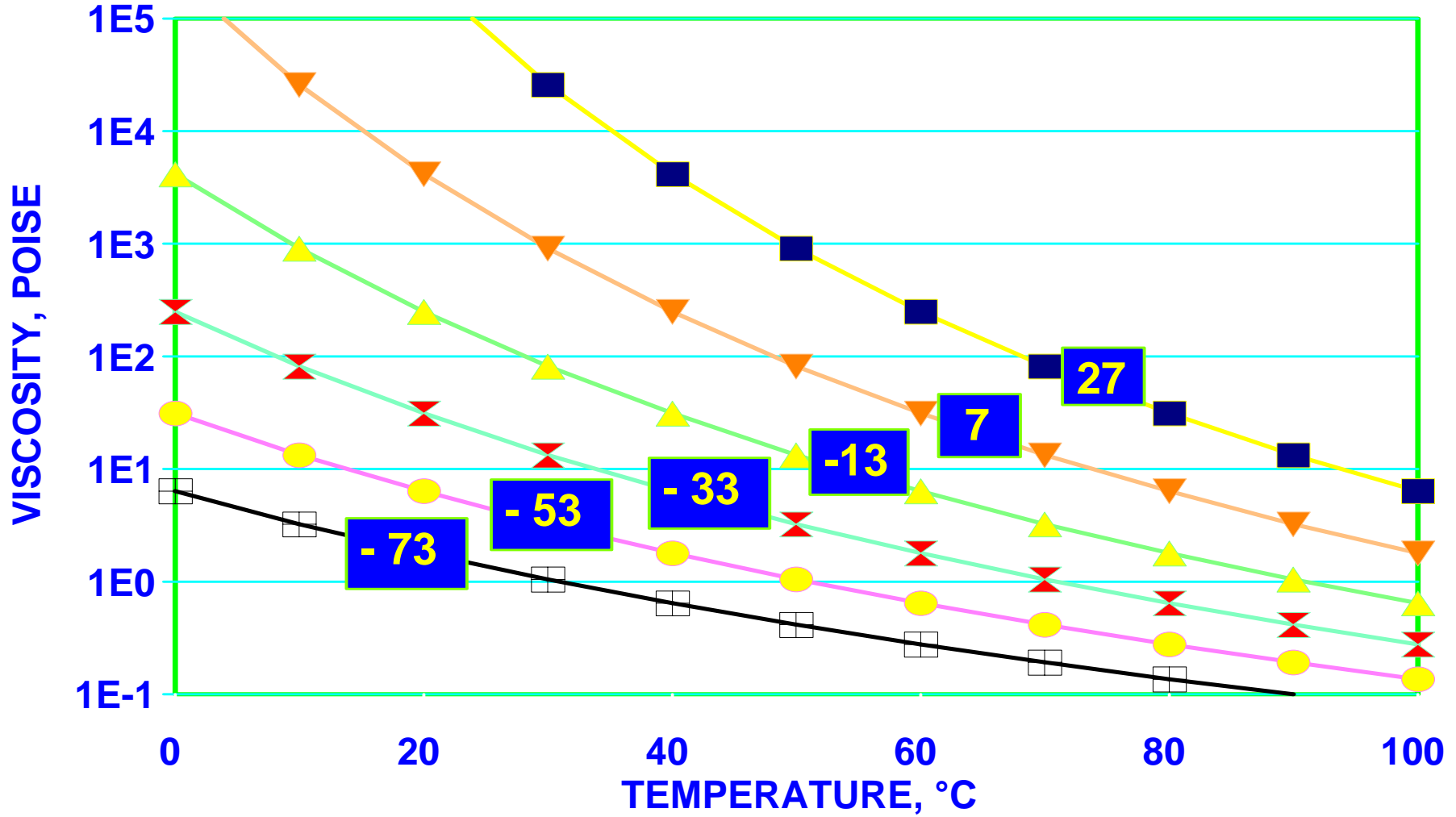


NETWORK FORMATION

A4 + B2



VISCOSITY as a FUNCTION OF T_g, WLF EQUATION



CATALYST PROPERTIES

POTLIFE / REACTIVITY

SELECTIVITY

DELAYED ACTION

LOW TEMPERATURE

HIGH TEMPERATURE

WATER

HIGH RATE (RIM)

EXTERIOR DURABILITY

RESISTANCE PROPERTIES

ENVIRONMENT - TOXICITY

ACTIVATION OF CATALYST



TRIGGER



HEAT

MOISTURE

UV RADIATION

OXIDATION

EQUILIBRIUM

MIXING

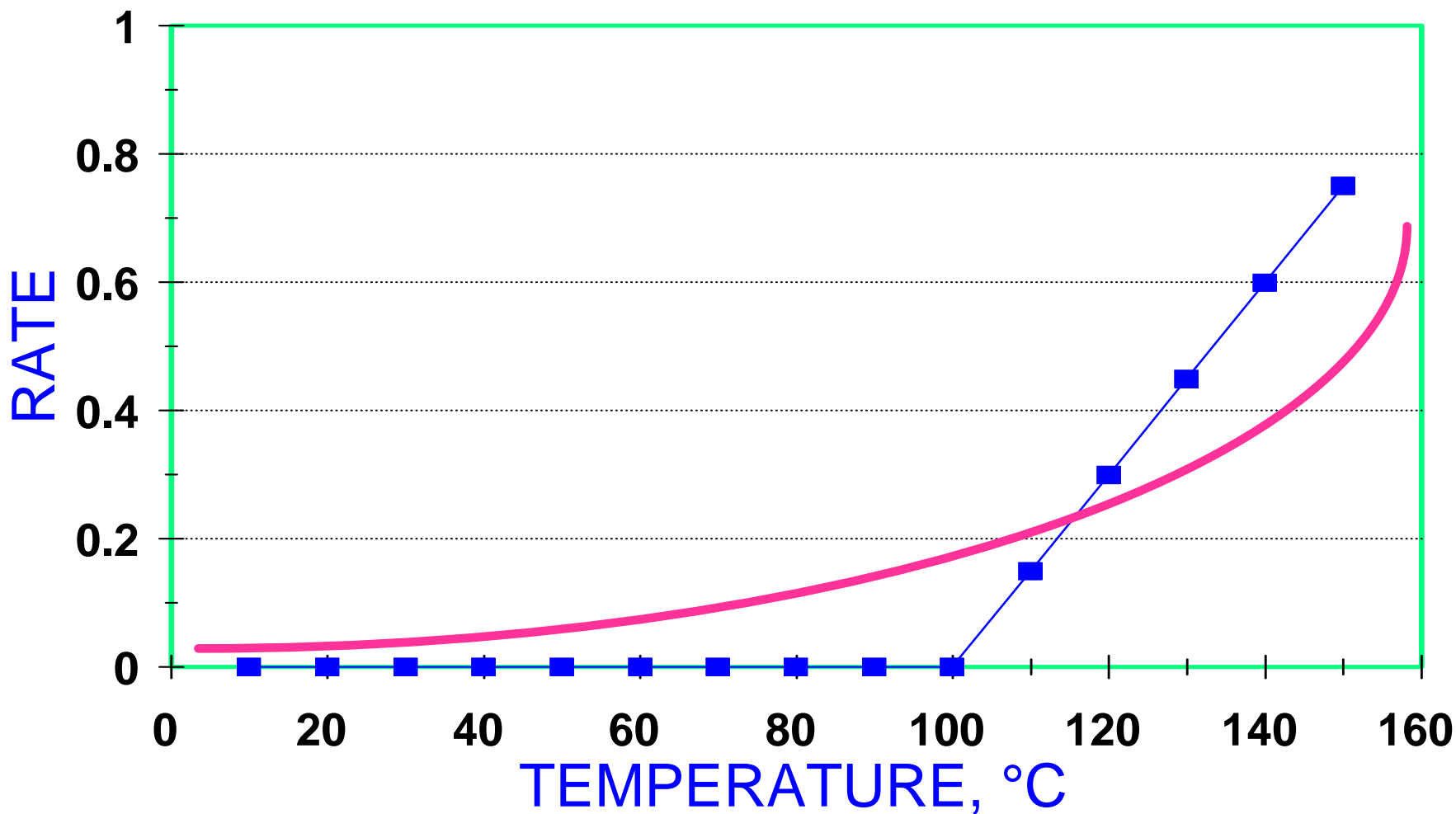
**POTLIFE
STABILITY**



**X-LINKING
REACTION**

REACTION RATES

AS A FUNCTION OF TEMPERATURE



CATALYSTS FOR ISOCYANATES

ENVIRONMENTALLY ACCEPTABLE CATALYSTS

REACTION RATE OF CATALYSTS WITH OH

SELECTIVE CATALYSTS FOR OH

IMPROVED POTLIFE/REACTIVITY

REDUCED WATER REACTION

CATALYSTS USED

DIBUTYLTIN DILAURATE / DIACETATE

DIBUTYLTIN OXIDE

MERCURY COMPOUNDS

LEAD COMPOUNDS

AMINES

ZINC SALTS

MANGANESE SALTS

SCREENING OF CATALYSTS

APPLICATION TESTS FORMULATION

POTLIFE (2X VISC.)

GEL TIME

TACK FREE

DRY-THROUGH

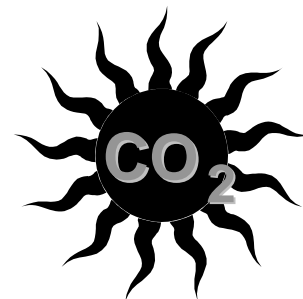
MODEL SYSTEMS (ANALYTICAL)

DISAPPEARANCE OF NCO

FORMATION OF URETHANE / UREA

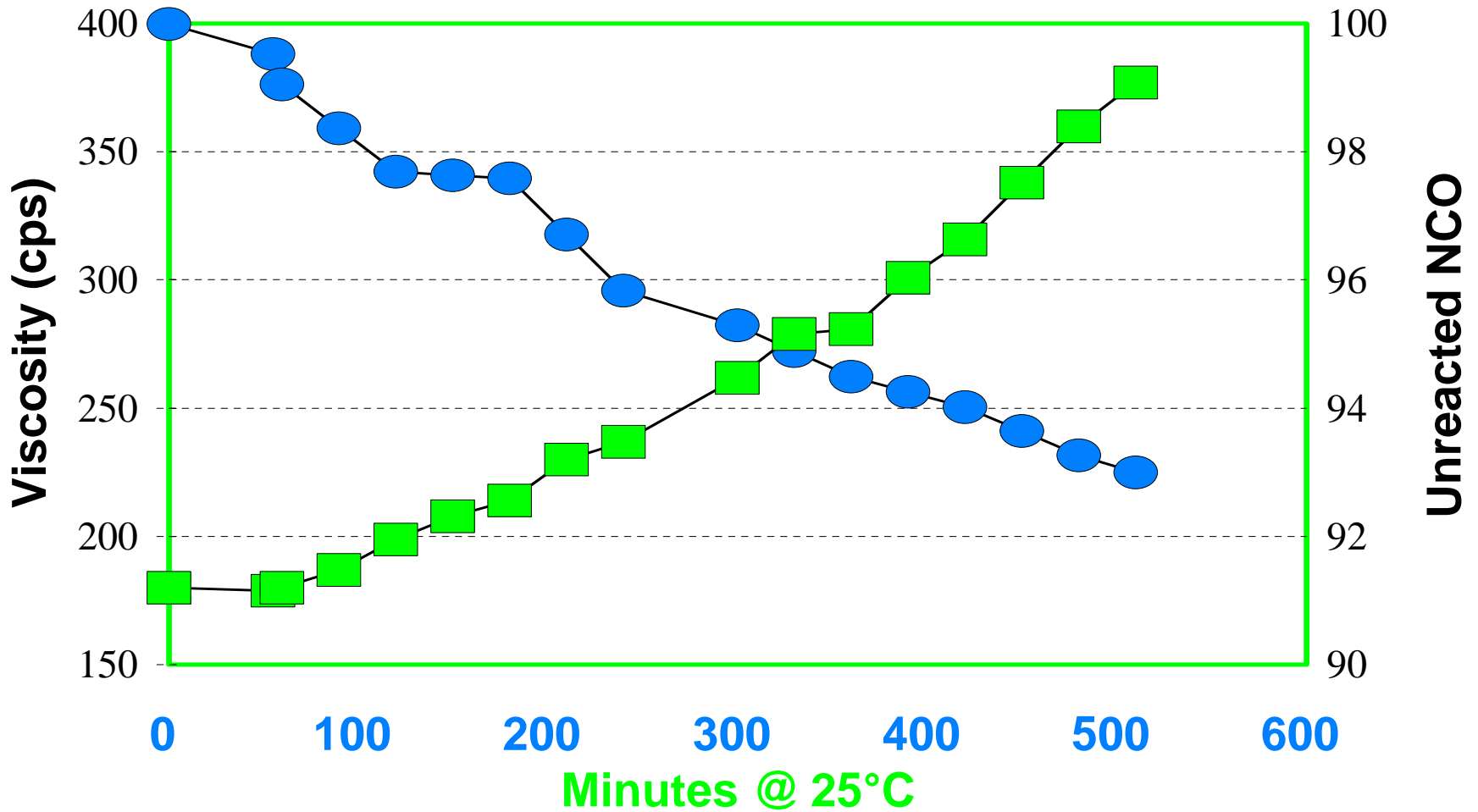
MW

Isocyanate-Hydroxyl Reactions



PE/HDI-TRIMER

No Catalyst



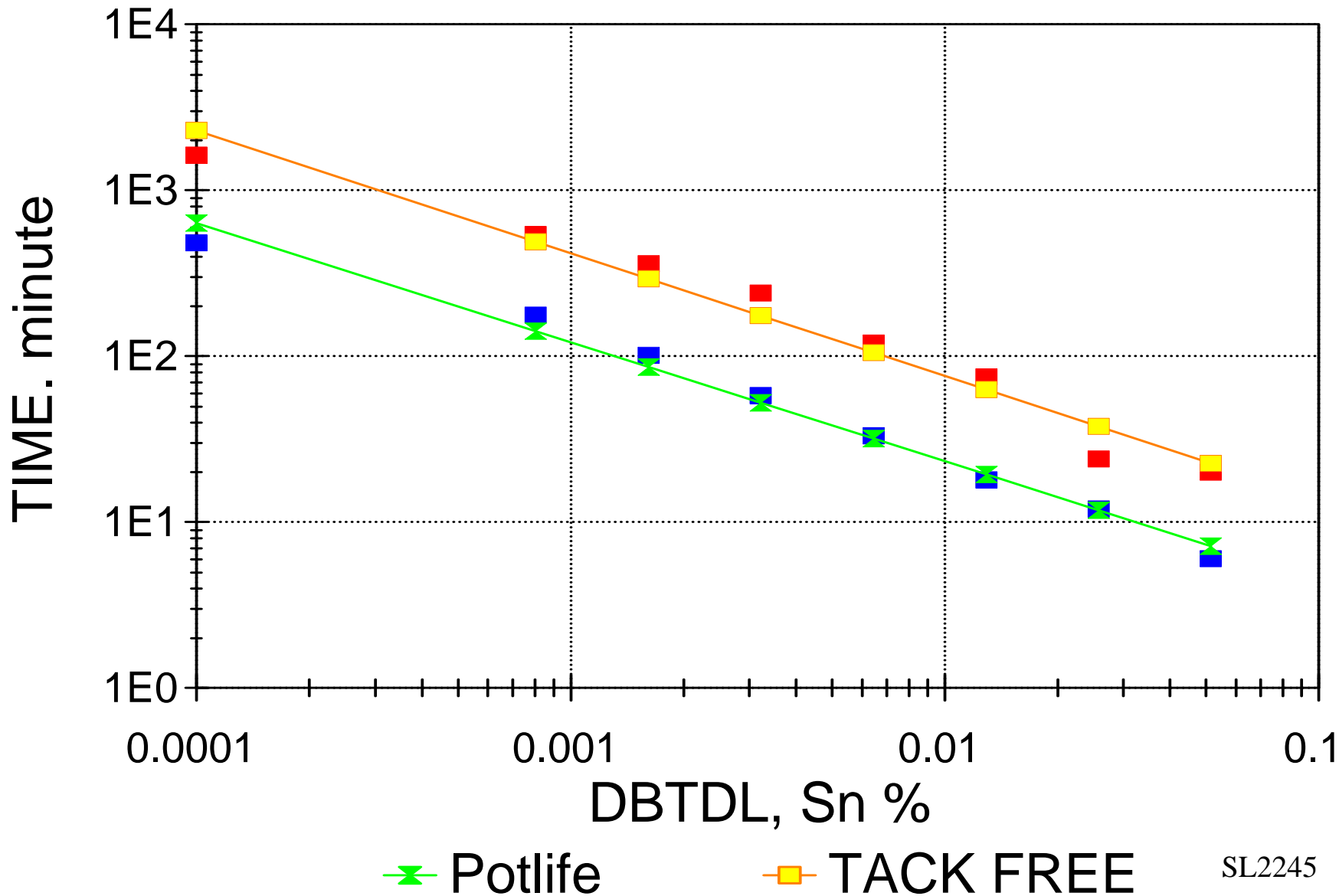
● % NCO

■ VISCOSITY

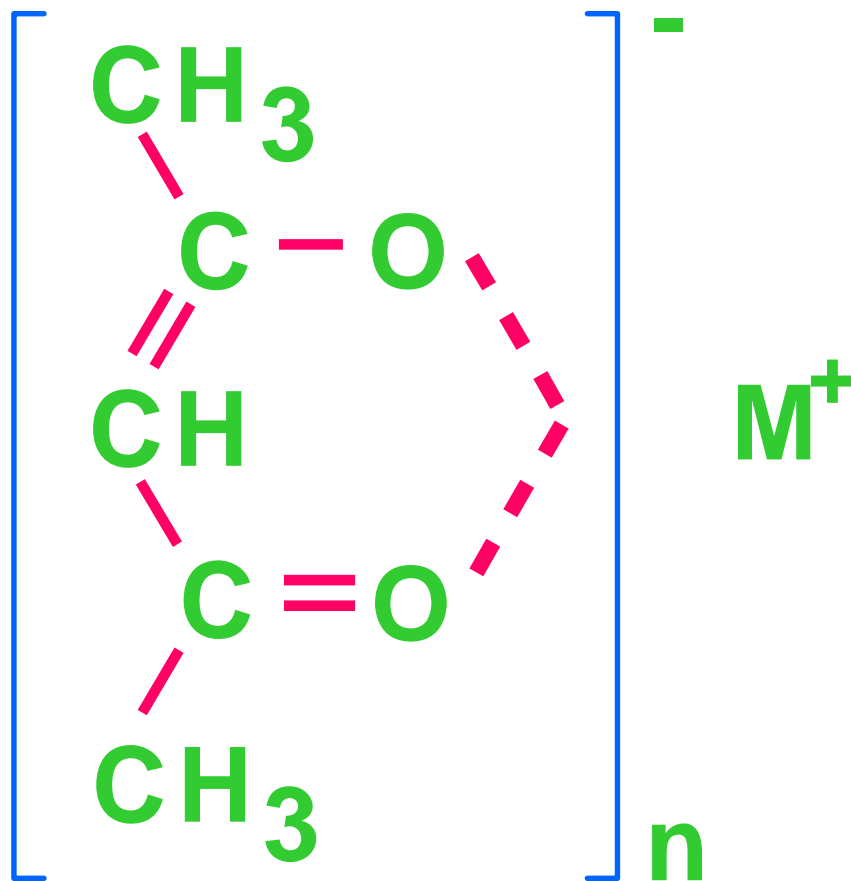
SL2017

PE/HDI-TRIMER

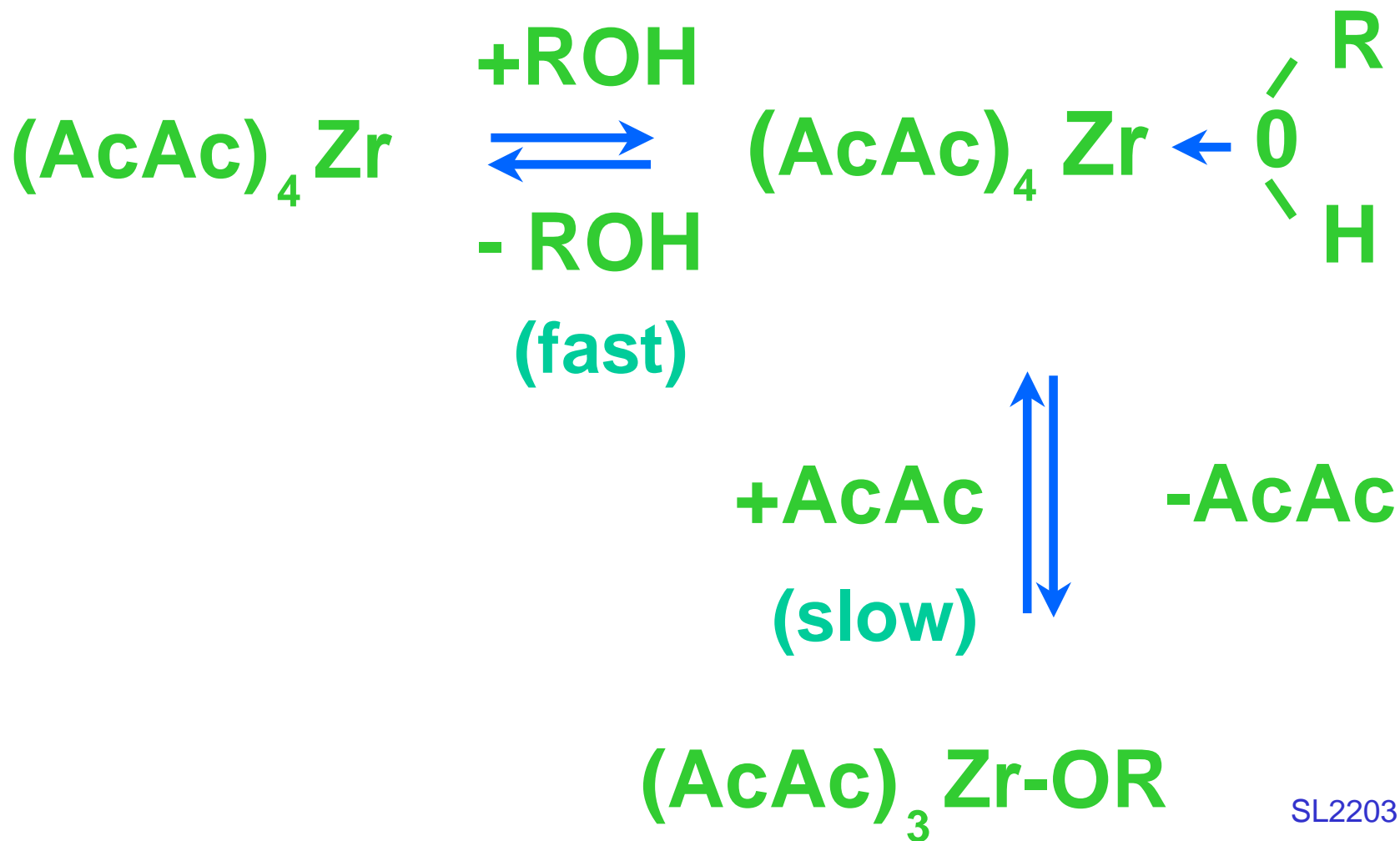
CATALYST REACTION RATE



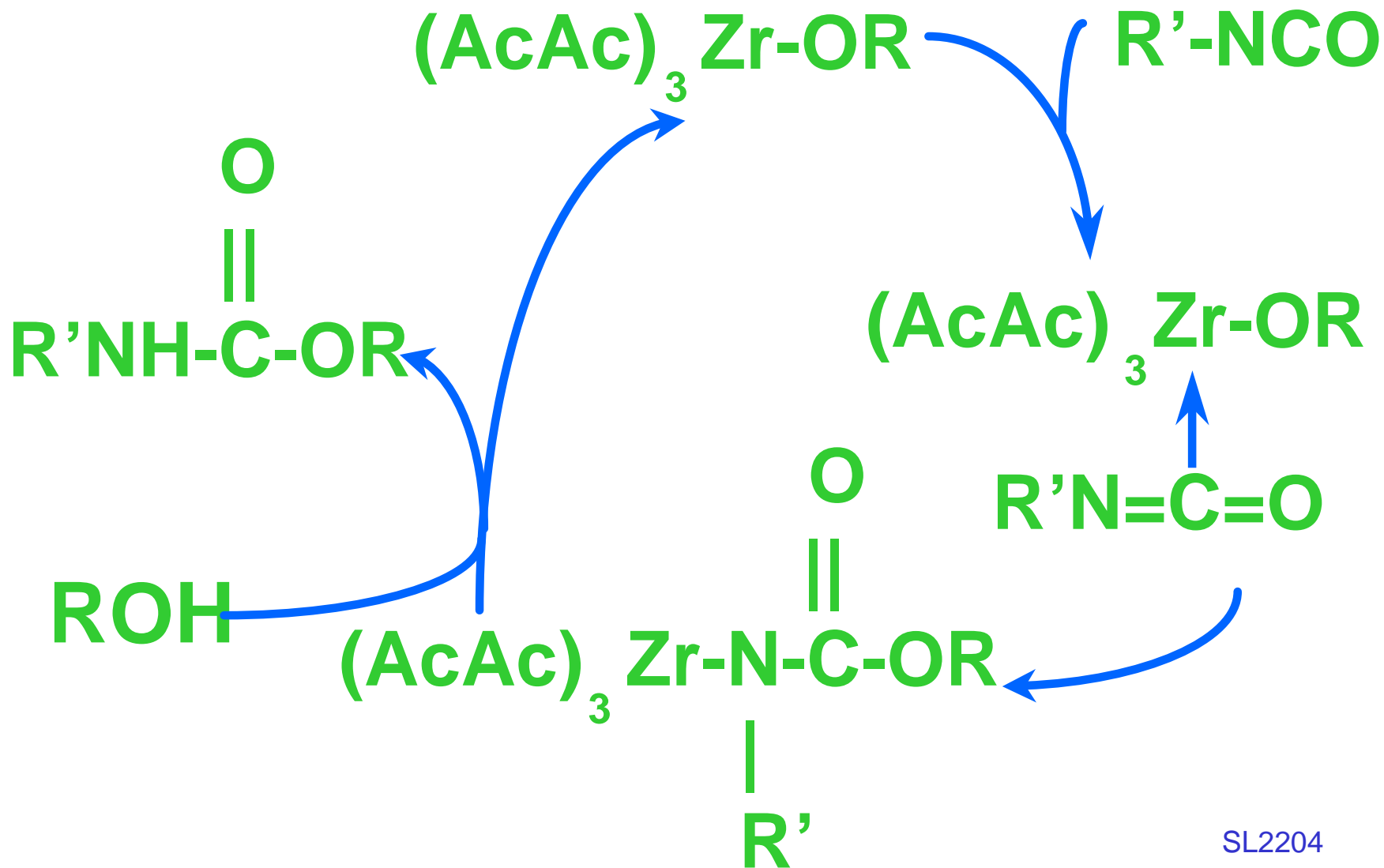
Metal Chelate with 2,4-PD



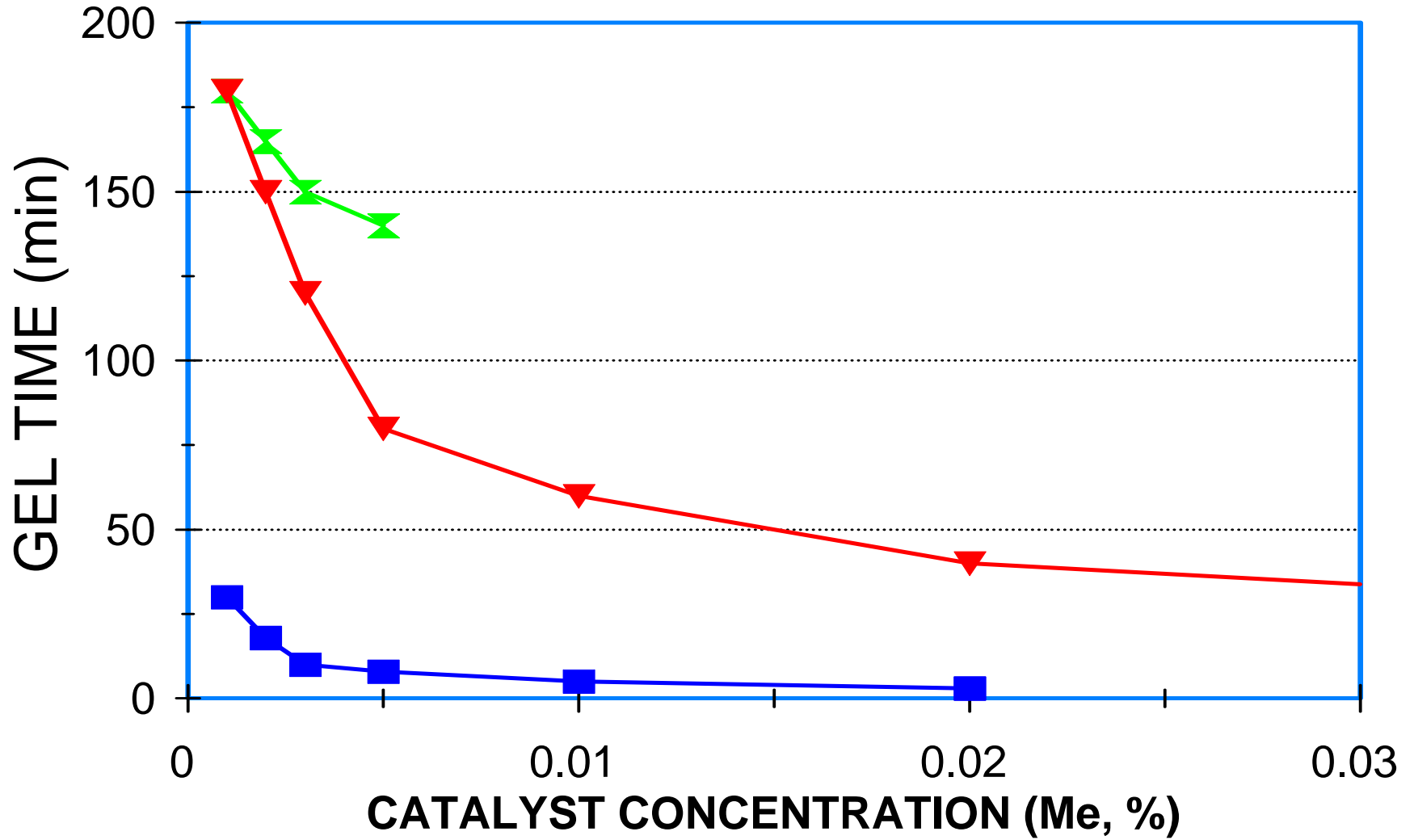
ZIRCONIUM CHELATE CATALYSIS



ZIRCONIUM CHELATE CATALYSIS

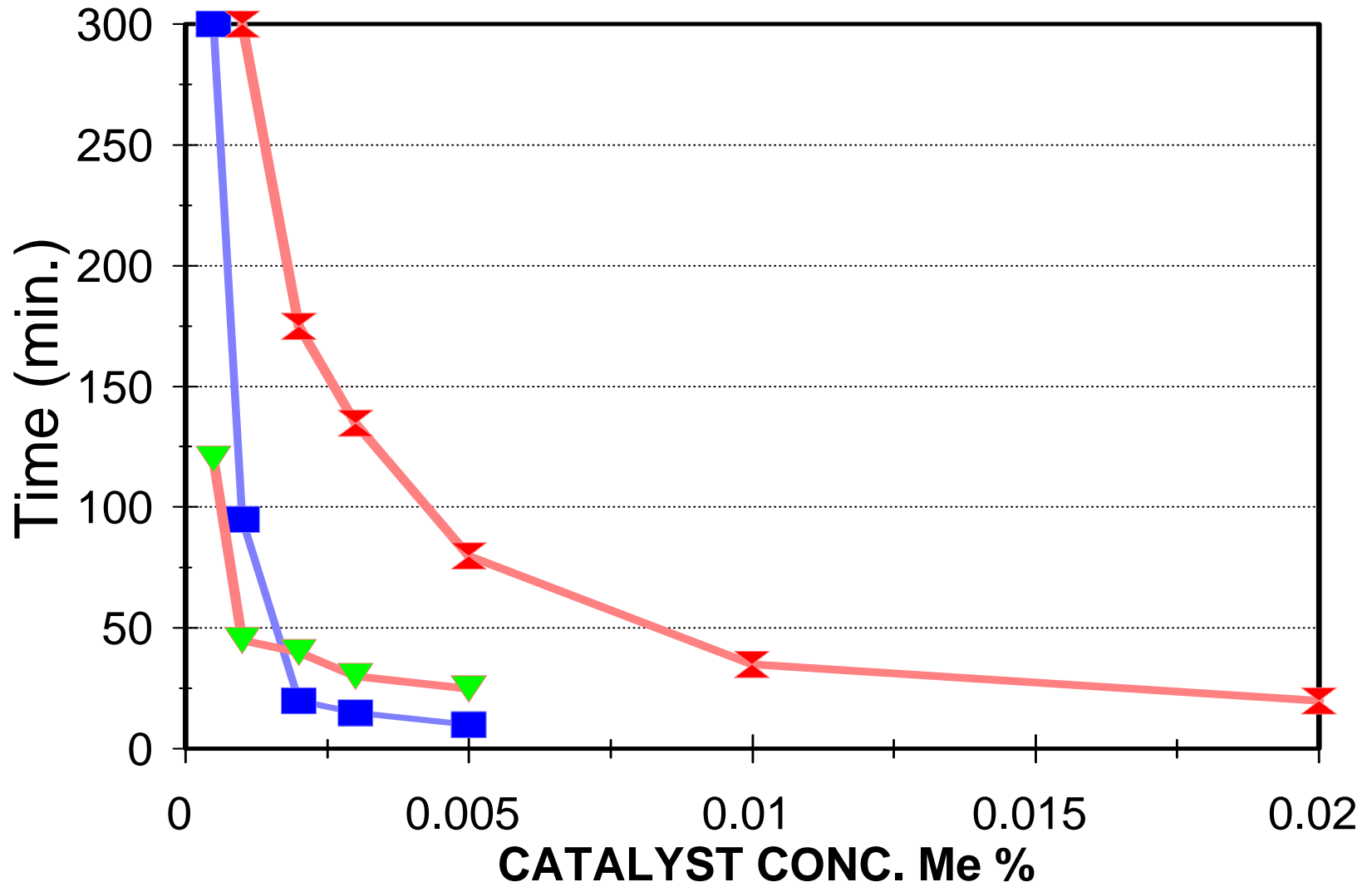


GEL TIME ACRYLIC/HDI-TIMER



■ XC-6212 × XC-4205 ▼ DBTDL

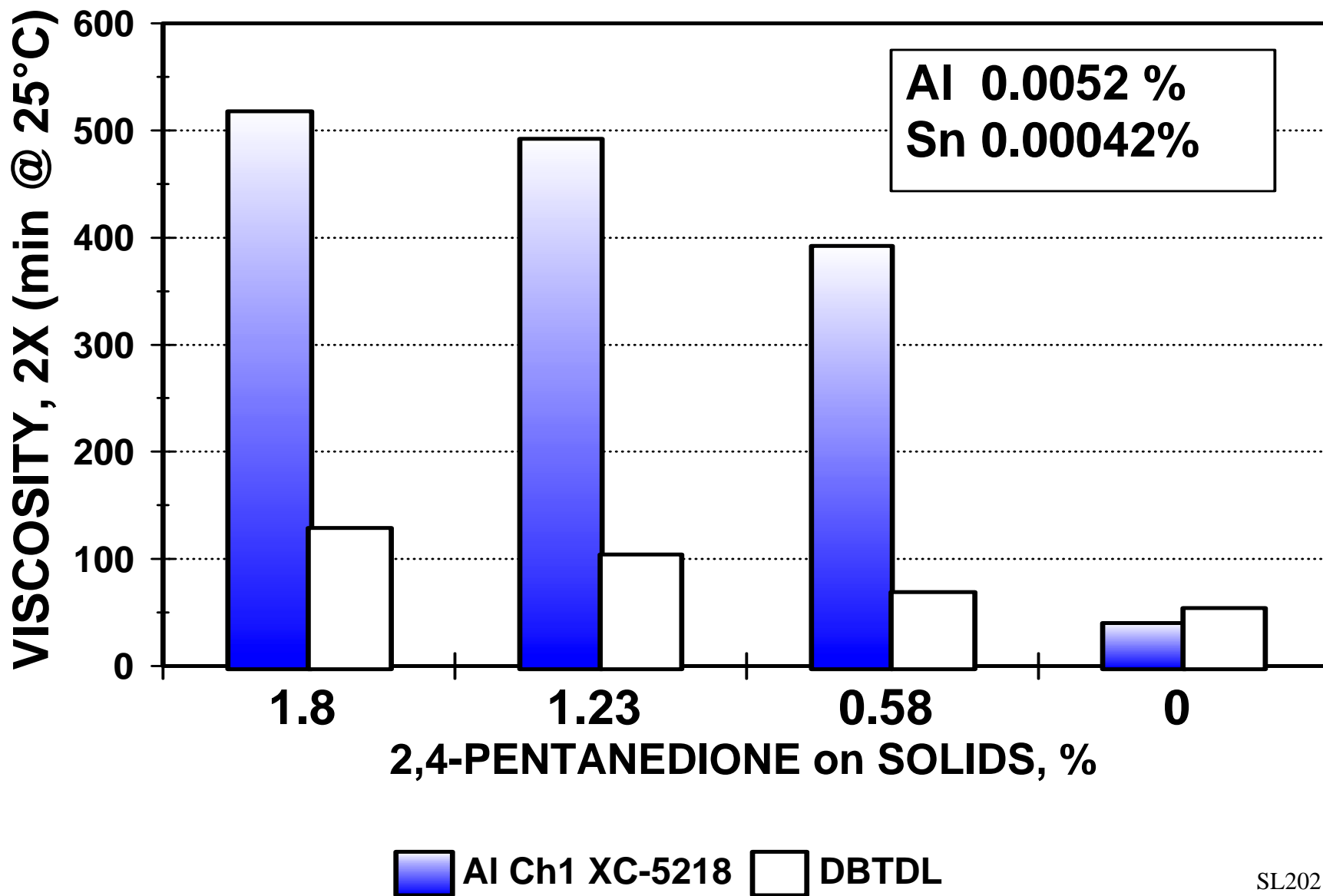
Tack Free time



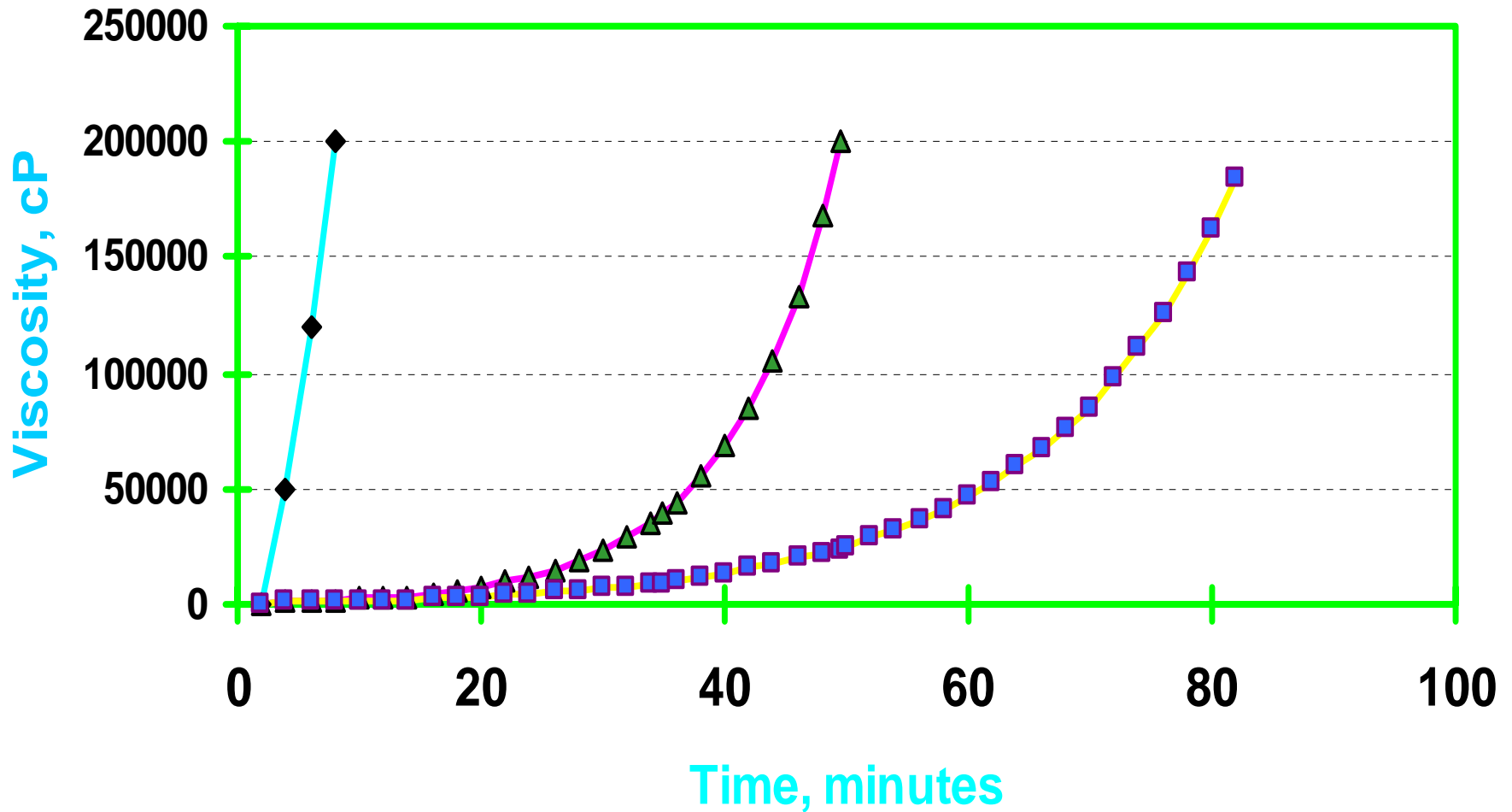
■ Zr B XC6212 ▼ Zr A XC4205 × DBTDL

POLYESTER/HDI-TRIMER

TACK FREE TIME 3.0-4.0 HOURS



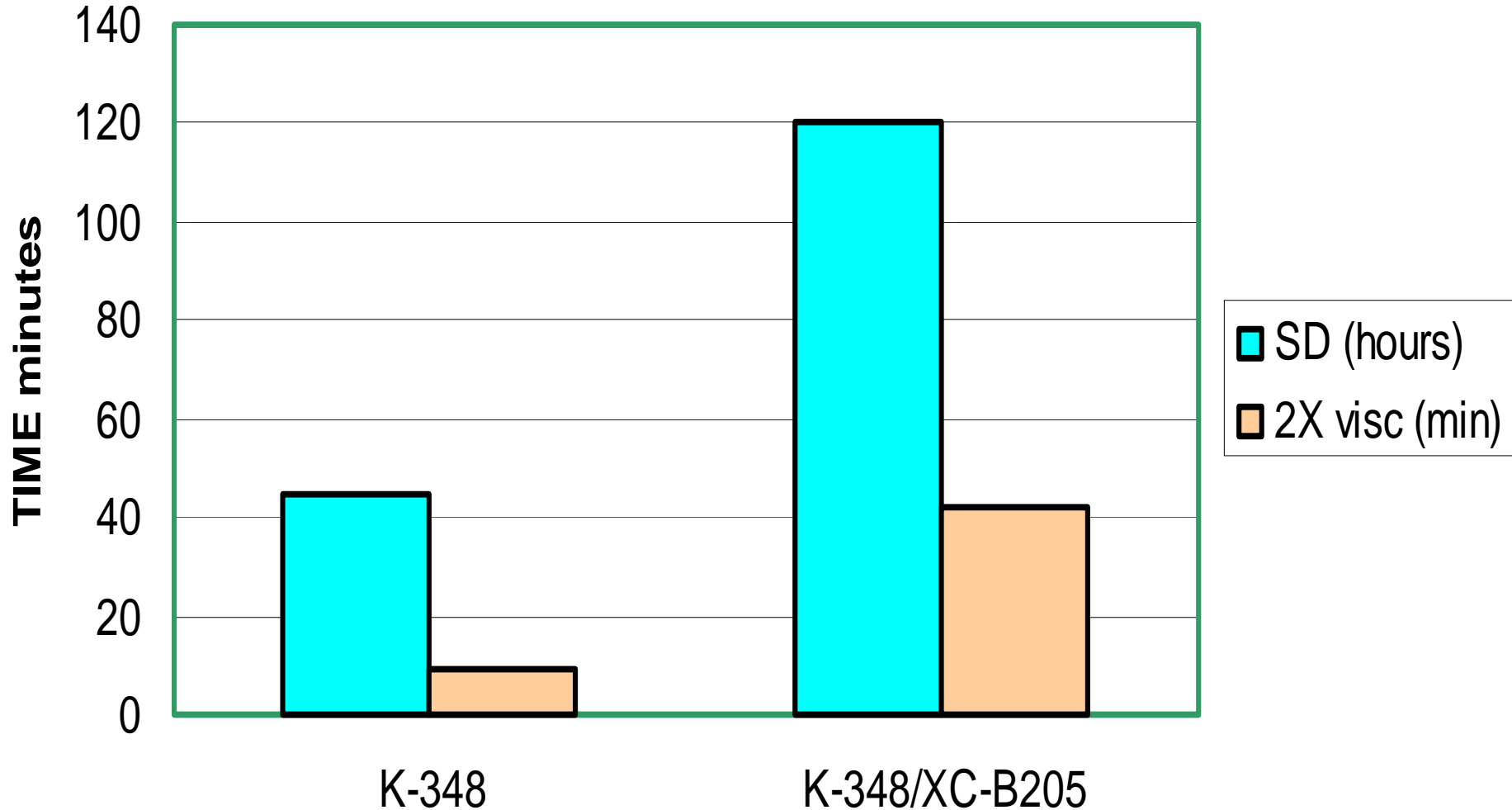
Polyether MDI Elastomer Bi Oct. 1/5 mol WATER



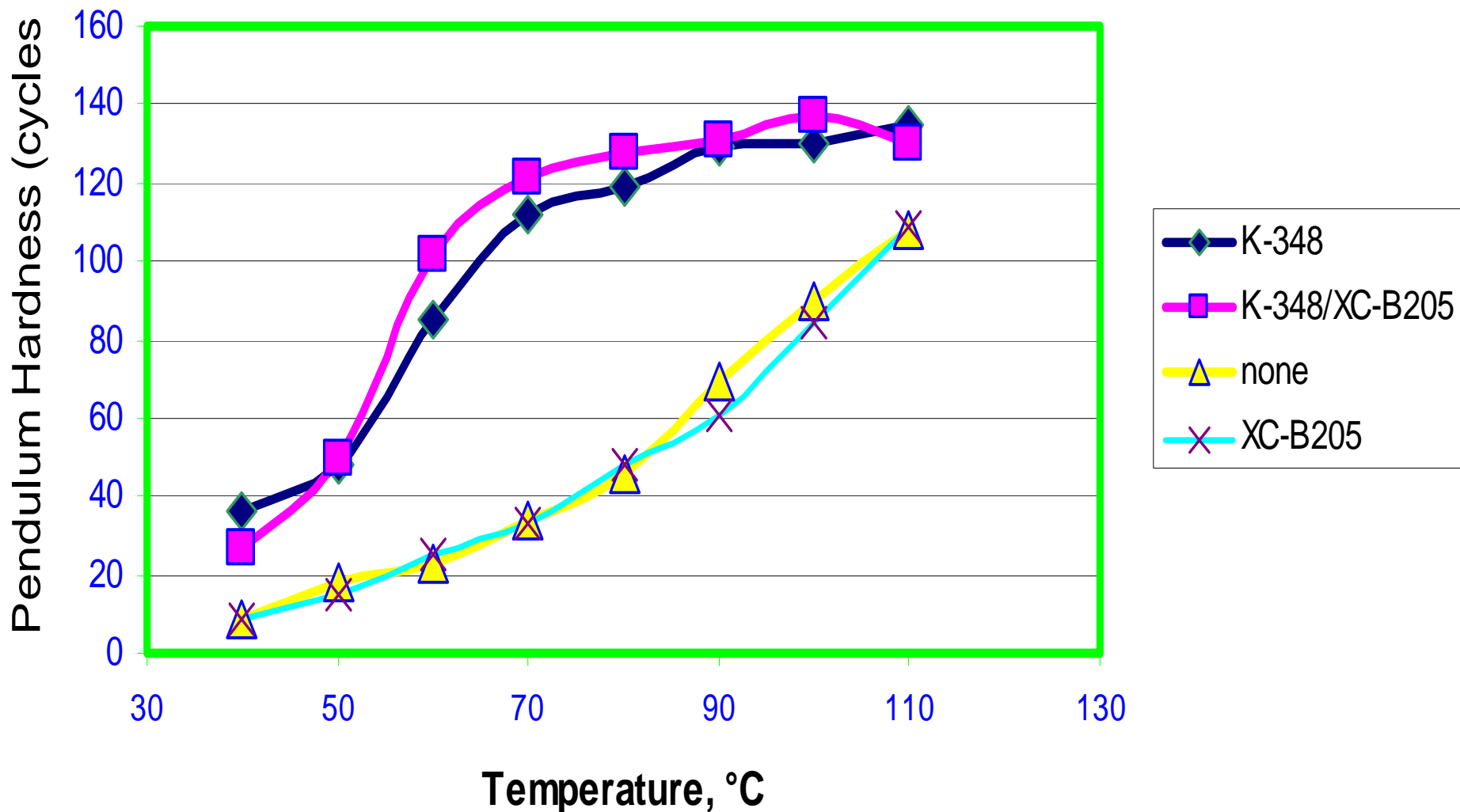
◆ Bi Oct. Initial ▲ Bi Oct. 2 days ■ Bi Oct. 7 days

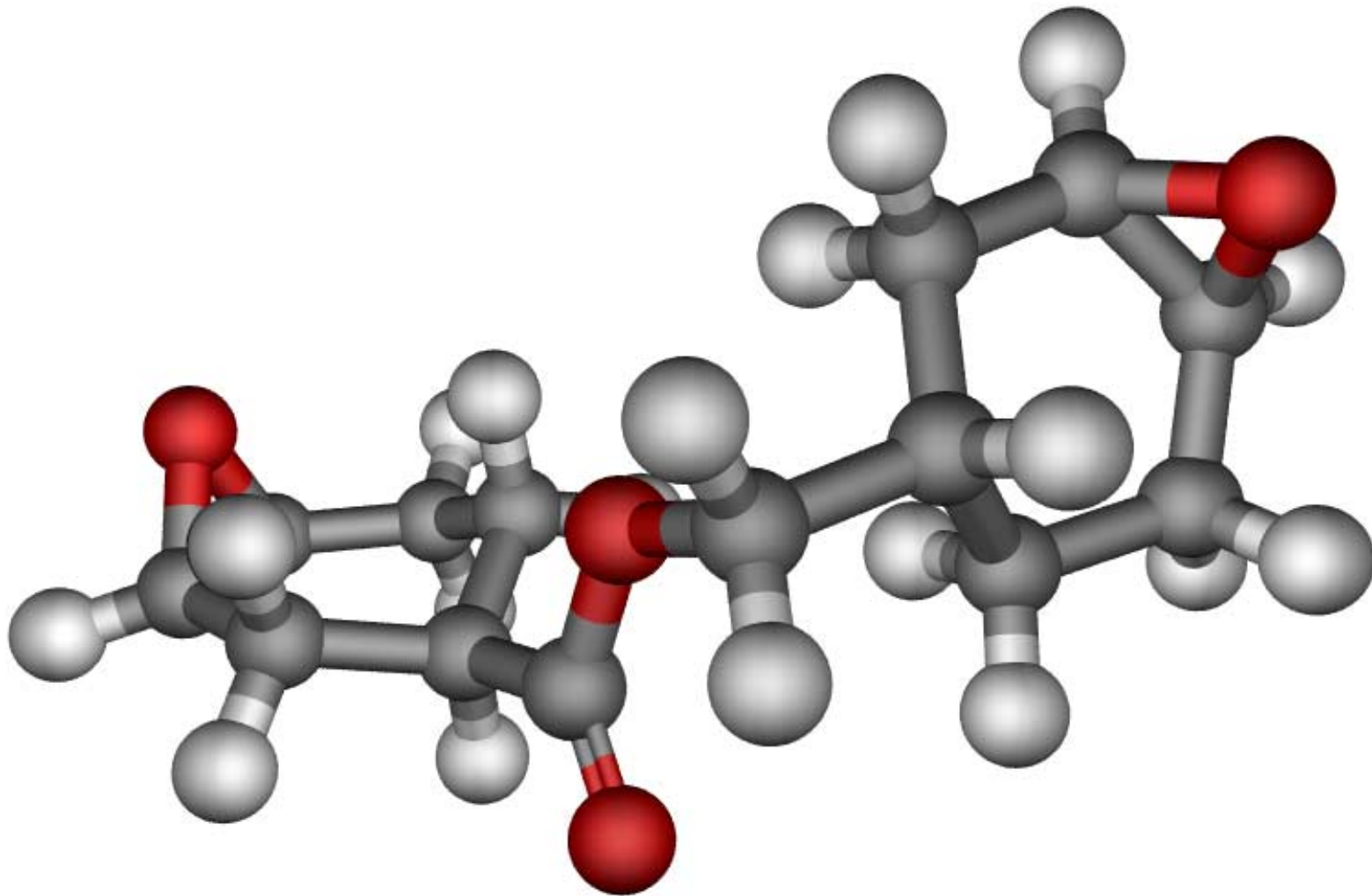
ACRYLIC/HDI-TRIMER

Dry Time/Pot Life at 25°C



Acrylic/HDI-Trimer 2K Potlife Extender Pendulum Hardness, 15 Minute Cure

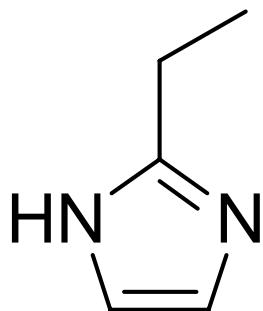




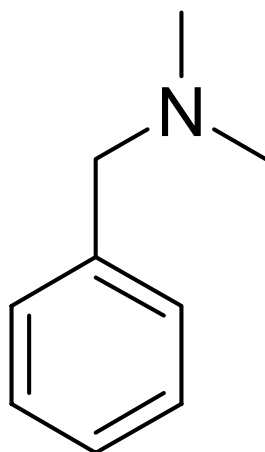
Epoxy Catalysts

for Thermal Cure Epoxy Based Systems

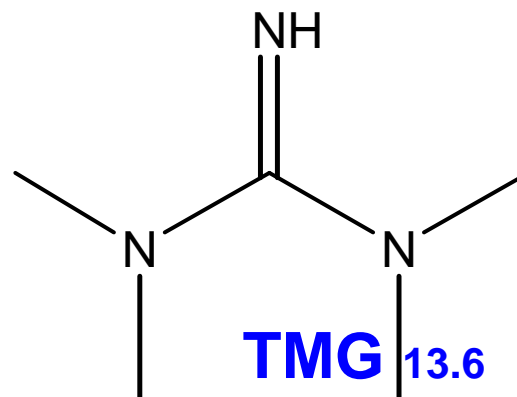
AMINE CATALYST USED IN THIS STUDY



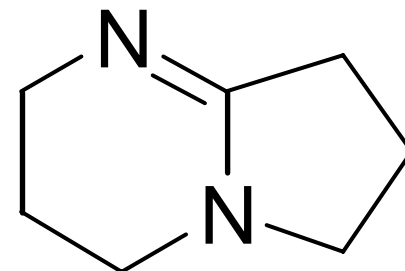
2E-IMID 7.0



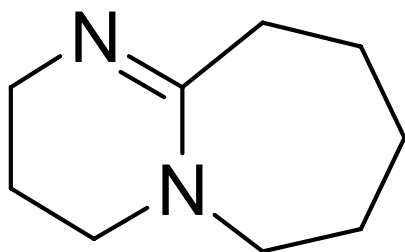
DMBA 8.8



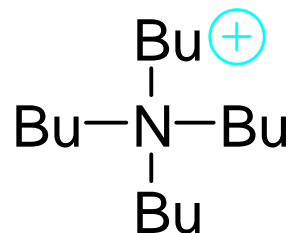
TMG 13.6



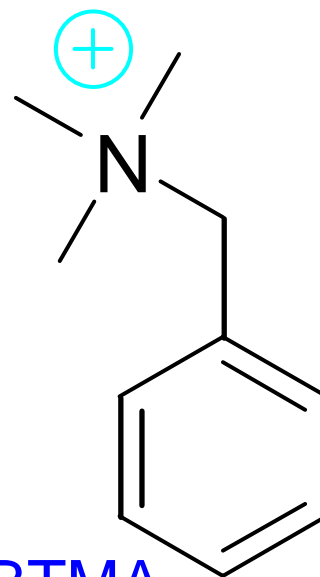
DBN 13.1



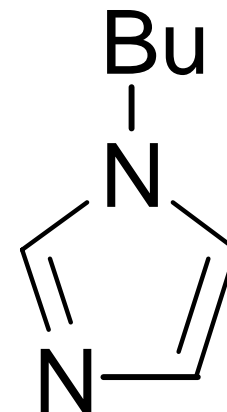
DBU 12.8



TBA

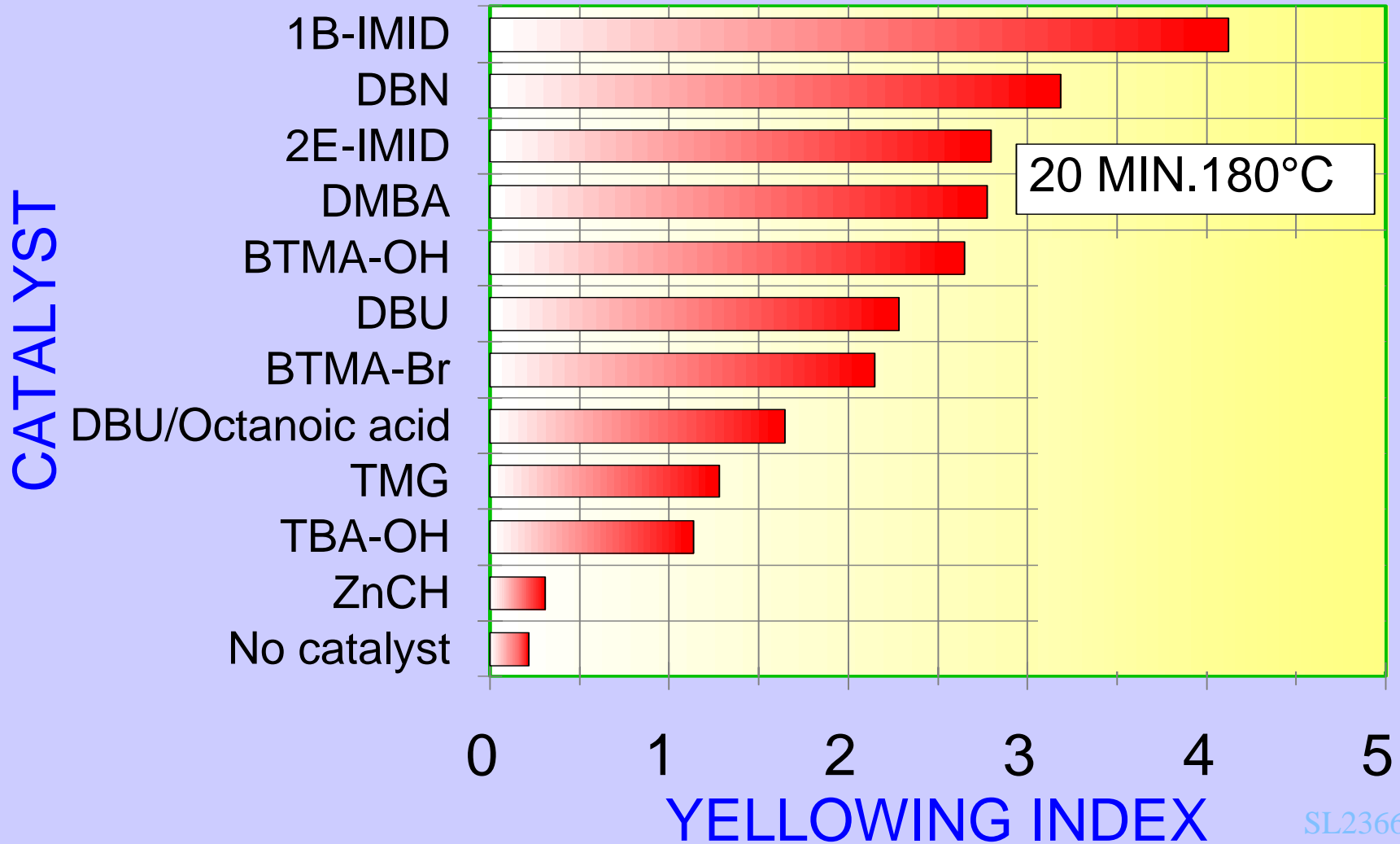


BTMA



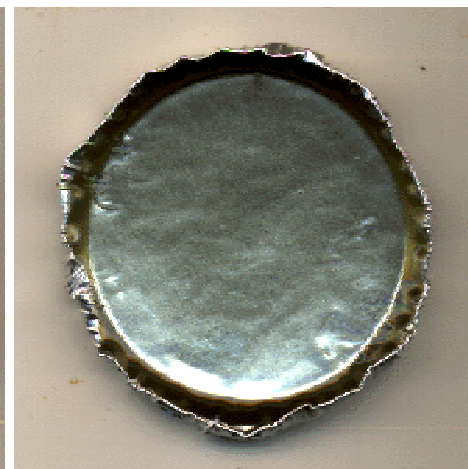
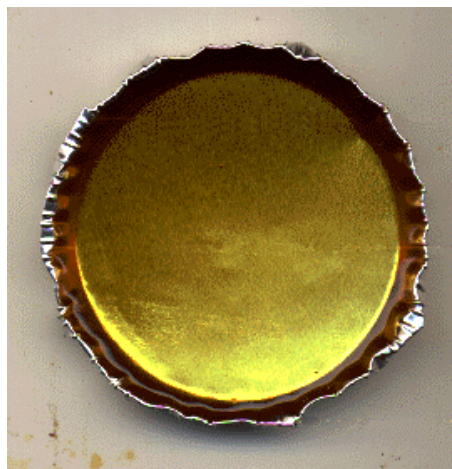
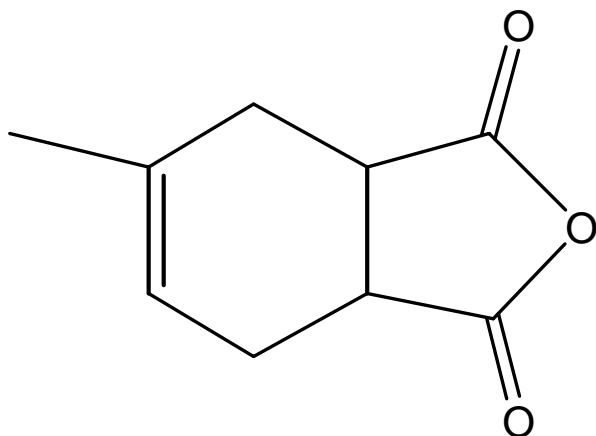
1B-IMID 7.1

YELLOWING EPOXY/CARBOXYL GLYCIDYL ESTER -COOH ACRYLIC

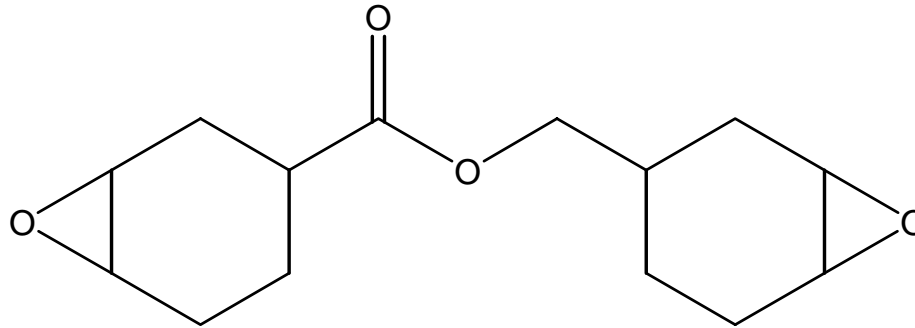


BIS A EPOXY LIQUID/ MTHPA

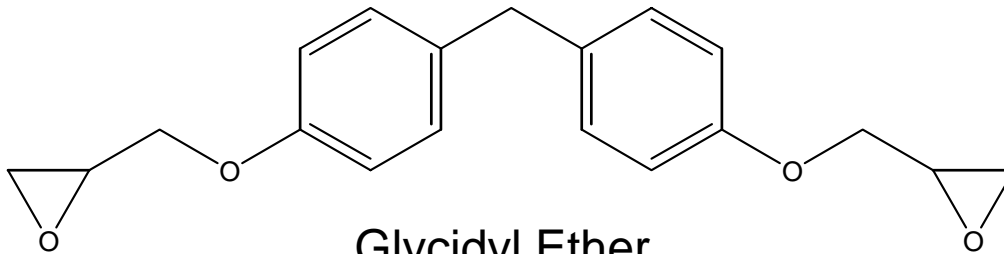
	NO CAT.	2E-IMID	ZnCH
VISC. 25°C, CPS	900	900	900
VISC. 24hrs	900	4200	900
POTLIFE, DAYS	>14	3	>14
CURE 1hr. 80°C 3 hr.. 150 °C			
HARDN. SHORE D	LIQUID	95	95



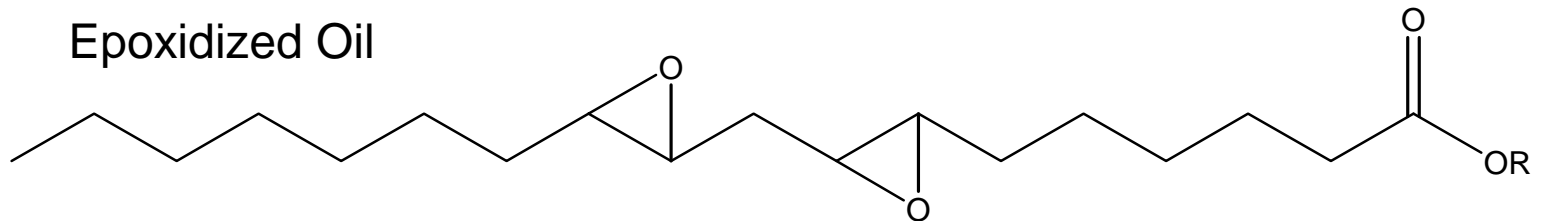
TYPICAL EPOXY RESINS



Cycloaliphatic



Glycidyl Ether



Epoxidized Oil

SUPERACID CATALYST

	ACID	AMINE
XC-7231	SbF ₆	Quat.
XC-9223	SbF ₆	t-Amine
XC-A230	Triflic	Quat.
A218	Triflic	Zn
A233	Triflic	DEA
BF ₃ Amine		

Cure Response - Cycloaliphatic

Time to Obtain 200+ MEK Double Rubs

	<u>100</u>	<u>120</u>	<u>140</u>	<u>160</u>
XC-7231*	6	2	2	1
XC-9223	Gel			
XC-A230	15	8	6	2
A218	15	6	4	2
A233		10	6	4
BF ₃ Amine				30+

1% catalyst solids on Epoxy solids

* Cures at 90C in 8 minutes

Cure Response - Glycidyl ether

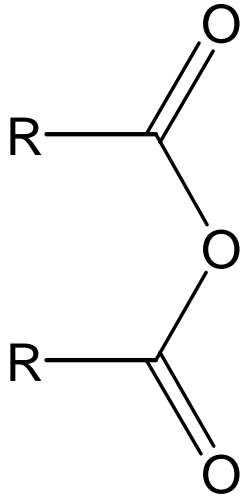
Time to Obtain 200+ MEK Double Rubs

	<u>100</u>	<u>120</u>	<u>140</u>	<u>160</u>
XC-7231	15	6	6	2
XC-9223*	6	4	2	2
XC-A230				20
A218				20
A233				20

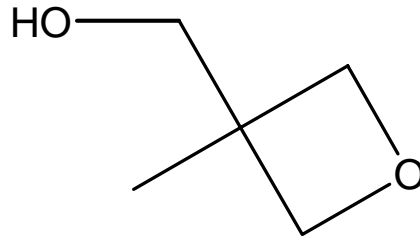
1% catalyst solids on Epoxy solids

*works at 90 C in 10 minutes

Diluents & Reactants



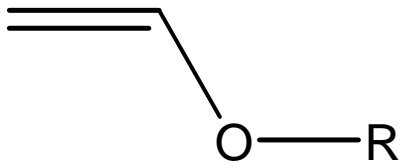
Anhydride



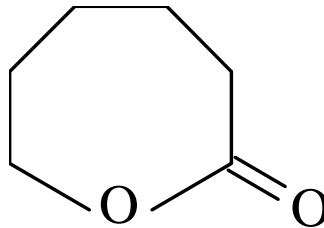
Oxetane



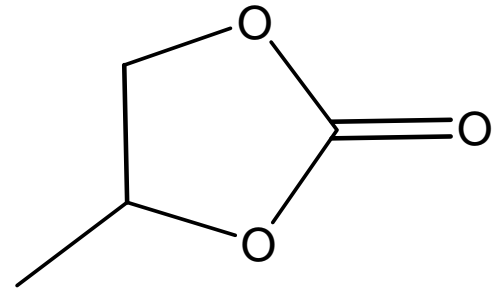
Polyester



Vinyl ether

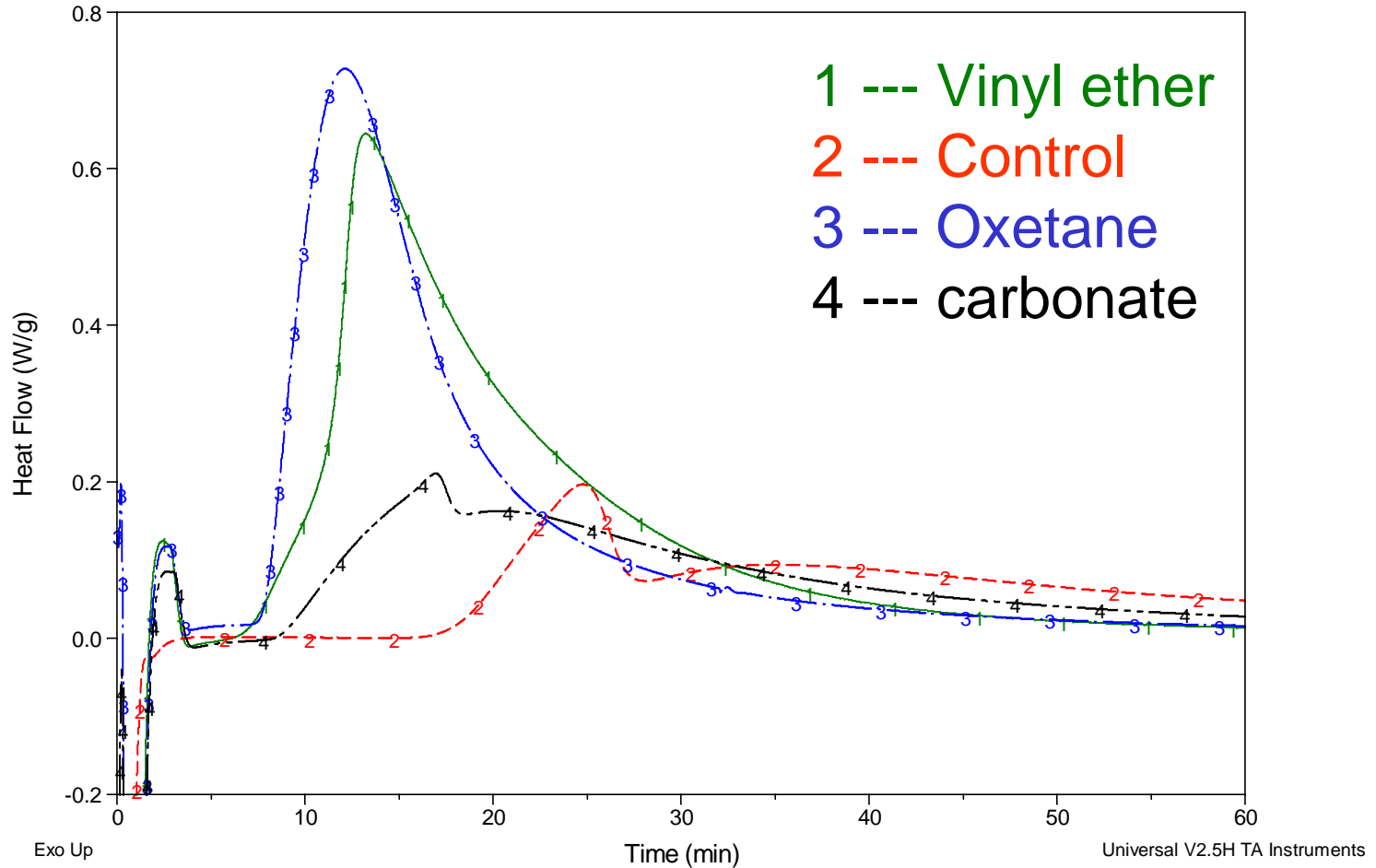


Lactone



Carbonate

Enhanced Reactivity with 25% Reactive Diluent Isothermal at 80°C

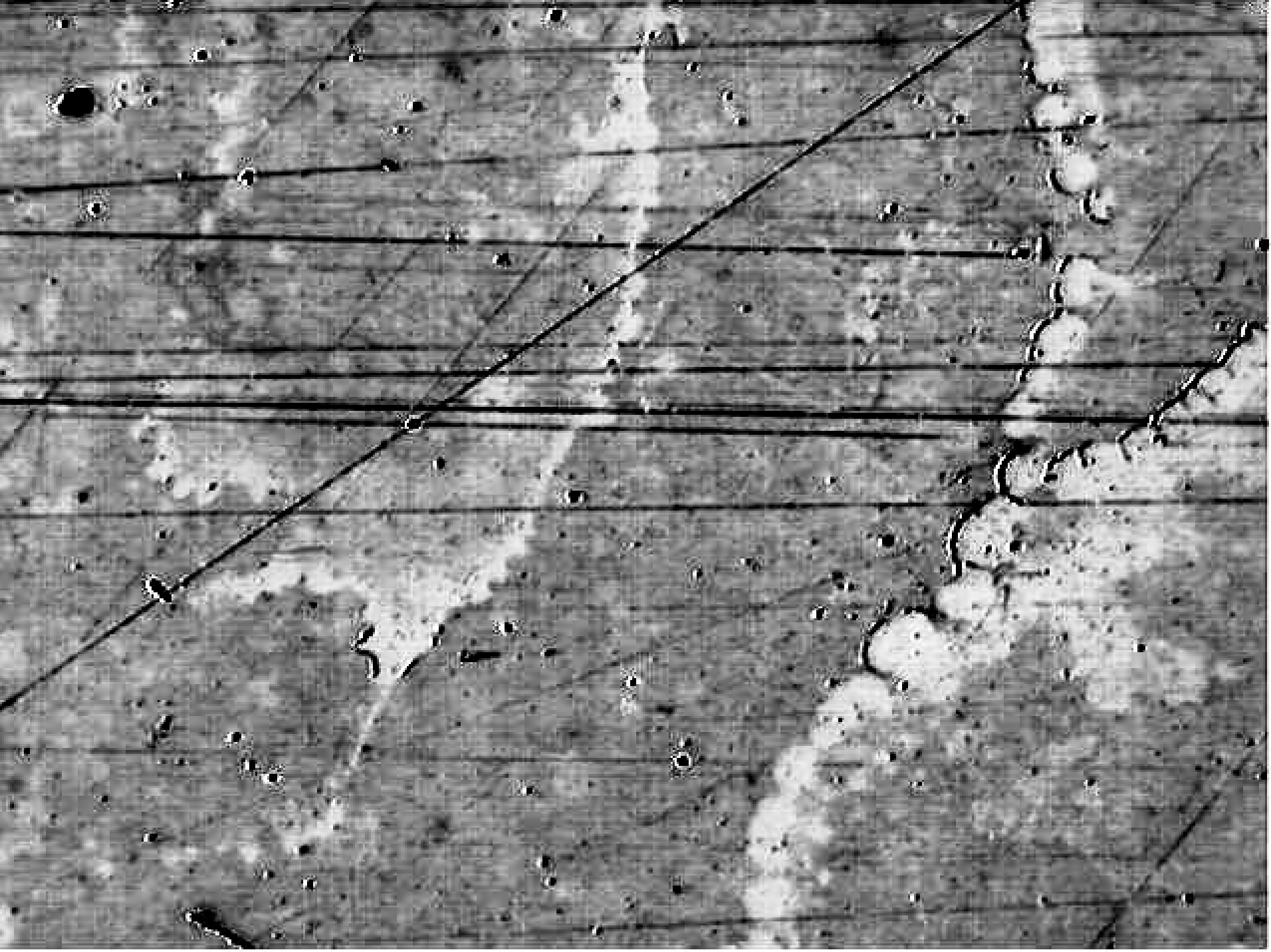


Catalyst XC-7231 at 1% on TRS

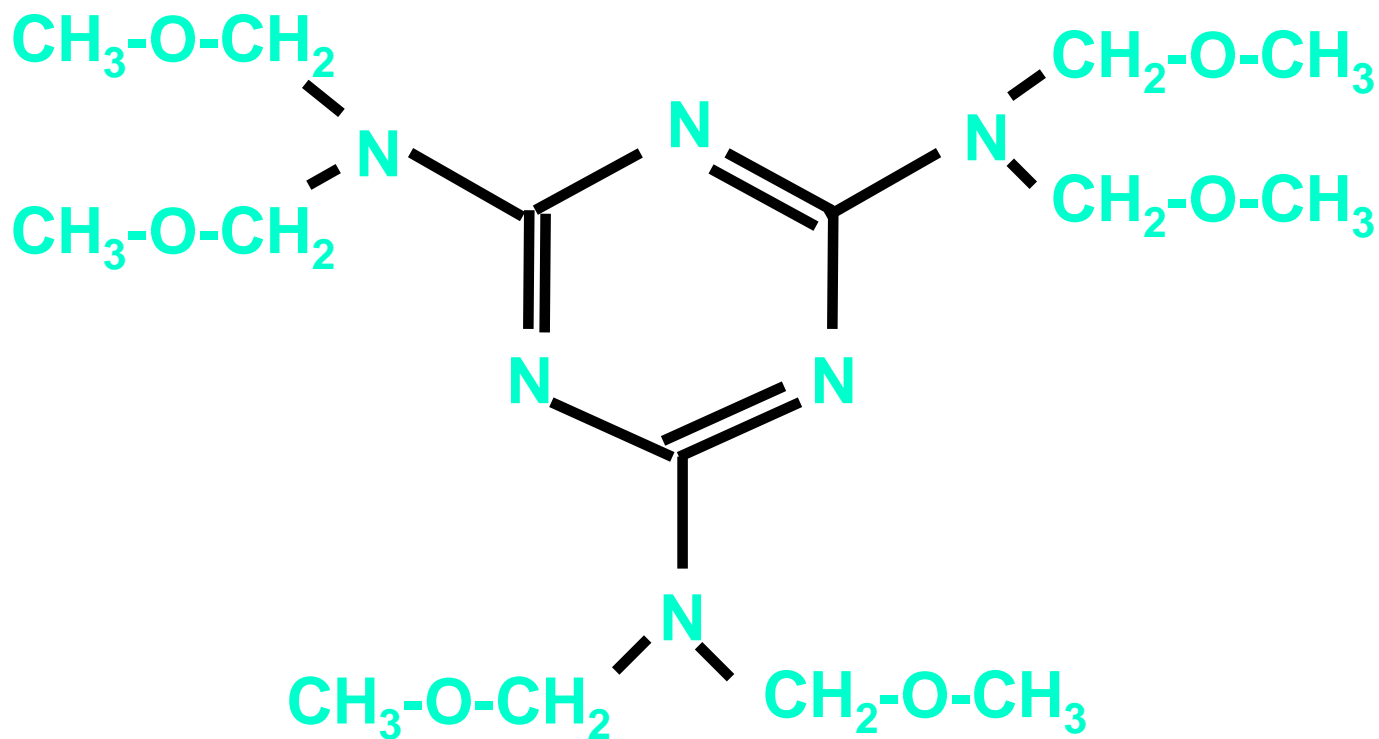


**MELAMINE FORMALDEHYDE
NETWORKS WITH IMPROVED
CHEMICAL RESISTANCE**

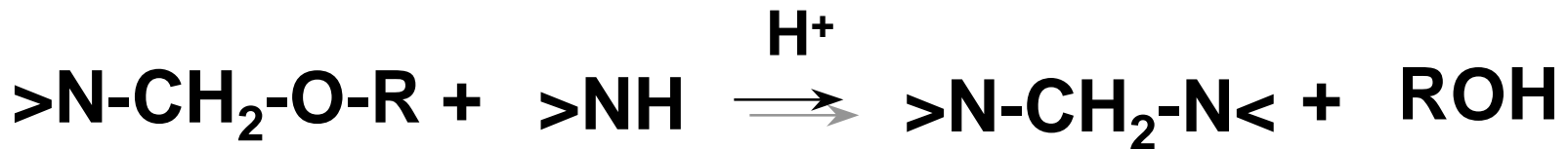
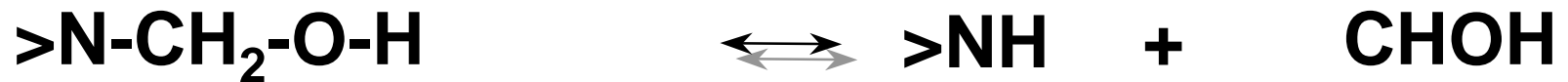
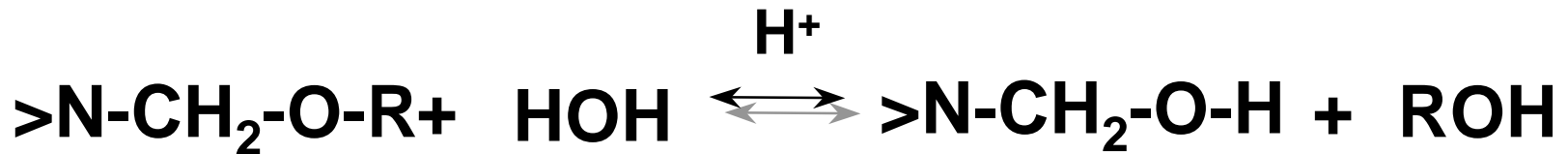
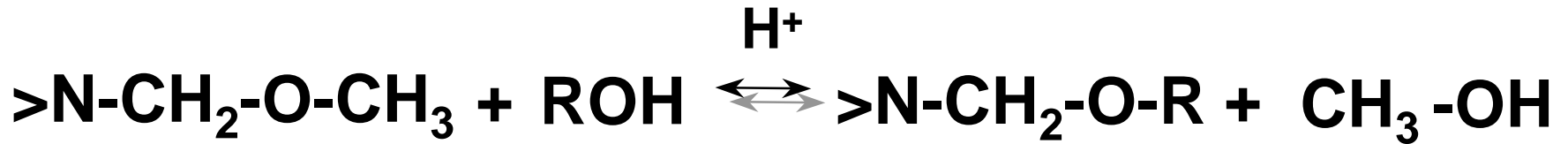
**CHEMICAL RESISTANCE
NETWORKS WITH IMPROVED
MELAMINE FORMALDEHYDE**



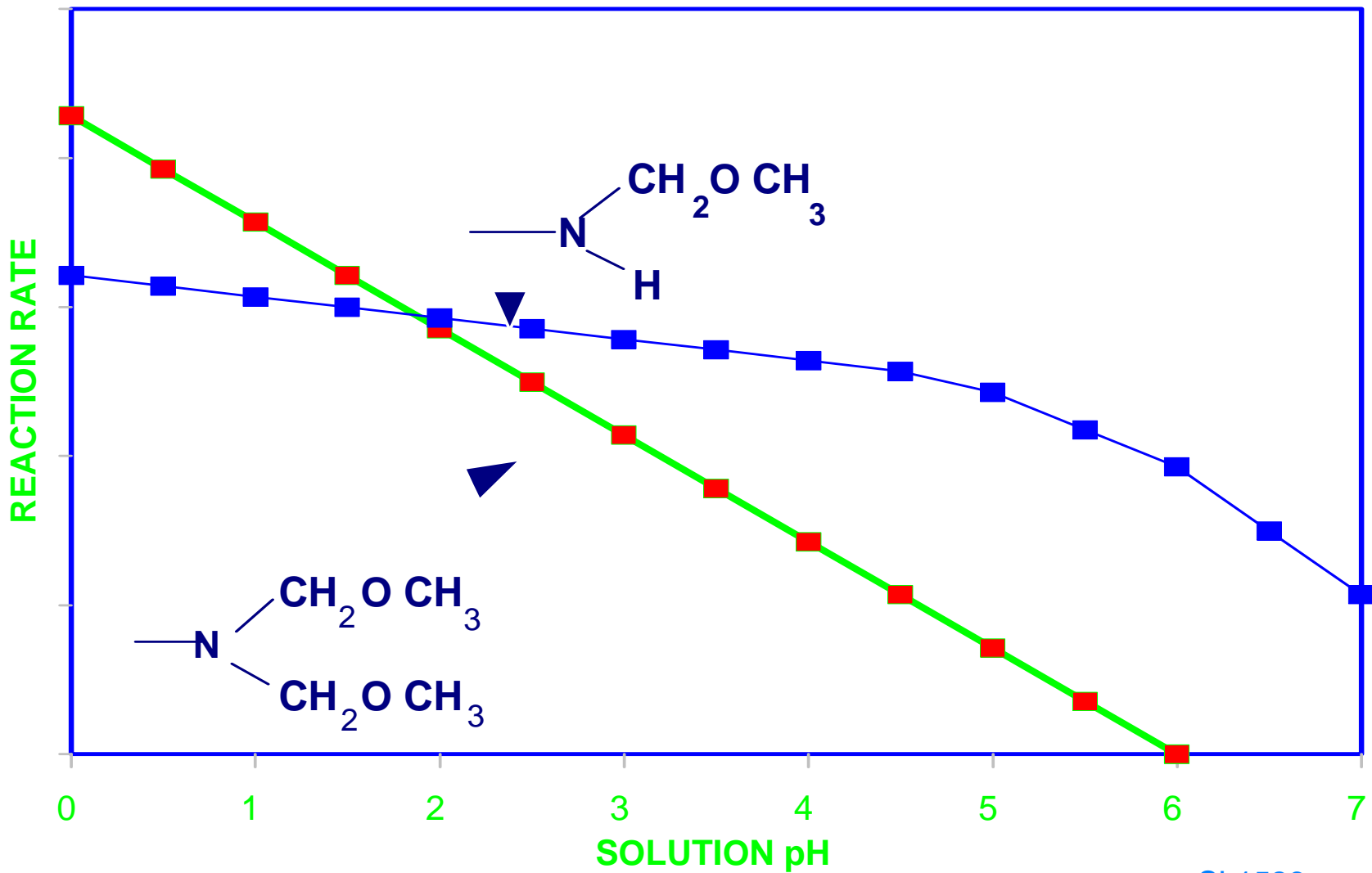
HMMM



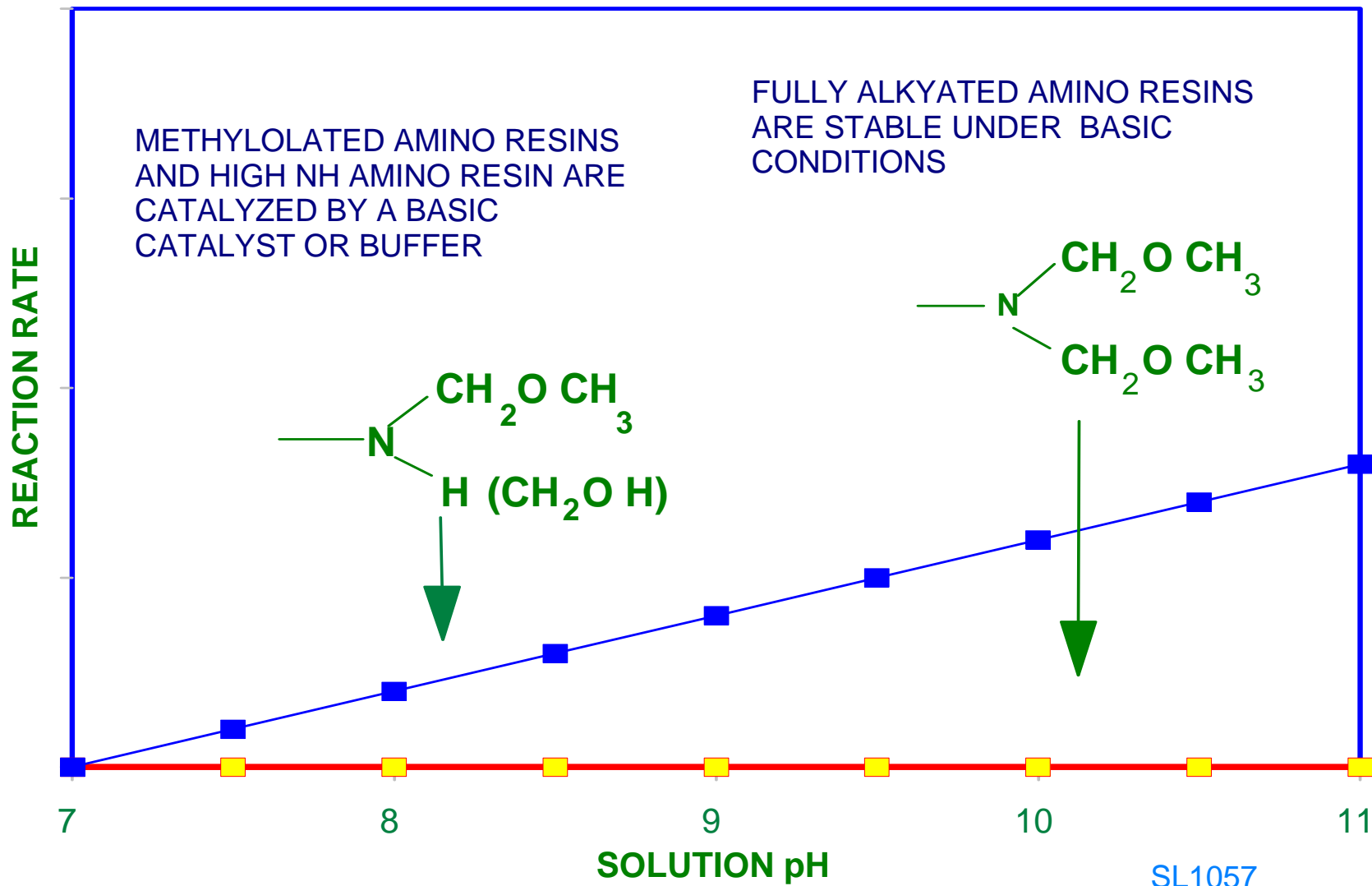
X-LINK and SELF-CONDENSATION



RATE OF REACTION OF MELAMINE RESIN



STABILITY OF MELAMINE RESIN pH 7-11



SL1057

IMPROVED NETWORKS

MORE STABLE NETWORK

NH CROSSLINKS

CARBAMATE pri, sec

AMIDE

UREA

CH CROSSLINKS

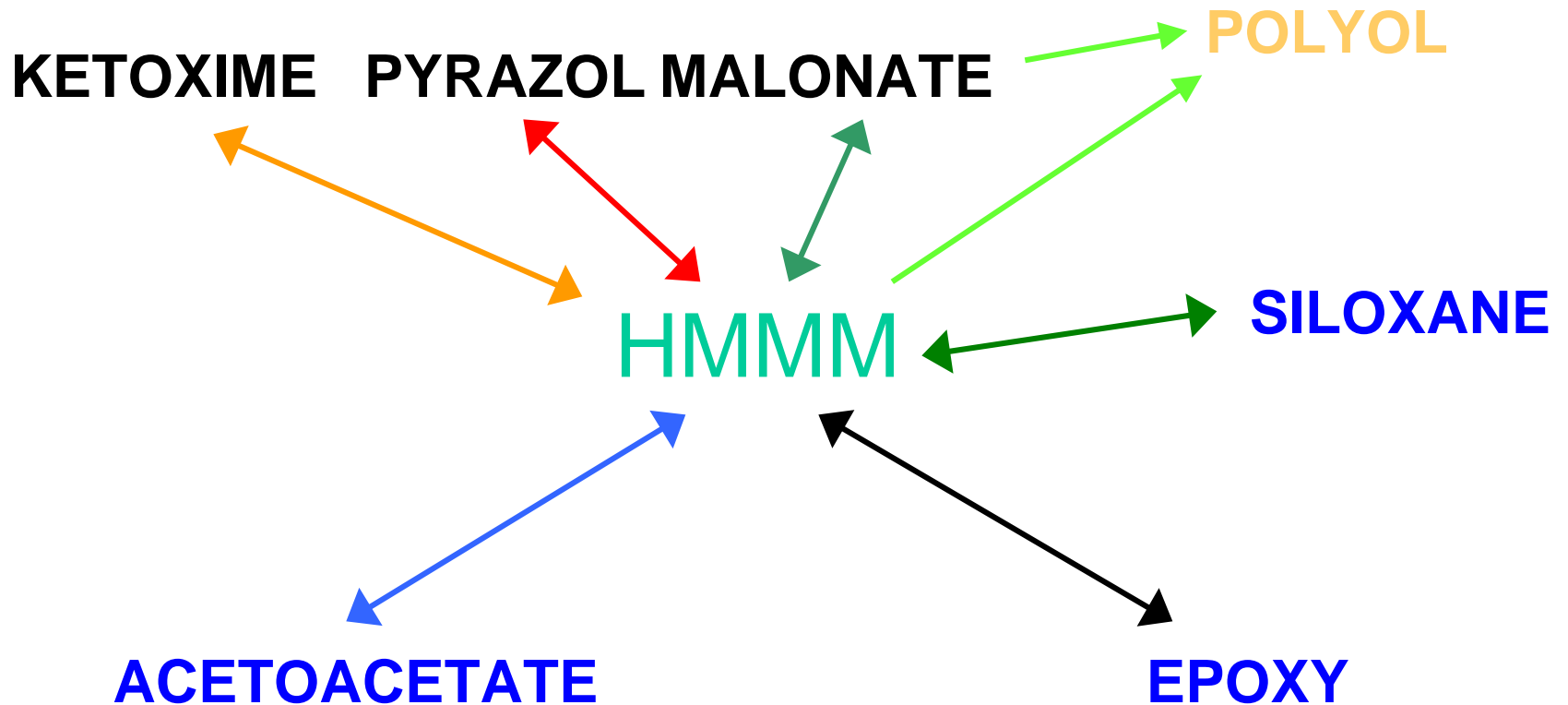
PHENOL

MALONATE BL.

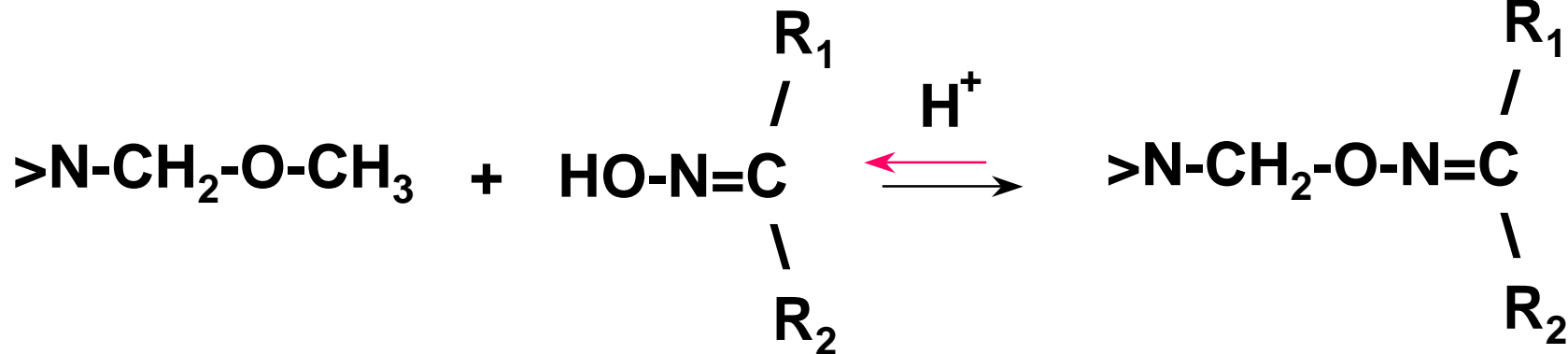
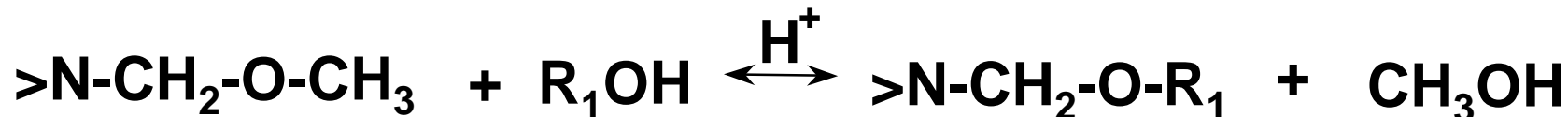
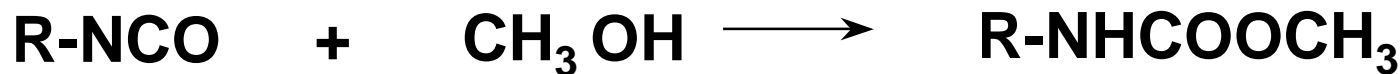
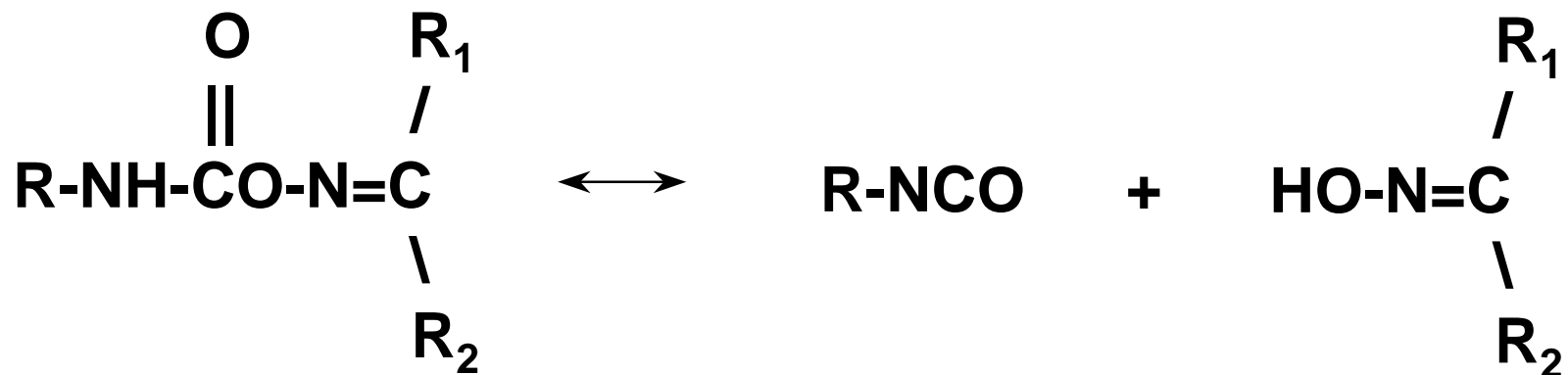
MERCAPTO

MULTIPLE CURE MECHANISM

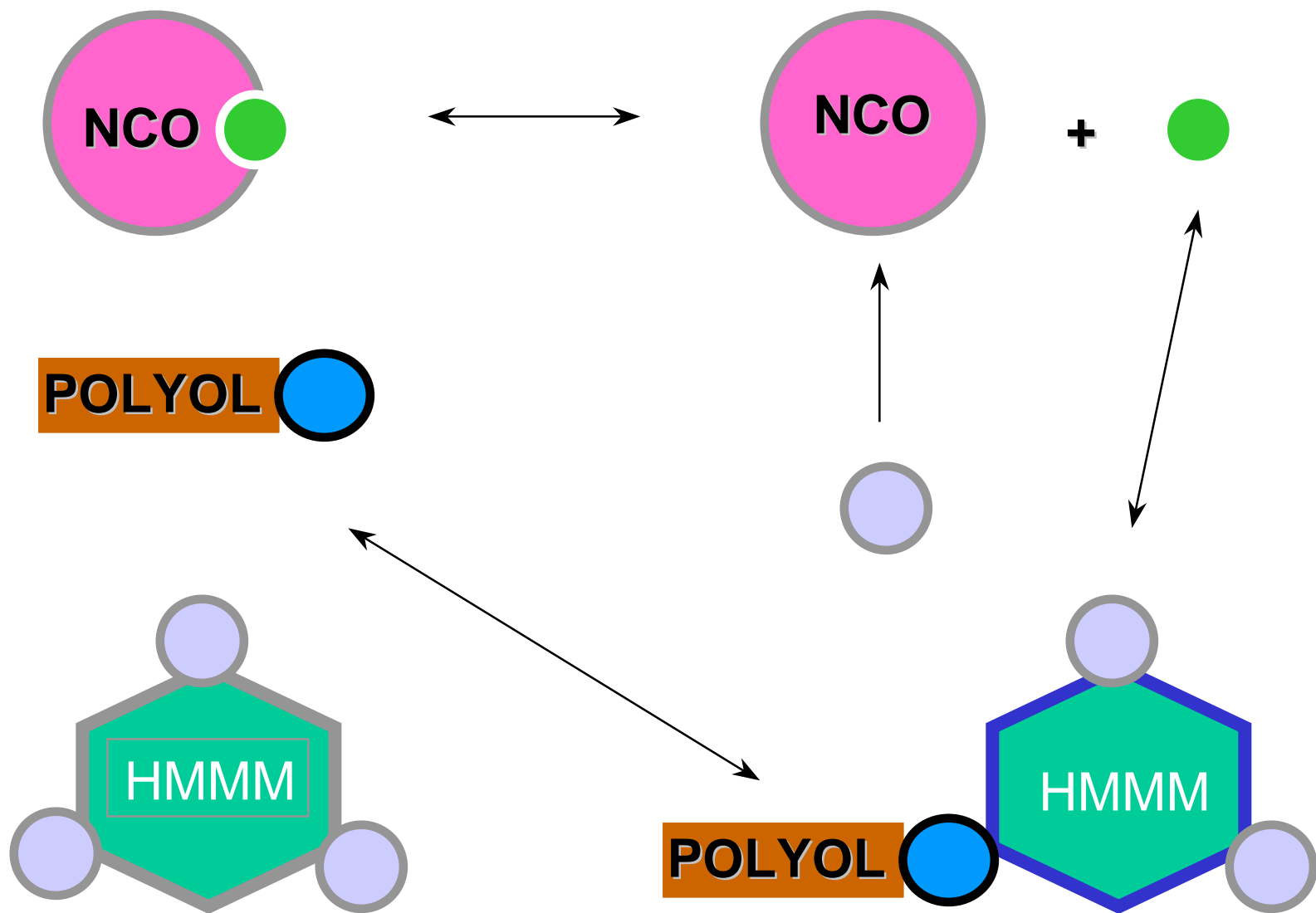
BLOCKED ISOCYANATE



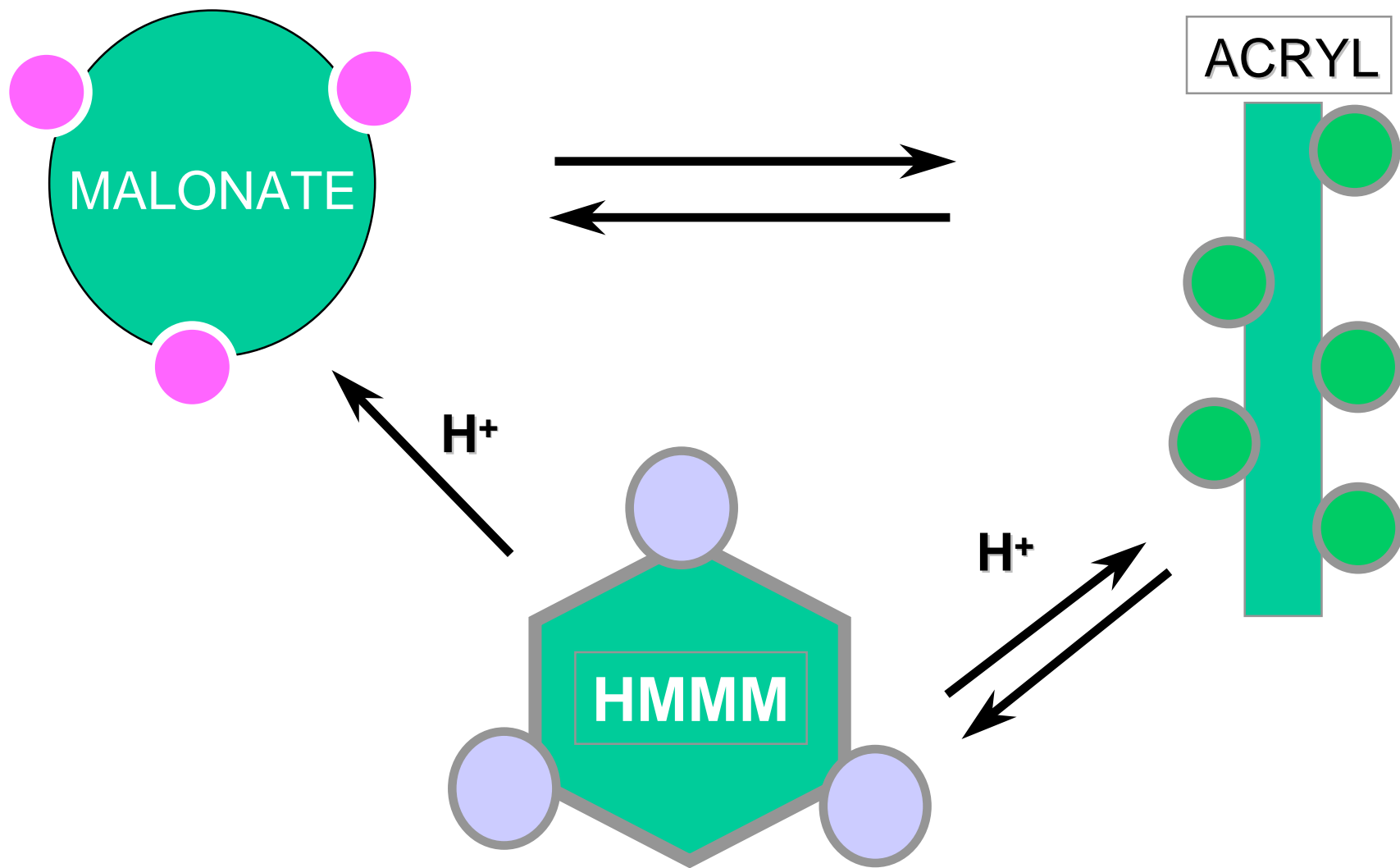
BL-NCO/HMMM/POLYOL



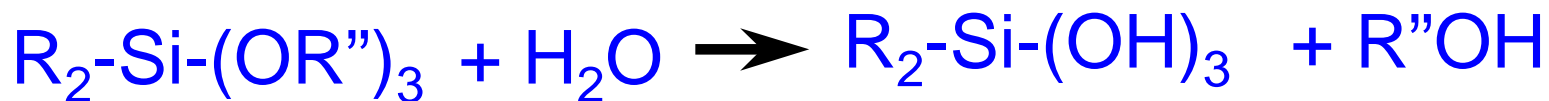
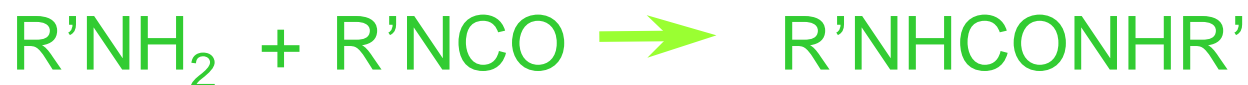
BL-NCO/HMMM/POLYOL



MALONATE BLOCKED NCO

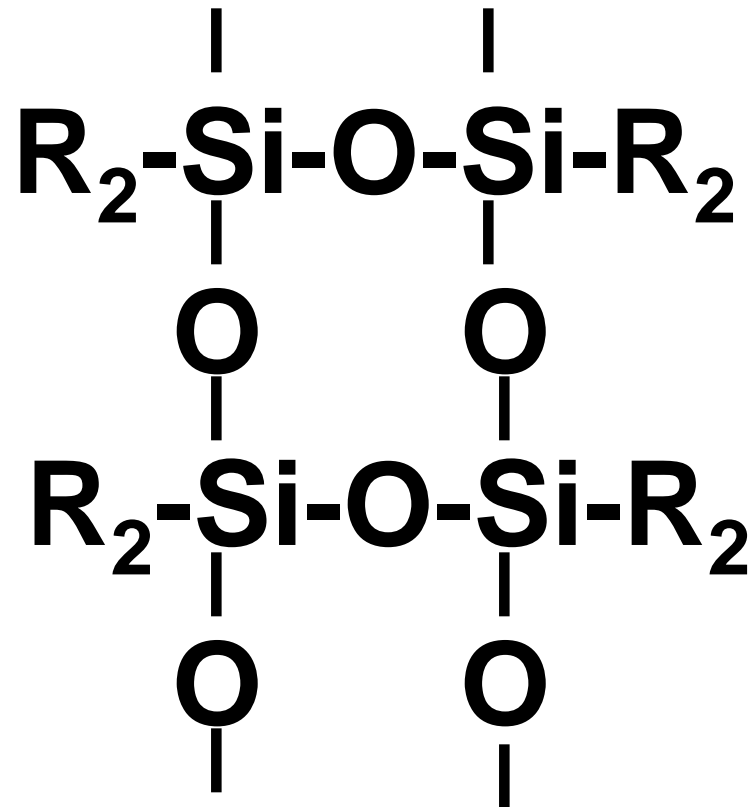


Isocyanate-Siloxane



SILOXANE REACTION

DBTDL



Acknowledgment

Co-worker

R. SUBRAYAN

J. J. FLORIO

D. MILLER

M. PICCI

M. EMMET

A. HE

R. COUGHLIN

CUSTOMER

KING INDUSTRIES