CPI 2010

Houston, TX
October, 2010

Susterra® Propanediol – Renewability, Sustainability, and Differentiating Performance in Urethane Applications

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DuPont Tate & Lyle BioProducts™

The Leading Edge of Industrial Biotech: Susterra® Production at Loudon, Tennessee, USA

- *Manufacturing plant start-up in November 2006*
- *100 MM lb. capacity*

Since 2006, the joint venture DuPont Tate & Lyle Bio Products produces renewably sourced Susterra® 1,3-propanediol (Bio-PDO™) from corn sugar, a sustainable & renewable resource.

DuPont Tate & Lyle BioProducts

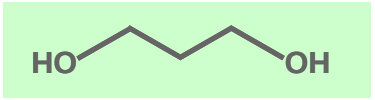
Loudon Production Fermentors

Susterra® delivers superior functionality and enables our customers to offer renewable, natural and sustainable products.

DuPont Tate & Lyle BioProducts

Agenda

- Background
  - Susterra® Propanediol: from a Renewable Source via a Small Footprint
  - Susterra® Propanediol in PolyUrethanes
- Thermal Transitions and the Odd Even Effect
  - Susterra® as Monomer in Polyester Polyol Prepolymers
  - Susterra® in Polyurethanes
- Susterra® PolyUrethane Applications: Beyond Green
  - Susterra® Possibilities in Polyester Polyols and Polyurethanes
  - Susterra® Propanediol in Footwear



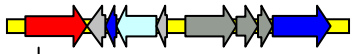
Susterra®

(Bio-derived 1,3-Propanediol)

DuPont Tate & Lyle BioProducts

History of Bio-PDO™ Development – A Highly Collaborative Endeavor

PDO Genes Isolated



Broad Biocatalyst Patent Allowed

Gen II biocatalyst milestone

Tate & Lyle-DuPont Joint Venture started

TATE & LYLE

Detailed engineering design started

Ground breaking Loudon, TN

1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007

Genencor-DuPont collaboration started

Genencor

Gen I biocatalyst milestone

Process development team formed

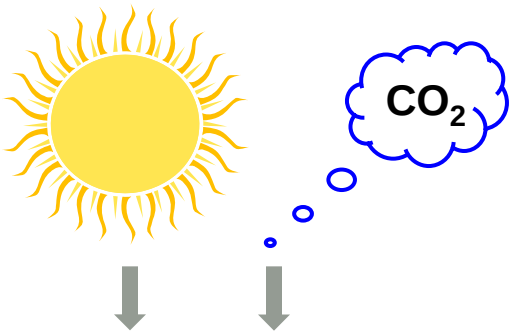
Polymer-grade Bio-PDO

Commercial biocatalyst delivered

100MM ppy Loudon plant start up

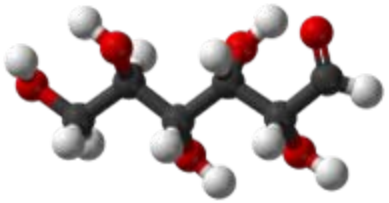
DuPont Tate & Lyle BioProducts

Susterra® Process



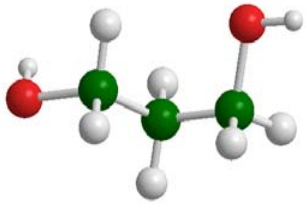
Corn

Fermentation process
using patented biocatalyst



Glucose

Refinement
to 99.7% purity



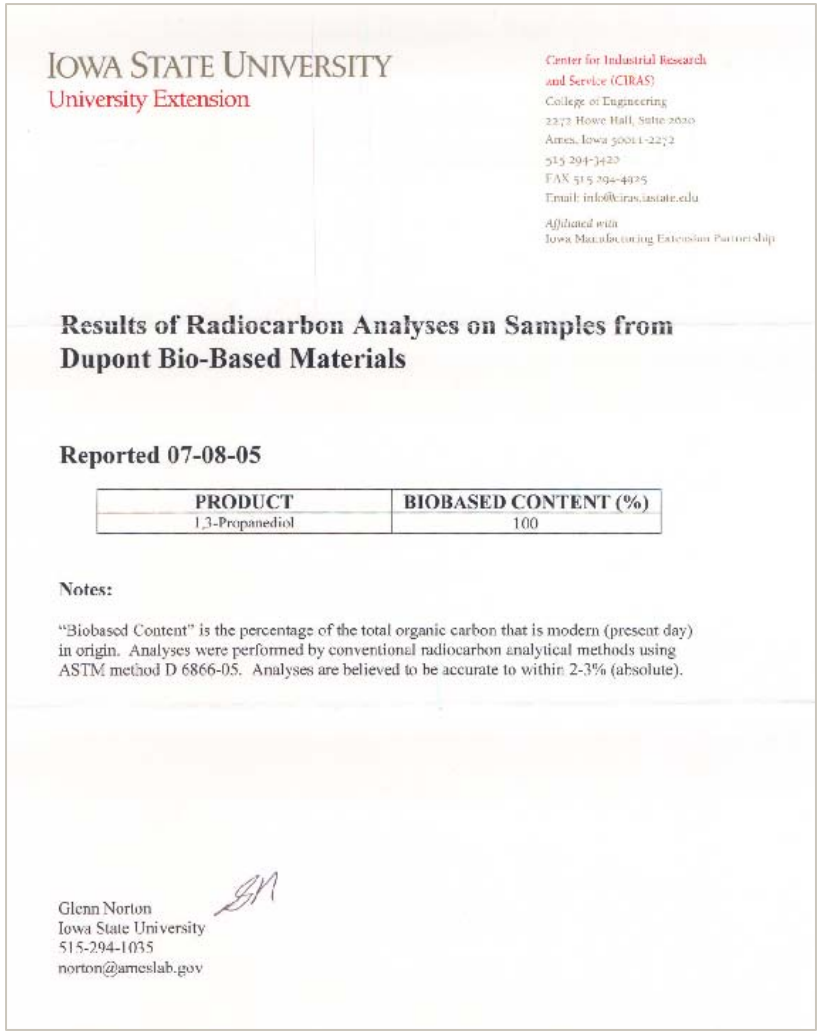
Susterra®
(Bio-derived 1,3-Propanediol)

Susterra® propanediol is a **renewably sourced** offering from DuPont Tate & Lyle Bio Products and manufactured via a proprietary corn sugar fermentation process.

DuPont Tate & Lyle BioProducts

100% Bio-Based Content

- "Biobased Content" is the percentage of the total organic carbon that is modern (present day) in origin.
- Analyses were performed by conventional radiocarbon analytical methods using ASTM method D6866.



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Iowa Manufacturing Extension Partnership

Results of Radiocarbon Analyses on Samples from Dupont Bio-Based Materials

Reported 07-08-05

PRODUCT	BIOBASED CONTENT (%)
1,3-Propanediol	100

Notes:

"Biobased Content" is the percentage of the total organic carbon that is modern (present day) in origin. Analyses were performed by conventional radiocarbon analytical methods using ASTM method D 6866-05. Analyses are believed to be accurate to within 2-3% (absolute).

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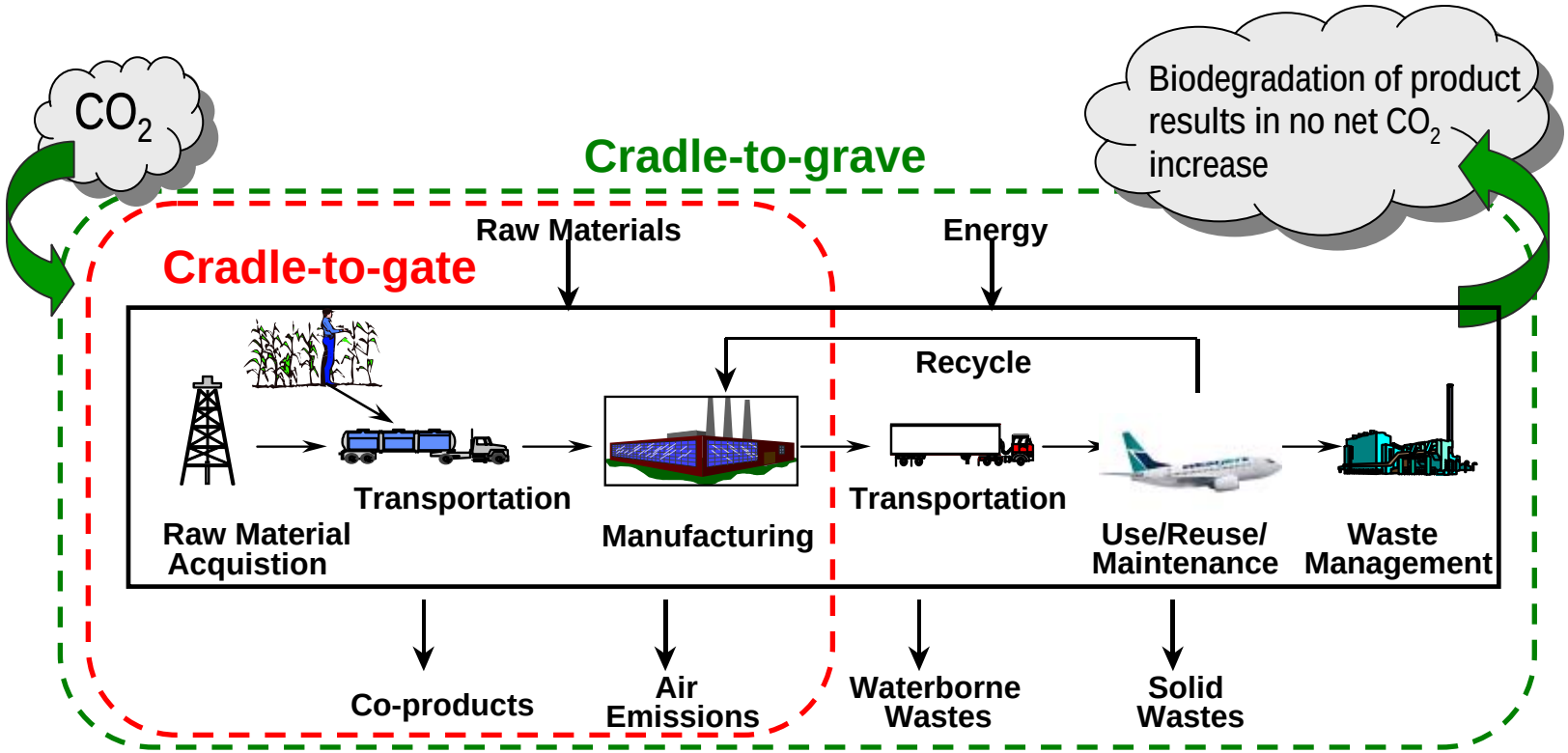
DuPont Tate & Lyle BioProducts

Life Cycle Analysis Approach

LCA is the only standardized method to evaluate the environmental footprint of a whole supply chain. Energy consumption and Green House Gas (CO_2) emissions are key factors in determining environmental footprint.

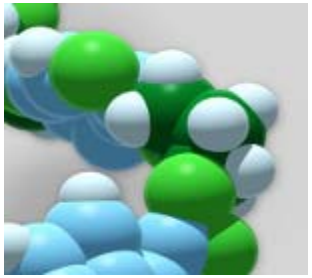


The corn-based process for Susterra® propanediol hass a **small footprint** compared to the petroleum-based processes for 1,3-propanediol and 1,2-propanediol.

DuPont Tate & Lyle BioProducts

Polyurethanes – Clear Differentiation

	Miscible in Polyols	Handling Issues (viscosity/heating)	Controlled Substance in US	Renewably Sourced
Susterra®	Yes	No	No	Yes
BDO (1,4-butanediol)	Yes	Yes	Yes	No
DEG (diethylene glycol)	Yes	No	No	No
EG (ethylene glycol)	No	No	No	No



- Susterra® propanediol offers polyurethane formulators and manufacturers a renewably sourced substance, that is non-controlled in the US.
- Susterra® is an alternative short chain diol that offers improved handling at lower temperatures, and has a higher reactivity per pound compared to BDO.

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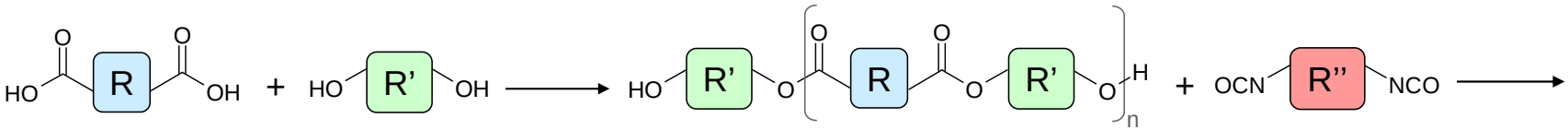
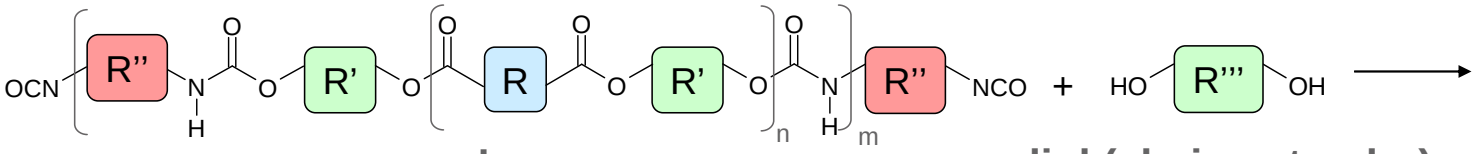
Polyurethane Synthesis

Polyester polyol formation:

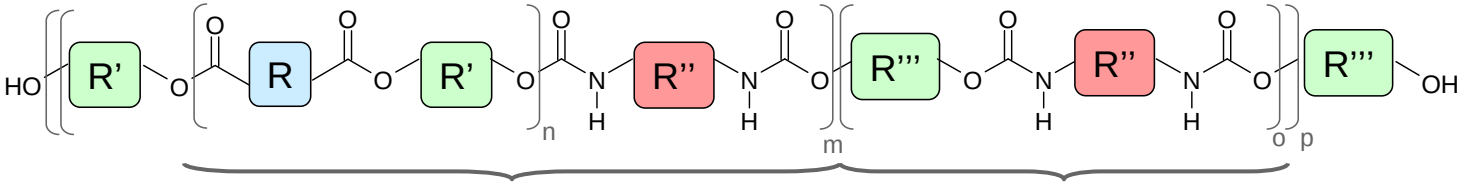


Diacid diol (monomer) polyester polyol di-isocyanate

2 shot method:



prepolymer diol (chain extender)



soft block hard block

block polyurethane

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Bio Content in Susterra® based Polyurethanes

Susterra® can yield a final product containing up to 33% renewably sourced material.

Susterra® Based Material	Bio-Content of Material	Contribution to Final PU
Polyester Polyol	up to 40 wt%	23 - 30 wt%
Chain Extender	up to 100 wt%	3 - 10 wt%
Polyurethane	----	up to 33 wt%

- Some renewably sourced content can be obtained using Susterra® as a chain extender.
- More Susterra® is incorporated when used as monomer in the polyester prepolymer.

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Susterra™
renewably sourced™ propanediol

Bio-content expressed as a percentage on all atoms C, H, O, N.

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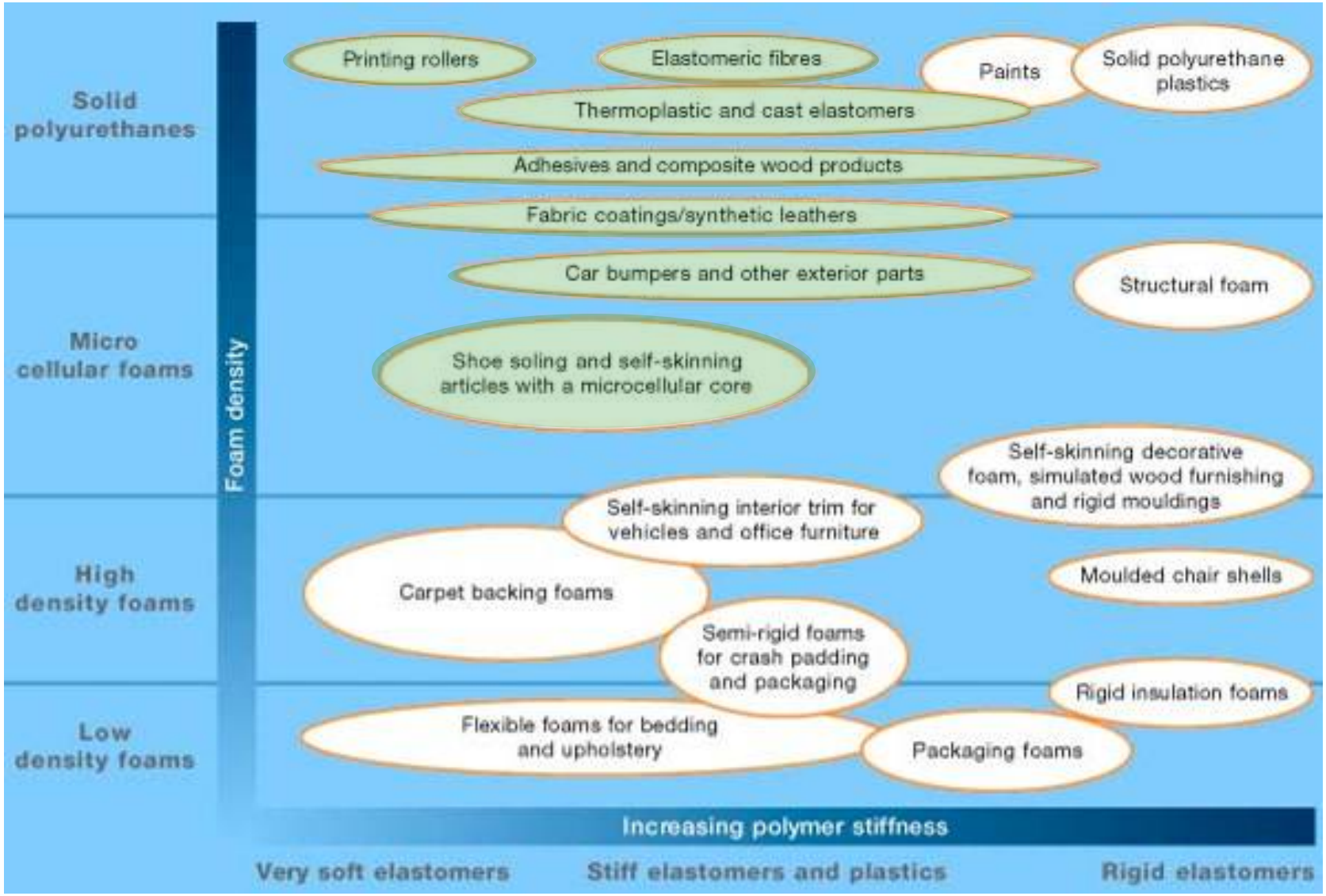
Polyurethane Product Map

Current areas of focus



Many urethane markets, applications, and products exist…..
that could possibly contain 33 wt% renewably sourced Susterra®.

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Susterra® Strengths in Cast Elastomers

No.	Polyester Polyol	Prepolymer Isocyanate	Curative	Renewable Content	Observed Strengths	Envisioned Applications
1	•EG AA •EG/BG AA •BG AA	•MDI	•Susterra® •BDO	~30 wt%	• Abrasion resist. • Pot life	High wear appl. Increased catalyst loading for improved performance
2	•Susterra® AA	•MDI	•Susterra® •Susterra® AA	~30wt%	• Resilience • Abrasion resist. • Compr. set • Potlife	High wear appl. Maximize cat. load.
3	•Susterra® AA •EG AA	•TDI 80/20 •TDI 100	•DMTDA	25-30 wt%	• Resilience • Abrasion resist. • Compr. set • Potlife	High wear appl. Maximize cat. load.

- Susterra® can be used in PU's as curative and building block giving renewably sourced products without extensive re-formulation.
- Susterra® strengths (e.g., improved abrasion resistance and pot life / catalyst loading) are general trends observed in a range of elastomeric materials.

Co-presented with ITWC during the CPI 2009 Polyurethanes Technical Conference, Oct. 5-7, 2009, National Harbor, MD

PDO in Polyurethanes in the Product Literature

Cast Polyurethanes
Piggott et al.

- "*number of carbons in the straight chain diol chain extender has relatively **little effect on the room temperature properties**.*"

TPU's
SHELL

- "***similar physico-mechanical properties at room temperature** when chain extended with either 1,3-PDO or BDO"*
- "***coefficient of thermal expansion is much lower** for the 1,3-PDO than for the BDO based TPU"*

Solventborne PU's
DT&L

- "*mixed diol adipates based on Susterra® behave **as good or better** than EG/BDO adipate*"
- "*Susterra® as chain extender increases the **gelation** of the TPU in organic aprotic solvents*"

Hot Melt Adhesives
SHELL

- "***improved tensile strength, modulus, and lap shear strength**….when BDO was replaced as a chain extender by 1,3-PDO."*
- "***Mechanical properties** of hot melt adhesives based on PDO adipate are **better** than those of adhesives based on PTMG."*

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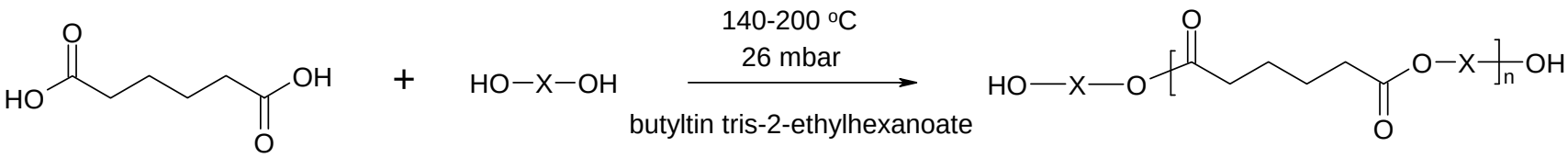
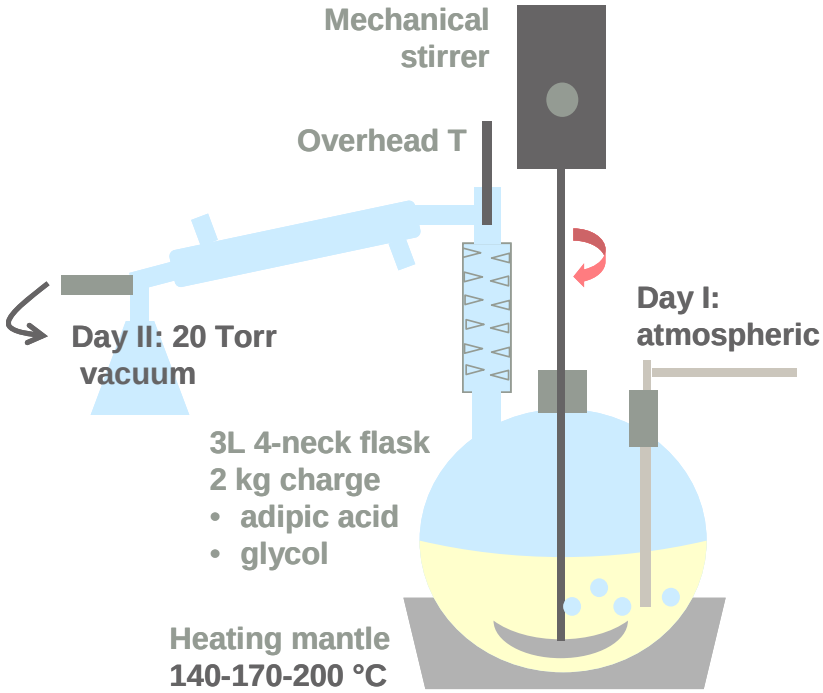
Polyester Polyol Synthesis



Poly adipate type (M_n = 2,000 g/mol)		
EG	1,2-ethylene-	-O-C_2H_4-O-
Susterra® PDO	1,3-propylene-	-O-C_3H_6-O-
BDO	1,4-butylene-	-O-C_4H_8-O-
PeDO	1,5-pentylene-	-O-C_5H_{10}-O-
HDO	1,6-hexylene-	-O-C_6H_{12}-O-

Parameters:
- Stoichiometry
- Heating Profile
- Vacuum Profile
- Catalyst

Polyol CTQ's:
- Molecular Weight
- Acid Number
- Color



Five straight chain diol polyadipates were synthesized via condensation at elevated temperature using a tin catalyst.

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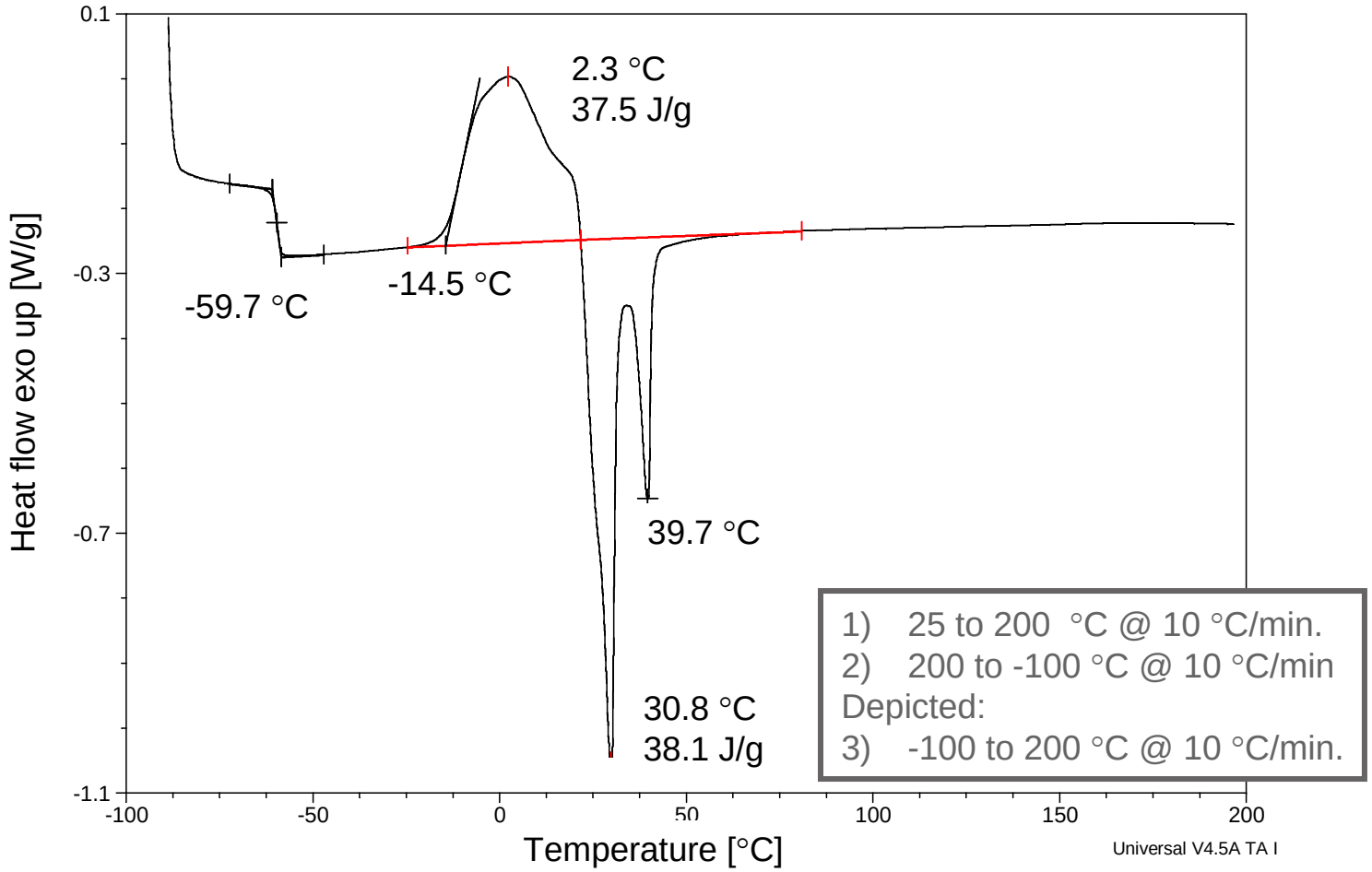
DSC of Susterra® Adipate



Susterra® adipate shows mutiple melt transitions: a glass transition, cold crystallization, and a melt transition with two minima.

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Thermal Transitions of Five Adipates

Diol	T_g [°C]	T_c [°C]	ΔH_{Tc} [J/g]	T_m [°C]	ΔH_{Tm} [J/g]
EG	-46.9	8.96 +31.1	56.9	48.0	59.4
Susterra®	**-59.7**	**2.26**	**37.5**	**30.8 + 39.7**	**38.1**
BDO	**-53.7**	**none**	**none**	**48.0 + 53.3**	**76.0**
PeDO	-61.8	none	none	0.66 + 31.1 + 38.6	76.3
HDO	none	none	none	51.8	96.1

M_n = 2,000 g/mol

- The thermal transitions of Susterra® adipate are compared to those of the four other straight chain diol adipates.
- Susterra® has a lower glass transition and melt transition than BDO adipate.
- The relationship between both glass and melt transition and the number of carbons in the straight chain glycol follows the **odd even effect**.

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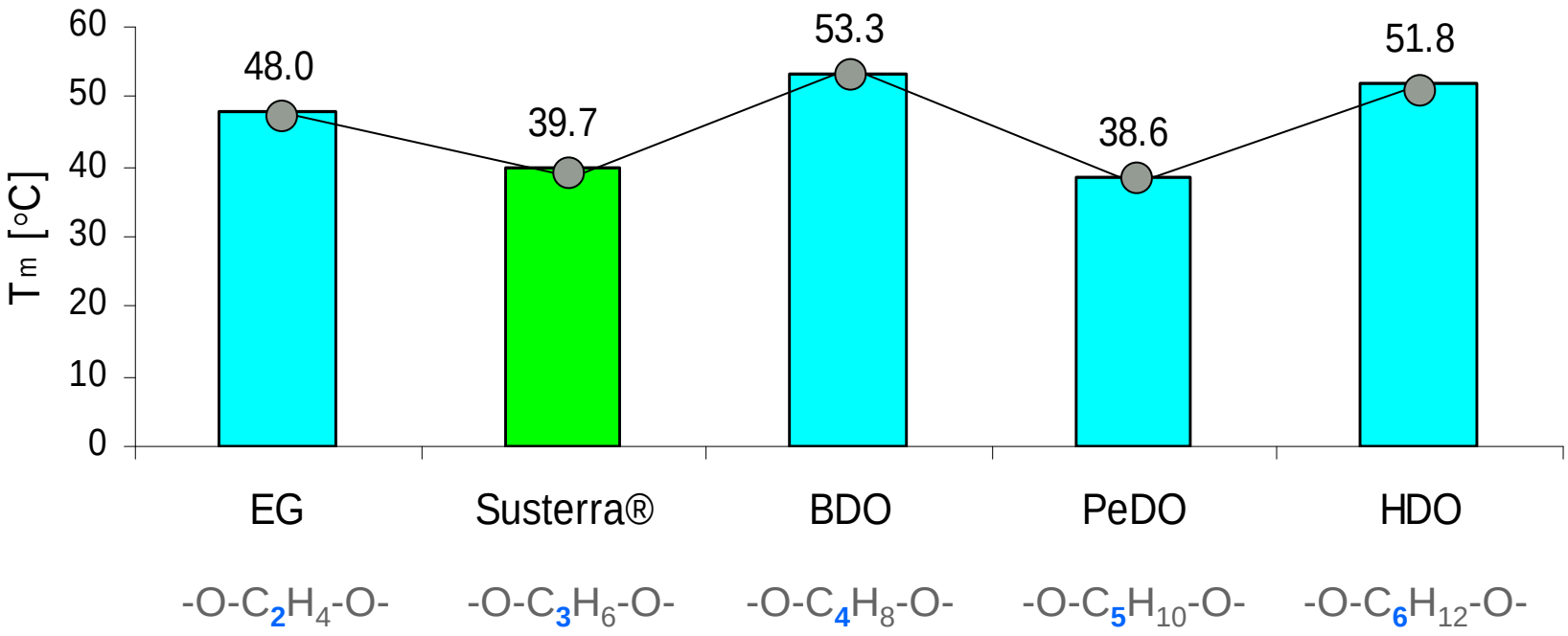
Melting Points of Five Adipates: Odd Even Effect



- The melt behavior of Susterra® adipate is consistent with the odd number of carbons in its diol fragment.
- The melting points of adipates based on glycols with increasing number of carbons follow the odd even effect.

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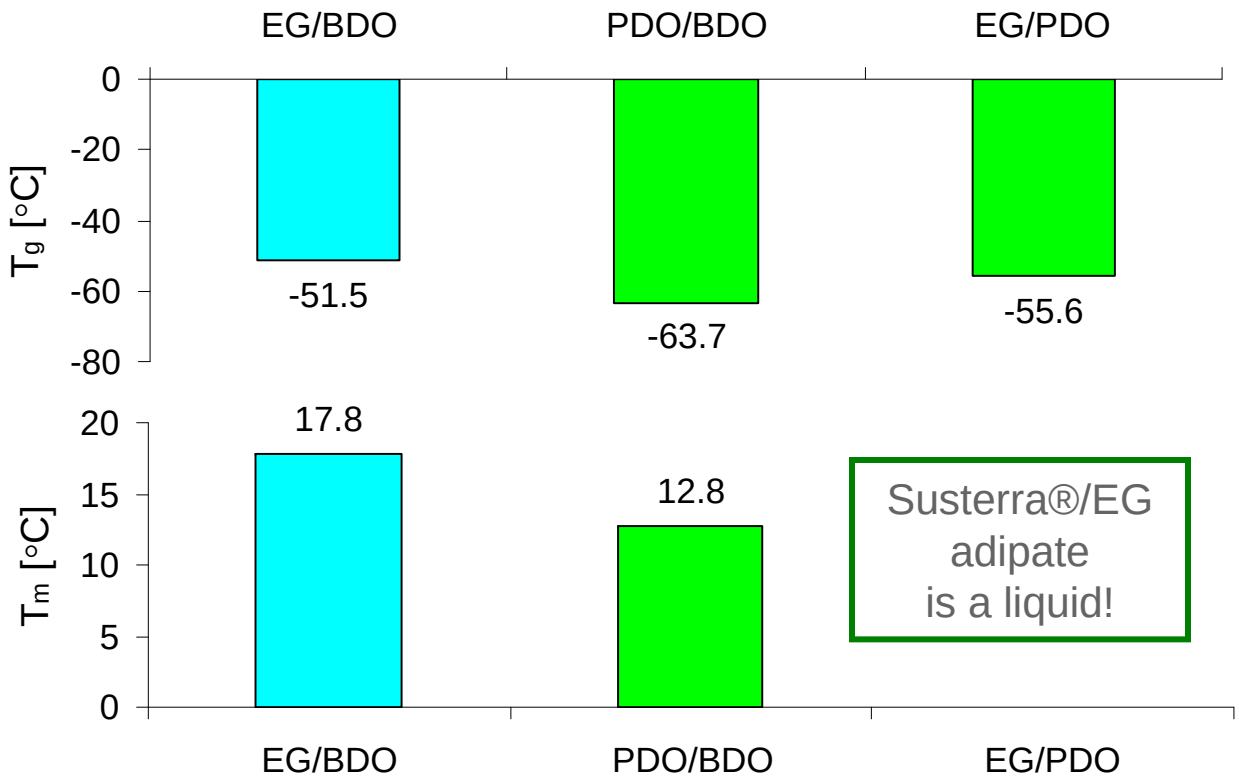
Thermal Transitions of Mixed Glycol Adipates

	Mixed Glycol Poly Adipate Reaction Charge	
	Mol% diol I	Mol% diol II
EG/BDO	50	50
EG/Susterra®	50	50
Susterra® /BDO	50	50



Susterra® Differentiation

Polyester Polyol (BDO Adipate vs Susterra® adipate)

Process

- It is straightforward to prepare a Susterra® adipate.
- Susterra® adipates are commercially available.
- The process to prepare Susterra® based polyester polyols can be optimized just as the process to prepare BDO based polyester polyols.
  - temperatures, level and type of catalyst, stoechiometry, additives

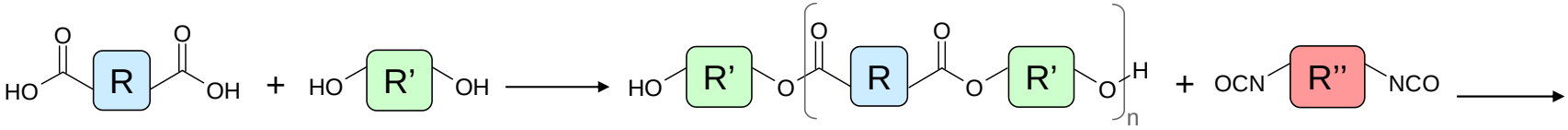
Properties

- The melting point of Susterra® adipate is 40 °C, vs 53 °C for BDO adipate.
  - *Some Susterra® based polyester polyols are liquid at room temperature.*
  - *Susterra® based polyester polyols may give improved handling.*
- The crystals formed by Susterra® adipate are less perfect; Susterra® adipate has a lower melting energy.
- Susterra® adipate crystallizes more slowly.
  - *Susterra® based polyester polyols may give transparent articles.*
- The non-crystalline portions of Susterra® adipate become glassy at lower temperatures. Susterra® adipate has a slightly lower glass transition.
  - *Susterra® based polyester polyols may improve the low temperature performance.*

Polyurethane Synthesis

Hard block content = 25 wt%
Prepolymer NCO/OH ratio = 1.03

Polyester polyol formation:



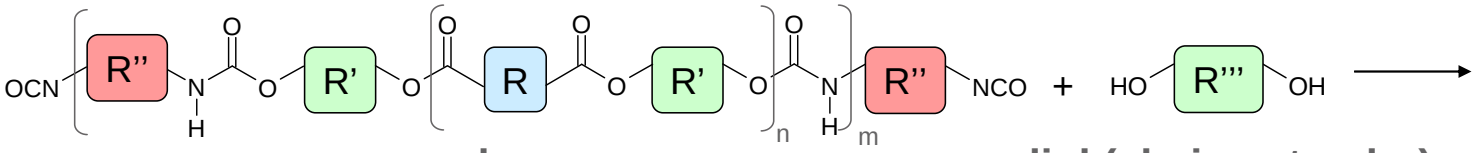
Diacid
adipate

diol (monomer)
Susterra® or BDO

polyester polyol
polyadipate

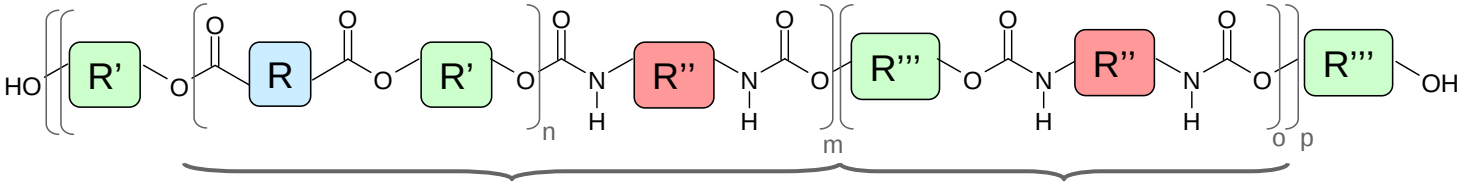
di-isocyanate
MDI

2 shot method:



prepolymer

diol (chain extender)
five straight chain glycols



soft block

hard block

block polyurethane

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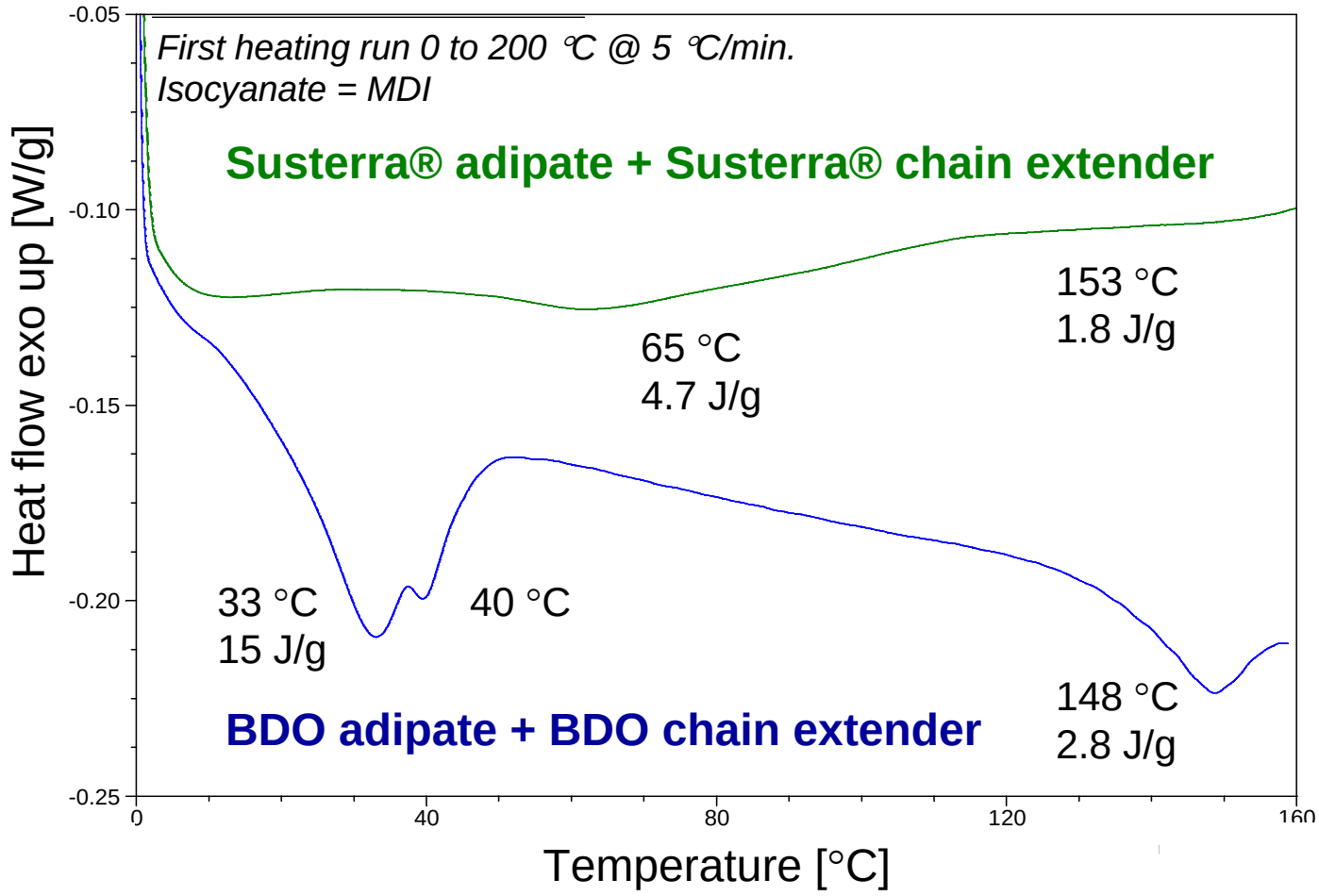
DSC of Susterra® and BDO based Polyurethane



Both the soft and hard segment in Susterra® based polyurethanes show little and slow crystallization.

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Thermal Transitions of PU's Extended With 5 Glycols

Chain Extender	Soft block		Hard block	
	T_m [°C]	ΔH_{Tm} [J/g]	T_m [°C]	ΔH_{Tm} [J/g]
BDO adipate/MDI				
EG	28.5 + 41.1	11	175	0.90
Susterra®	**36.1**	**19**	**145**	**0.43**
BDO	**32.8 + 39.5**	**15**	**148**	**2.8**
PeDO	13.5 + 52.6 + 98.9	40	167	0.14
HDO	25.5 + 38.9 + 87.4	14	156	0.69
Susterra® adipate/MDI				
EG	62.8	3.9	178	2.9
Susterra®	**65.4**	**4.7**	**153**	**1.8**
BDO	**63.5**	**3.8**	**140**	**3.7**
PeDO	62.0	4.9	none	0
HDO	61.9	8.0	171	0.33

The melt transitions of the soft and hard block show no odd even effect but the melt enthalpies do.

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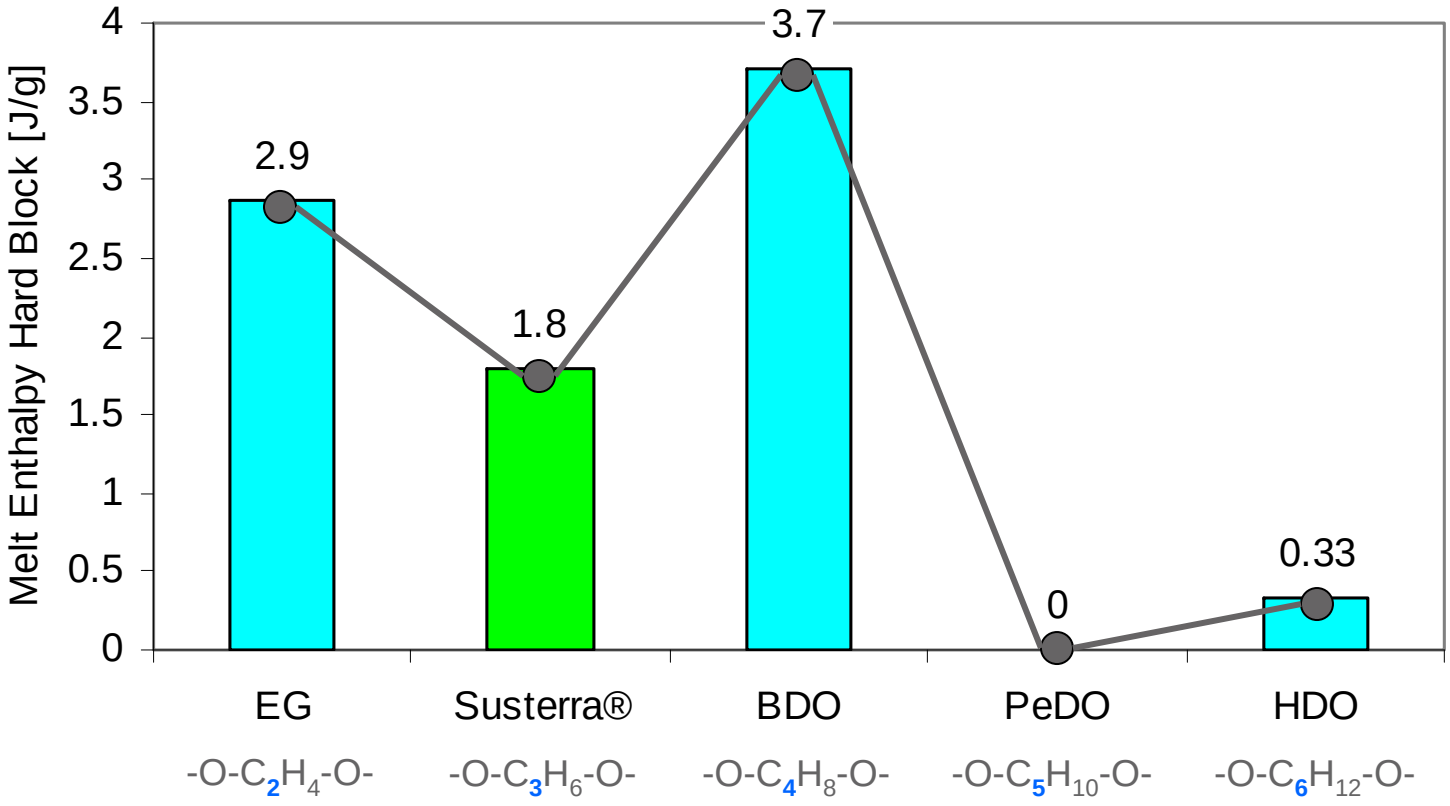
Melt Enthalpy of Polyurethane Hard Block



The melt enthalpies of the hard blocks of a Susterra® adipate based polyurethane follow the odd even effect.

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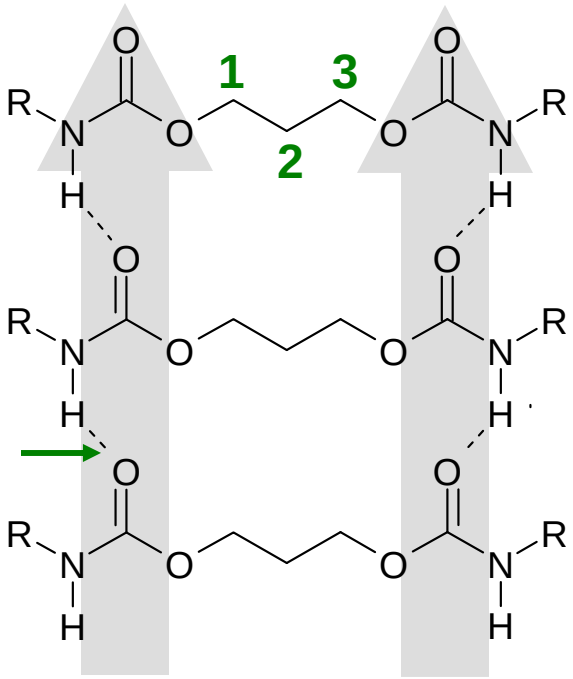
Odd-Even Effect in Di-Urethane Fragments

Susterra® hard block

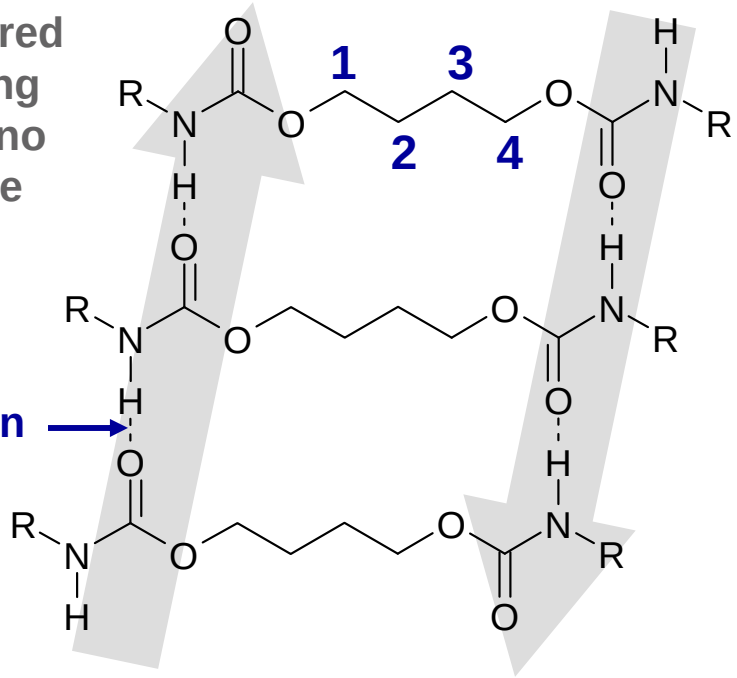
Dipole induces bending and strain



Long hydrogen bond

BDO hard block

Staggered packing gives no dipole



Short hydrogen bond

The odd even effect is explained by the packing of the hard block segments.

L. Born, H. Hespe, J. Crone, K.H. Wolf, Colloid and Polymer Science, 1982, 260(9), 819-828.
J. Blackwell, M.R. Najarajan, T.B. Hoitink Polymer, 1981, 22, 1534-1539.
O. Bayer, *Agnew. Chem.*, A59, 257 (1947)

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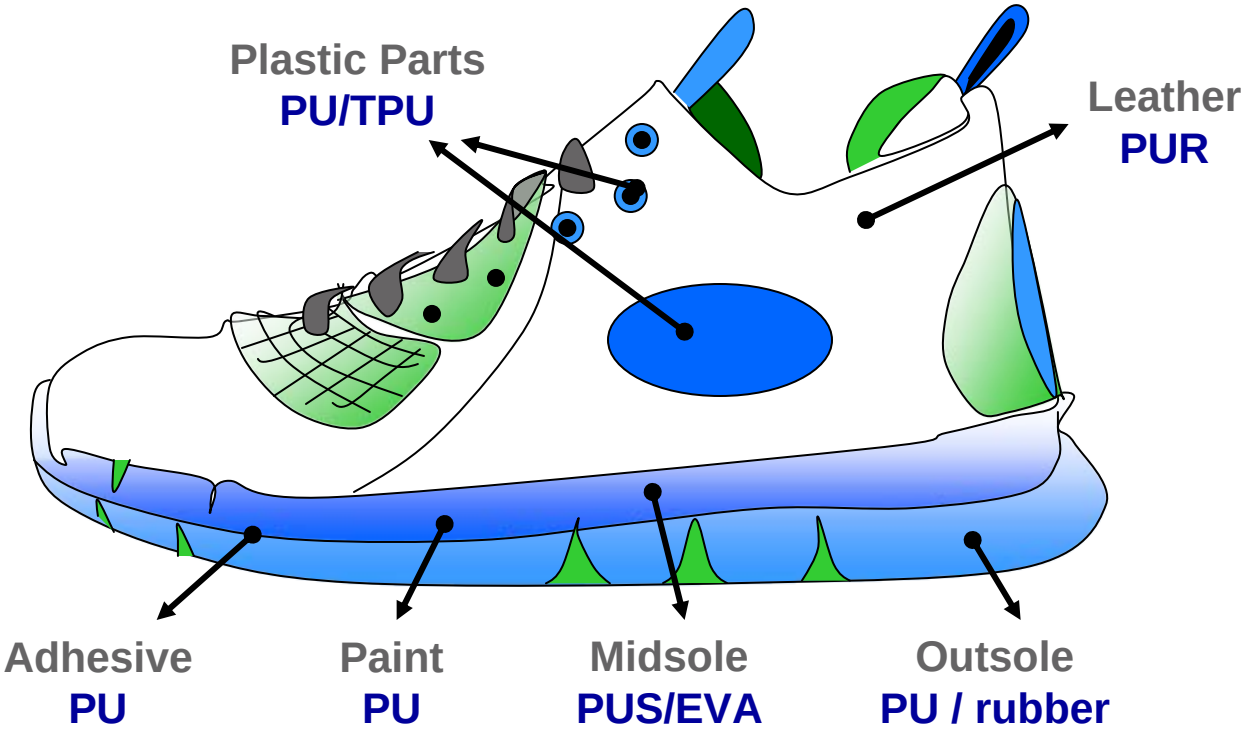
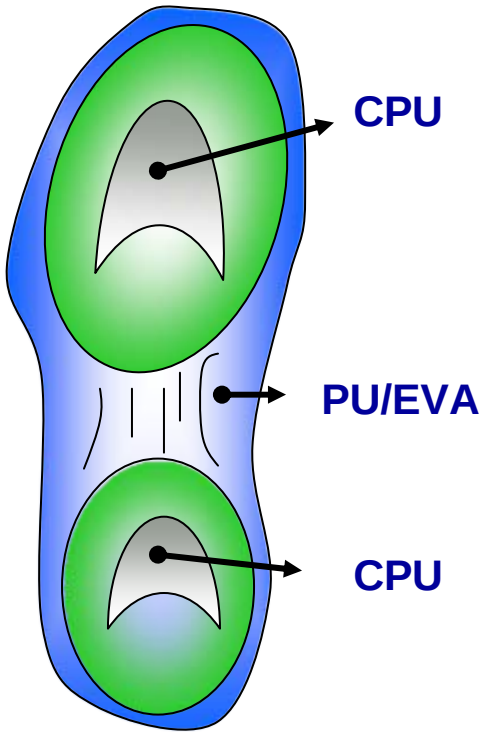
Potential Differentiation with Susterra® Propanediol in Footwear





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Susterra® Differentiation

Prepolymers / Hard blocks / Polyurethanes

Process

- Susterra® based prepolymers and polyurethanes are prepared as BDO based ones.
- Susterra® adipate prepolymers are commercially available.

Properties

- Susterra® hard blocks are less ordered & less “strong”. They have lower melt energies.
- Susterra® based PU’s show lower hardness at the same level of hard block.
- Cast elastomers based on Susterra® , Susterra® adipate and MDI are shown to have:
  - Improved abrasion resistance
  - Improved resilience
  - Improved compression set
  - Improved pot life
  - Balanced tensile properties
  - Balanced tear strength

What benefits can Susterra® give your customer?

DuPont Tate & Lyle BioProducts

Acknowledgement

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Mureo Kaku

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Matt Page

Ron Rawlins

Gordon Tseng

Judith van Gorp

DuPont Tate & Lyle BioProducts