FATTY-ACID CAPPED OLIGOMERIC PROPANEDIOL SUCCINATES

Note: This research was presented at the 2016 “in cosmetics” exhibition in Paris on April 13, 2016.

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Purpose:

- Successfully produced propanediol succinates of varying molecular weights with various fatty acids end-caps.
- These oligomers are 100% bio-based and show promise in several applications based on initial screening and property measurements.
- This technology can be considered for manufacturing of and to be used in a wide range of polymers for coatings, adhesives, sealants, elastomers, films, film formers, surfactants and end-use applications such as but not limited to:
  - Consumer: for example cosmetics, personal care, detergent & cleaning, food, flavors, pharmaceutical
  - Industrial: for example polyurethane, polyester saturated resins, polyester unsaturated resins, agricultural, paints, coatings and inks
- This approach demonstrates a “tunable” architecture with many possibilities.

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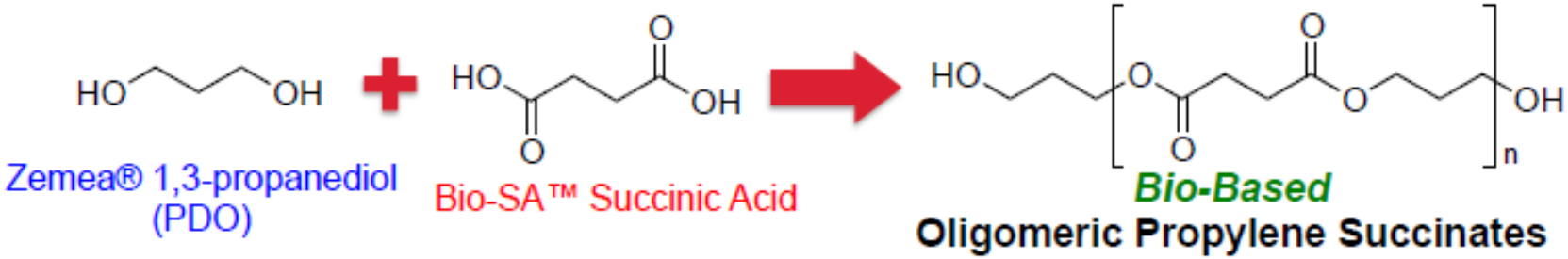
Synthesized 24 Fatty-acid End Capped Oligomeric Propanediol Succinates



Zemea® 1,3-propanediol (PDO)

Bio-SA™ Succinic Acid

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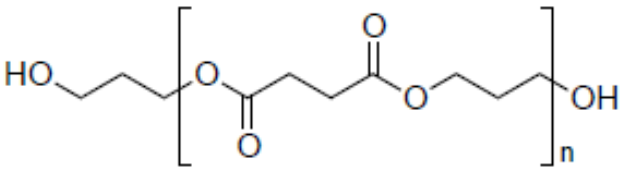
Oligomeric Propylene Succinates

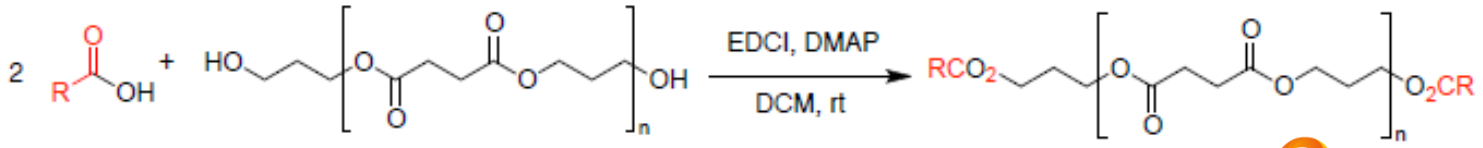
Oligomer synthesis

- Three classes of oligomeric propylene succinates have been synthesized



$M_w \approx 2700$ Da "high"
$M_w \approx 1800$ Da "medium"
$M_w \approx 900$ Da "low"

Fatty-acid endcapping – "Extreme" Examples



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Properties: from fully amorphous to semi-crystalline polymers, from viscous oils to waxy solids

	Fatty-acid end-capping											
	C8-Caprylic			C10 - Capric			C12-Lauric			C18		
	Low Mw	Medium Mw	High Mw	Low Mw	Medium Mw	High Mw	Low Mw	Medium Mw	High Mw	Stearic (unbranched)	Oleic (unsaturated)	Isostearic (branched)
Odor	odorless or faint odor (faint ethyl acetate-like)					garlic	odorless or faint odor			low odor (faint ethyl acetate odor)		
Color	colorless to pale yellow/amber			colorless/pale yellow		white	white to light yellow			colorless viscous liquid to waxy off-white/pale yellow solids	colorless viscous oil to off-white waxy solids	white viscous oily waxes to white waxy solids
Texture	oil	oil	oil	oil	oil	solid wax	waxy/paste-like					
Structure	amorphous (no melting temperature observed) with very low Tg (< -45 ºC) or no observable Tg						Semi crystalline with low melting temperatures (<25 ºC) and low Tg (-35 to -50 ºC)			Semi crystalline with melting temperatures around 40 ºC (at the high MW end) and low Tg (-40 to -60 ºC); low Mw oligomers do not exhibit observable Tm or Tg		amorphous (no Tm observed) with very low Tg (< -50 ºC) or no observable Tg (at lowest Mw)
Td	thermally stable to at least 200 ºC											

General Trends

Low M_w
viscous oil
colorless/white

High M_w
wax/solid
off-white/yellow

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Solubility: Opportunity or Challenge?

- Solubility assessed at **10 %** w/v, **1 %** w/v, and **0.1 %** w/v
- No differences observed for different Mw

	Solvent	Fatty-acid end-capping				
		C2-Acetate	C22-Behenate	C18		
				Stearic (unbranched)	Isostearic (branched)	Oleic (unsaturated)
Cosmetic	water	Insoluble	insoluble	insoluble	insoluble	insoluble
	glycerol	Insoluble	insoluble	insoluble	insoluble	insoluble
	1,3-Propanediol	Insoluble	insoluble	insoluble	insoluble	insoluble
	Propylene glycol	Insoluble	insoluble	insoluble	insoluble	insoluble
	Dimethicone	soluble	insoluble	insoluble	insoluble	insoluble
	Capric/Caprylic	Insoluble	insoluble	insoluble	insoluble	insoluble
	Triglycerides	N/A	N/A	insoluble	insoluble	insoluble
	Isopropyl palmitate	Insoluble	insoluble	insoluble	insoluble	insoluble
	mineral oil	soluble	insoluble	insoluble	insoluble	insoluble
	Tween 20	soluble	insoluble	insoluble	insoluble	insoluble
	Isopropyl alcohol	Insoluble	insoluble	insoluble	insoluble	insoluble
Organic	Chloroform	soluble	soluble	soluble	soluble	soluble
	Dichloromethane	soluble	soluble	soluble	soluble	soluble
	acetone	Slightly soluble	Slightly soluble	soluble	soluble	soluble
	ethyl acetate	Slightly soluble	Slightly soluble	Slightly soluble	Slightly soluble	Slightly soluble
	dimethyl sulfoxide	soluble	soluble	soluble	soluble	soluble
	n-hexane	N/A	N/A	insoluble	insoluble	insoluble

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Surface tension: Good surfactants, especially those based on long-chain fatty acids

Surface Tension of pure DMSO:
44 mN/m

Surface Tensions (mN/m) of DMSO solutions of FA-OPS

Increasing chain length ↓

	High M_w	Medium M_w	Low M_w
Acetic (C2)	37.8	41.6	41.9
Caprylic (C8)	37.0	38.9	40.6
Capric (C10)	37.7	39.7	39.9
Lauric (C12)	31.7	36.5	38.3
Stearic (C18)	30.6	29.1	31.0
Isostearic (C18)	30.4	28.4	29.4
Oleic (C18)	30.5	33.6	33.7
Behenic (C22)	27.6	31.4	34.6

Measurements taken after drop equilibration for ca. 5 min at RT

- Surface tension of 1 % w/w solutions of FA-capped oligomers measured by pendant drop shape analysis
- All oligomers reduce surface tension of DMSO
- Longer chain fatty-acids result in larger reduction of surface tension.

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Viscosity: Tunable property

Viscosities of dilute polymer solutions in dichloromethane were measured at different concentrations using an electromagnetic viscometer.

- **1 % w/v solutions of FA-capped OPS exhibited no change in the viscosity of the solution relative to pure solvent :**
  - Possibly good for cosmetic formulation purposes
  - Oligomers at 1 wt % may not significantly alter the viscosity of the formula

- **2.5 % w/v solutions of FA-capped OPS exhibited only a modest increase in solution viscosity :**
  - Relative viscosities were generally between 1.1 - 1.25.
  - Higher MW oligomers tended to yield higher solution viscosities
  - Little differences between different fatty acid-capped oligomers within same Mw range

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Summary: Formulate to Innovate

Alcohol-terminated oligomeric propanediol succinates of varying molecular weight were synthesized and end-capped with various fatty acids (a total of 24 unique oligomers were prepared) :

- FA-capped OPSs were characterized by NMR and FT-IR spectroscopies.
- Thermal properties (Tg, Tm, Td) were analyzed by DSC and TGA
- Solution behavior of these oligomers was studied
- Surface tension and viscosity of dilute polymer solutions were measured confirming that longer fatty acid chains had greater surfactant properties
- Viscosity of dilute solutions unchanged at low oligomer concentrations : at higher concentrations, viscosity changed more as a function of molecular weight than fatty acid chain length

Next step is formulation work on these unique materials, we are providing this data to accelerate innovation at our customers

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