



## Bio-Based Polyurethanes That Work



# Polyurethanes: The Case For Renewable Polyester Polyols

**Consumers of bio-based intermediates enjoy more stable costs than their competitors using petroleum-based intermediates.** Myriant's Developmental Polyester Polyols are made from bio-succinic acid, and will allow polyurethane manufacturers to make products with a smaller environmental footprint and no performance penalty, at a competitive cost.

## **POLYESTER POLYOLS - BUILDING BLOCKS FOR THE THINGS YOU USE EVERYDAY**

Petroleum-based polyester polyols are in everything from couches and mattresses to packaging and toys. As consumer demand grows for "greener" products, manufacturers seek solutions for producing polyester polyols that reduce their reliance on petroleum. Myriant has that solution.

Myriant has produced a line of developmental polyester polyols using bio-succinic acid as a raw material. While Myriant will not be manufacturing or selling polyester polyols, we are offering these materials in an effort to assist polyol formulators in exploring the advantages of bio-succinic acid in polyurethanes.



# Polyester Polyol Chemistry

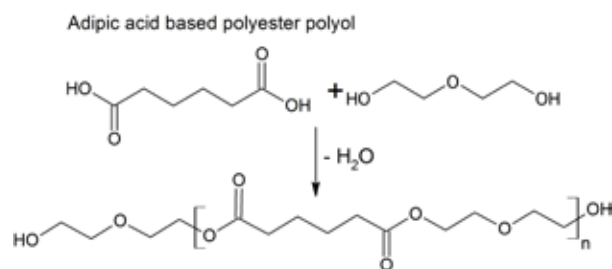
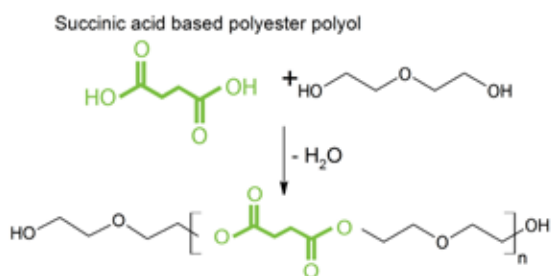
## Making Polyurethanes Greener

### Myriant's Bio-Succinic Acid Can Replace Adipic Acid in Polyols, Which Increases the Renewable Content Up to 100% Based on the Choice of Diol.

Adipic acid is the most common aliphatic diacid used to make polyester polyols. Succinic acid has the same chemical properties as adipic acid and thus can generally be used without changes to the manufacturing process. Myriant's bio-succinic acid can replace adipic acid in polyols, which increases the renewable content up to 66%.

The renewable content of Myriant's Developmental Polyester Polyols available for sampling are shown in the table below. Also shown are the corresponding adipic acid-based polyester polyols used for comparison, along with their bio-based carbon content.

Succinic Polyols			Adipic Polyols		
Product Code	Diol	Bio-Based Carbon Content	Control Sample ID	Diol	Bio-Based Carbon Content
DGTA-56	DEG/PEG/TMP	47	APTA-56	DEG/TMP	0
DGTB-56	DEG/PEG/TMP	47	ABTB-56	DEG/TMP	0
EG-110	EG	66	APEG-110	EG	0
DG-110	DEG	50	APDG-110	DEG	0
HD-110	HDO	40	APHD-110	HDO	0



# Bio-Based Polyurethanes

## Higher Renewable Content With Equal Performance

### All of Myriant's Developmental Polyester Polyols Work as Drop-In Replacements for Their Adipic Acid-Based Counterparts.

Polyester polyols, typically produced from adipic acid, are used to produce polyurethanes with good mechanical properties, abrasion resistance and chemical resistance. Succinic acid can be directly substituted for adipic acid in these polyester polyols. The polyols are then used to make polyurethanes with a higher renewable content that can be incorporated into standard formulations to give predictable performance in specialty foams, coatings, adhesives, elastomers and TPUs.

The tables below show the characterization of the succinic acid and adipic acid polyols.

Myriant's Developmental Polyester Polyols – Based on Bio-Succinic Acid				
Product Code	Diol	Type	OH Number	Viscosity (60 °C, cPs)
DGTA-56	DEG/PEG/TMP	Branched, f ~ 2.4	61	3150
DGTB-56	DEG/PEG/TMP	Branched, f ~ 2.7	64	4000
EG-110	EG	Linear, f = 2.0	107	400 (80 °C)
DG-110	DEG	Linear, f = 2.0	113	440
HD-110	HDO	Linear, f = 2.0	108	450

Adipic Polyester Polyols				
Control Sample ID	Diol	Type	OH Number	Viscosity (60 °C, cPs)
APTA-56	DEG/TMP	Branched, f ~ 2.4	76	440
APTB-56	DEG/TMP	Branched, f ~ 2.7	60	1340
APEG-110	EG	Linear, f = 2.0	90	415
APDG-110	DEG	Linear, f = 2.0	116	250
APHD-110	HDO	Linear, f = 2.0	95	450

# Bio-Based Polyurethanes

## Higher Renewable Content With Equal Performance

### Myriant's Developmental Polyester Polyols Have Similar Thermal and Mechanical Properties to Adipic Acid Polyols.

To evaluate the performance of the higher renewable content Developmental Polyester Polyols, polyurethane plaques were made using Bayer MaterialScience Desmodur 3200, a liquid aliphatic isocyanate based on hexamethylene diisocyanate with an NCO content of 23.0%, a viscosity of 2500 cPs and a functionality of 3.2.

Elastomer samples were prepared by preheating the components to 70 °C, mixing for one minute, pouring the mixture into a preheated dog bone mold and curing overnight at 85 °C. Test specimens from Myriant's Developmental Polyester Polyols and control specimens from the adipic acid polyester polyols were prepared. These formulations were not optimized for any specific application but were chosen to give the most direct physical property comparison between succinic acid and adipic acid when used in a polyurethane application.

### Thermal Properties

The thermal properties of the polyurethanes made from Myriant's Developmental Polyester Polyols, as well as the corresponding adipic acid controls, are shown in the table below. Two of the polyurethanes crystallized: Myriant's EG-110, with a melting point ( $T_m$ ) of 60 °C, and the adipic acid version of HD-110, with a melting point of 30 °C. In general, polyurethanes made from succinic acid-based polyester polyols have slightly higher glass transition temperatures than the adipic acid-based controls. This is the result of the slightly shorter four-carbon diacid causing a small increase in the rigidity of the backbone.

Succinic Polyols		Adipic Polyols	
Product Code	$T_g$ ( $T_m$ ) - °C	Control Sample ID	$T_g$ ( $T_m$ ) - °C
DGTA-56	-17	APTA-56	-28
DGTB-56	-16	APTB-56	-29
EG-110	-6 (60)	APEG-110	-30
DG-110	-12	APDG-110	-26
HD-110	-33	APHD-110	-44 (30)

# Bio-Based Polyurethanes

## Higher Renewable Content With Equal Performance

### Mechanical Properties

The data shown in the table below illustrates the similarity in properties between the succinic and adipic-based polyols. The Shore A and D hardness values were essentially the same, with the exception of the materials that showed crystallinity. In those cases, the crystalline elastomers exhibit higher hardness values than their amorphous counterparts.

Succinic Acid			Adipic Acid		
Product Code	Shore A	Shore D	Control Sample ID	Shore A	Shore D
DGTA-56	55	16	APTA-56	54	17
DGTB-56	54	16	APTB-56	66	20
EG-110	87	31	APEG-110	55	17
DG-110	61	21	APDG-110	65	20
HD-110	56	16	APHD-110	68	25

Tensile properties for the polyurethanes derived from Myriant's Developmental Polyester Polyols are shown below.

Succinic Acid				Adipic Acid			
Product Code	Break Strain (%)	Break Stress (MPa)	Tensile Modulus (MPa)	Control Sample ID	Break Strain (%)	Break Stress (MPa)	Tensile Modulus (MPa)
DGTA-56	39	0.9	3.0	APTA-56	25	0.6	2.9
DGTB-56	36	0.7	2.7	APTB-56	14	0.7	6.0
EG-110	44	2.9	36	APEG-110	33	0.9	3.4
DG-110	26	0.9	4.3	APDG-110	23	1.0	5.5
HD-110	16	0.5	4.0	APHD-110	25	1.1	5.6

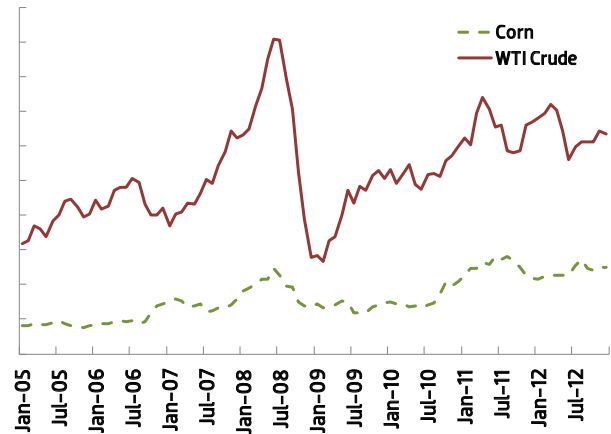
Theoretically, the shorter backbone of succinic acid should result in better abrasion resistance, giving succinic polyols an advantage in applications where abrasion resistance is required.

# Bio-Based Polyurethanes

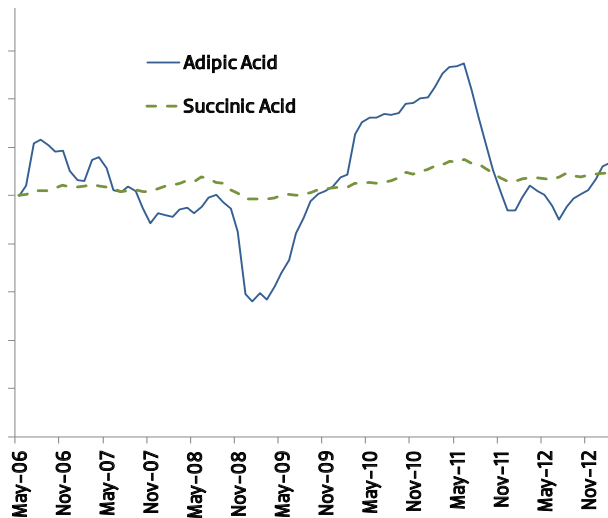
## Long Term Price Stability With No Green Premium

### Raw Material Cost for Myriant's Developmental Polyester Polyols is Lower and More Stable Than Petroleum-Derived Polyols.

Traditionally, polyurethanes are derived from raw materials that use petroleum as their carbon source, for which crude oil price is a primary cost driver. Myriant's Developmental Polyester Polyols are based on bio-succinic acid, which uses industrial sugar as its carbon source. Corn pricing is an historic indicator of the cost of these sugars. This chart shows the price of crude oil over a seven year period compared to the price of corn. The price of crude oil has had very large price peaks and valleys, with a generally increasing trend. The price line for corn is much flatter, indicative of a more stable pricing history.



### Myriant's Developmental Polyester Polyols Use Raw Materials That are Cost Competitive With Adipic Acid.



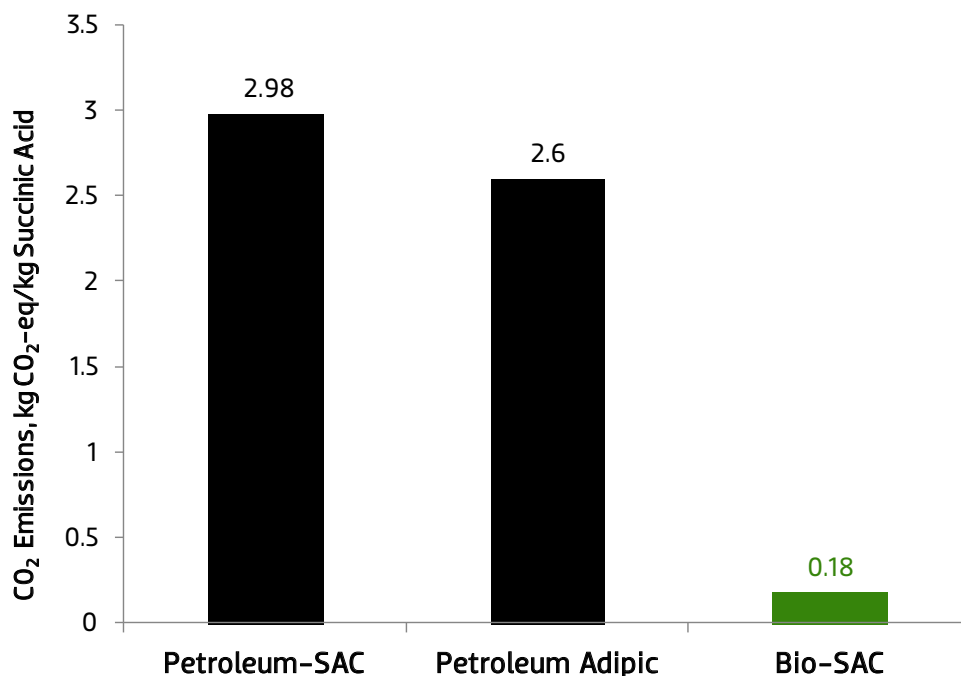
Many chemical intermediates used to produce polyurethanes are priced based on an index relating to their primary raw material cost drivers. As an example, adipic acid is typically priced based on a formula tied to benzene and ammonia prices, both of which follow crude oil prices. As the chart shows, the resulting price is highly volatile, driven primarily by fluctuations in oil prices. To illustrate the advantage of agricultural-based feedstocks, we used an example of a succinic acid price formula based on corn prices. This results in a more stable long term price and predictable cost for users of chemical intermediates. The result? Consumers of bio-based intermediates will enjoy more stable costs than their competitors using petroleum-based intermediates.

# Bio-Based Polyurethanes

## Smaller Environmental Footprint

### Polyurethanes Made From Renewable Raw Materials Will Have a Smaller Environmental Footprint Than Those Made From Petroleum-Based Raw Materials.

The life cycle analysis of Myriant's bio-succinic acid process shows that the carbon dioxide emissions of the bio-based process are substantially lower than either the existing petroleum-based process to make succinic acid from maleic anhydride, or the process to make adipic acid from benzene. Polyester polyols made from bio-succinic acid will enjoy a similar reduction in their environmental footprint compared to those made from adipic acid.





# APPENDIX: DEVELOPMENTAL POLYESTER POLYOLS

## Product Data Sheets

### Linear Polyester Polyols

DG-110 Developmental Polyester Polyol

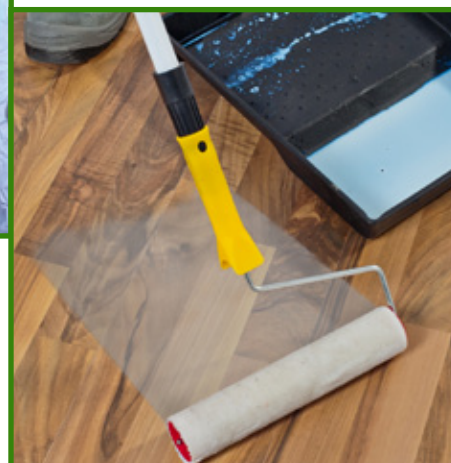
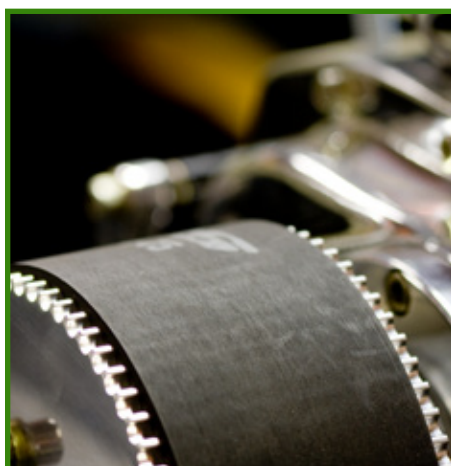
EG-110 Developmental Polyester Polyol

HD-110 Developmental Polyester Polyol

### Branched Polyester Polyols

DGTA-56 Developmental Polyester Polyol

DGTB-56 Developmental Polyester Polyol



# DG-110 DEVELOPMENTAL POLYESTER POLYOL

For Elastomers, Coatings and Adhesives

**Consumers of bio-based intermediates enjoy more stable costs than their competitors using petroleum-based intermediates. Myriant's Developmental Polyester Polyols are made from bio-succinic acid, and will allow polyurethane manufacturers to make products with a smaller environmental footprint and no performance penalty, at a competitive cost.**

## Derived From Succinic Acid and Diethylene Glycol CAS No. 26183-02-8

Myriant's DG-110 developmental linear polyester polyol, made from bio-succinic acid and diethylene glycol, provides renewable content and good properties for elastomers, coatings and adhesives. As with any product, the performance of Myriant's DG-110 polyol in any application must be verified by the end user.

Product Properties	Value
Hydroxyl Number	113
Functionality	2.0
Viscosity (60 °C, cPs)	440
Moisture (wt%)	0.04
Acid Value	0.8
Color (APHA)	300
Calculated Bio-Based Carbon Content (%)	50

## Storage and Handling

Myriant's DG-110 developmental linear polyester polyol is hygroscopic and may absorb water. Containers should be kept tightly closed and protected from contamination, especially by moisture. The product should be stored in a cool, dry location. The product may be heated prior to use to reduce the viscosity for processing.

## Health and Safety Information

Before working with this product, read and become familiar with the hazards, proper use and handling characteristics of the product. When using this product, the information and advice given in the Material Safety Data sheet, available on request, should be observed.

## Packaging

Samples are available in 1-quart containers.

# EG-110 DEVELOPMENTAL POLYESTER POLYOL

For Elastomers, Coatings and Adhesives

**Consumers of bio-based intermediates enjoy more stable costs than their competitors using petroleum-based intermediates. Myriant's Developmental Polyester Polyols are made from bio-succinic acid, and will allow polyurethane manufacturers to make products with a smaller environmental footprint and no performance penalty, at a competitive cost.**

## Derived From Succinic Acid and Ethylene Glycol CAS No. 25569-53-3

Myriant's EG-110 developmental linear polyester polyol, made from bio-succinic acid and ethylene glycol, provides renewable content and good properties for elastomers, coatings and adhesives. As with any product, the performance of Myriant's EG-110 polyol in any application must be verified by the end user.

Product Properties	Value
Hydroxyl Number	107
Functionality	2.0
Viscosity (80 °C, cPs)	400
Moisture (wt%)	0.01
Acid Value	0.52
Color (APHA)	245
Calculated Bio-Based Carbon Content (%)	66

## Storage and Handling

Myriant's EG-110 developmental linear polyester polyol is hygroscopic and may absorb water. Containers should be kept tightly closed and protected from contamination, especially by moisture. The product should be stored in a cool, dry location. The product may be heated prior to use to reduce the viscosity for processing.

## Health and Safety Information

Before working with this product, read and become familiar with the hazards, proper use and handling characteristics of the product. When using this product, the information and advice given in the Material Safety Data sheet, available on request, should be observed.

## Packaging

Samples are available in 1-quart containers.

# HD-110 DEVELOPMENTAL POLYESTER POLYOL

For Elastomers, Coatings and Adhesives

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## Derived From Succinic Acid and 1,6-Hexanediol CAS No. 27516-89-8

Myriant's HD-110 developmental linear polyester polyol, made from bio-succinic acid and 1,6 Hexanediol, provides renewable content and good properties for elastomers, coatings and adhesives. As with any product, the performance of Myriant's HD-110 polyol in any application must be verified by the end user.

Product Properties	Value
Hydroxyl Number	108
Functionality	2.0
Viscosity (60 °C, cPs)	450
Moisture (wt%)	0.02
Acid Value	0.7
Color (APHA)	110
Calculated Bio-Based Carbon Content (%)	40

## Storage and Handling

Myriant's HD-110 developmental linear polyester polyol is hygroscopic and may absorb water. Containers should be kept tightly closed and protected from contamination, especially by moisture. The product should be stored in a cool, dry location. The product may be heated prior to use to reduce the viscosity for processing.

## Health and Safety Information

Before working with this product, read and become familiar with the hazards, proper use and handling characteristics of the product. When using this product, the information and advice given in the Material Safety Data sheet, available on request, should be observed.

## Packaging

Samples are available in 1-quart containers.

# DGTA-56 DEVELOPMENTAL POLYESTER POLYOL

## For Foams

**Consumers of bio-based intermediates enjoy more stable costs than their competitors using petroleum-based intermediates. Myriant's Developmental Polyester Polyols are made from bio-succinic acid, and will allow polyurethane manufacturers to make products with a smaller environmental footprint and no performance penalty, at a competitive cost.**

### Derived From Succinic Acid, Diethylene Glycol and Polyethylene Glycol CAS No. 380894-87-1

Myriant's DGTA-56 developmental non-linear polyester polyol, made from bio-succinic acid, diethylene glycol and polyethylene glycol, provides renewable content and useful properties for foams. As with any product, the performance of Myriant's DGTA-56 polyol in any application must be verified by the end user.

Product Properties	Value
Hydroxyl Number	61
Functionality	2.4
Viscosity (60 °C, cPs)	3150
Moisture (wt%)	0.03
Acid Value	1.4
Color (APHA)	430
Calculated Bio-Based Carbon Content (%)	47

### Storage and Handling

Myriant's DGTA-56 developmental non-linear polyester polyol is hygroscopic and may absorb water. Containers should be kept tightly closed and protected from contamination, especially by moisture. The product should be stored in a cool, dry location. The product may be heated prior to use to reduce the viscosity for processing.

### Health and Safety Information

Before working with this product, read and become familiar with the hazards, proper use and handling characteristics of the product. When using this product, the information and advice given in the Material Safety Data sheet, available on request, should be observed.

### Packaging

Samples are available in 1-quart containers.

# DGTB-56 DEVELOPMENTAL POLYESTER POLYOL

## For Foams

**Consumers of bio-based intermediates enjoy more stable costs than their competitors using petroleum-based intermediates. Myriant's Developmental Polyester Polyols are made from bio-succinic acid, and will allow polyurethane manufacturers to make products with a smaller environmental footprint and no performance penalty, at a competitive cost.**

### Derived From Succinic Acid, Diethylene Glycol and Polyethylene Glycol CAS No. 380894-87-1

Myriant's DGTB-56 developmental non-linear polyester polyol, made from bio-succinic acid, diethylene glycol and polyethylene glycol, provides renewable content and useful properties for foams. As with any product, the performance of Myriant's DGTB-56 polyol in any application must be verified by the end user.

Product Properties	Value
Hydroxyl Number	64
Functionality	2.7
Viscosity (60 °C, cPs)	4000
Moisture (wt%)	0.01
Acid Value	1.2
Color (APHA)	480
Calculated Bio-Based Carbon Content (%)	47

### Storage and Handling

Myriant's DGTB-56 developmental non-linear polyester polyol is hygroscopic and may absorb water. Containers should be kept tightly closed and protected from contamination, especially by moisture. The product should be stored in a cool, dry location. The product may be heated prior to use to reduce the viscosity for processing.

### Health and Safety Information

Before working with this product, read and become familiar with the hazards, proper use and handling characteristics of the product. When using this product, the information and advice given in the Material Safety Data sheet, available on request, should be observed.

### Packaging

Samples are available in 1-quart containers.

# Bio-Based Polyurethanes

Higher Renewable Content, Equal Performance, No Green Premium

## Summary

Myriant's Developmental Polyester Polyols perform as direct drop-in replacements for adipic acid polyols in polyurethanes with applicability to specialty foams, elastomers, coatings, adhesives and TPUs. The long-term cost advantage of renewable feedstocks compared to crude oil results in more stable prices for polyurethane raw materials. The real environmental benefit of renewable chemicals comes from the reduced emissions during manufacture, a benefit that provides end products with smaller environmental footprints.

## Storage and Handling

Myriant's Developmental Polyester Polyols are hygroscopic and may absorb water. Containers should be kept tightly closed and protected from contamination, especially by moisture. The product should be stored in a cool, dry location. The product may be heated prior to use to reduce the viscosity for processing.

## Health and Safety Information

Before working with this product, read and become familiar with the hazards, proper use and handling characteristics of the product. When using this product, the information and advice given in the Material Safety Data Sheet should be observed. Normal precautions for the handling of chemicals, including wearing proper personal protective equipment, should be followed at all times. A Material Safety Data Sheet is available on request.

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