

# PET Modification with 2-Methyl-1,3-Propanediol

## “MPDiol-co-PET”: A Novel Copolymer for Fiber Applications

**Steven A. Schwartz** and **Paul M. Puckett**, Lyondell Chemical Company;  
**Anil W. Saraf**, Equistar Chemicals, L.P.;  
**Joseph E. Spruiell**, Materials Science and Engineering, University of Tennessee

*Presented at Polyester 2003, December 1-3, 2003 – Zurich, Switzerland  
The Polyester & PET Chain, 8th World Congress, Maack Business Services*



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**Abstract:** Glycols other than ethylene glycol and dicarboxylic acids other than terephthalic acid are used routinely in copolymerization reactions to modify the properties and the processability of PET (polyethyleneterephthalate). The objective of this paper is to describe the effects of a new comonomer, 2-methyl-1,3-propanediol (MPDiol® glycol), on the structure, properties, and processing characteristics of PET copolymers. Specific advantages for MPDiol-modified copolyester fibers will be reviewed, including effects on spinning and dye absorption characteristics as well as the mechanical properties of the fibers obtained.



# Lyondell Chemical Company Enterprise



## Lyondell Chemical

Intermediate Chemicals & Derivatives

- \$3.2 Billion (2002)
- 3,300 Employees
- HQ in Houston, TX
- R&D in Newtown Square, PA
- 6 Manuf Sites
- Leading Producer of PO, SM, MTBE, PG, POD, TDI, **BDO**, **MPDiol® Glycol**



## Equistar Chemicals

Petrochemicals & Polymers

- \$5.5 Billion (2002)
- 3,400 Employees
- HQ in Houston, TX
- R&D in Cincinnati, OH
- 16 Manuf Sites in U.S.
- Leading Producer of Ethylene, Propylene, Butadiene, Benzene, EO, **EG**, EOD, PE, PP, Toluene



## Lyondell-Citgo Refining

Refining

- \$3.4 Billion (2002)
- 1,000 Employees
- HQ in Houston, TX
- Refine Extra-Heavy Crude Oil (Venezuelan Crude)
- 268,000 bbl/d Capacity
- Major Products are Gasoline, Diesel, Benzene, **Paraxylene (PX)**, Orthoxylene

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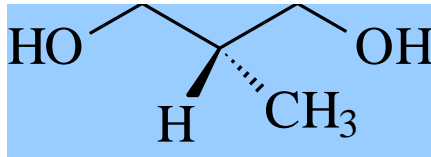
• Intermediate Chemicals and Derivatives in formerly **ARCO Chemical Company**

• Equistar Chemicals is ~71% owned by Lyondell Chemical Company

• **Lyondell Chemical Company Fits into the Supply Chain of Polyester**

- **PX**
- **BDO (PBT)**
- **EG (PET)**

## MPDiol® Glycol



### 2-methyl-1,3-propanediol

CAS Number	2163-42-0
Molecular Weight	90.1g/mole
Melting Point	< -60 C
Boiling Point	213 C
Density (20 C)	8.47 lb/gal (1.02 g/cc)
Viscosity (20 C)	174 cP
Vapor Pressure @ 100C	4.3 mm Hg

Miscible w/EG; Stable Slurry

Comparable Reactivity

Safe, Easy to Handle, Clear Liquid



**MPDiol is Compatible  
with Existing PET  
Materials and  
Manufacturing**

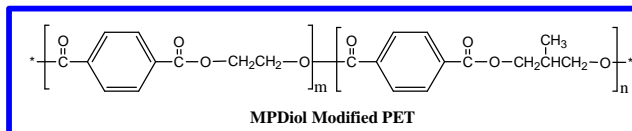
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MPDiol is a “drop-in” to conventional PET production:

- Miscible w/EG
- PET Reaction Conditions
- Comparable Reactivity

## MPDiol-co-PET



- Comonomer Feed Levels: 4 to 30 mole % (1.6 to 11.4 wt. %)
- Melt-Phase Polymerization (0.60-0.65 I.V.)
- Solid-State Polymerization (up to 10 mole % (3.9 wt. %) up to 0.80 I.V.)

**MPDiol® is a Straightforward “Drop-in” to Conventional Polymerization Processing**

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This type of modification chemistry is disclosed in several patents, including:

1. Toga, Y.; Shimada, T.; Okamoto, I., US Patent 4,415,727 (1983).
2. Chen, S.C.; Lin, F.S.; Chou, J.-Y.; Wang, H.Y.; Lee, M.S.; Chen, M.-S.; Huang, Y.J.; Sun, H.S., US Patent 5,916,677 (1999).

## MPDiol-co-PET

Broadens the Potential for PET  
(Fibers) Through

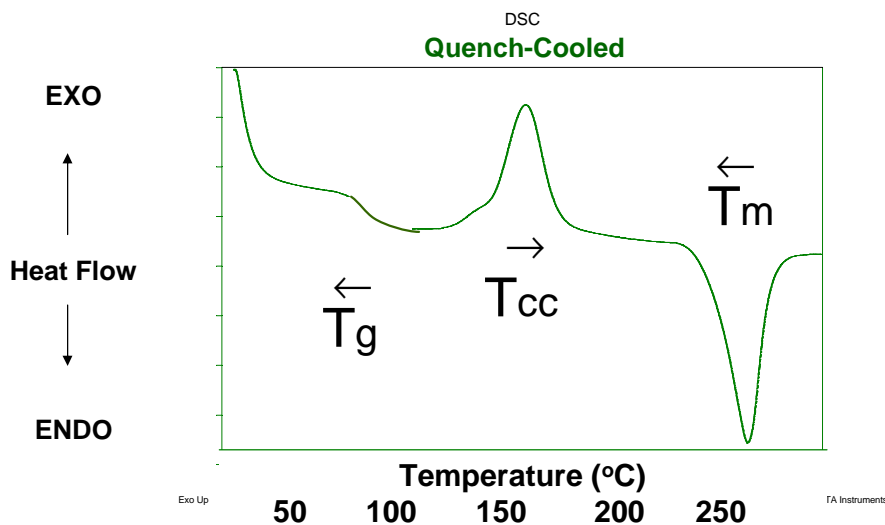
- **Processing Efficiencies**
- **Property Development**

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Our objective for this presentation is to demonstrate some features that we have observed for MPDiol-co-PET and relate them to the **substantial potential for exploiting these features to yield processing and property advantages.**

## Effect of Comonomer on Thermal Transitions



### **ADVANTAGES**

- **Process Efficiencies – Melt Spinning; Draw Texturing**
- **Properties – Dyeability; Hand; Aesthetics**

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AS EXPECTED:

Lowers both the glass transition temperature and the melting temperature

Raises the crystallization temperature

**T<sub>g</sub>:**

**More flexible MPDiol comonomer units cause a decrease in T<sub>g</sub> - less thermal energy required for molecular motion and rearrangement**

additional CH<sub>3</sub> group promotes main chain bond rotation

additional CH<sub>3</sub> group acts like a chain end - increases free volume

**T<sub>cc</sub>: CRYSTALLIZATION/MELT-PROCESSING**

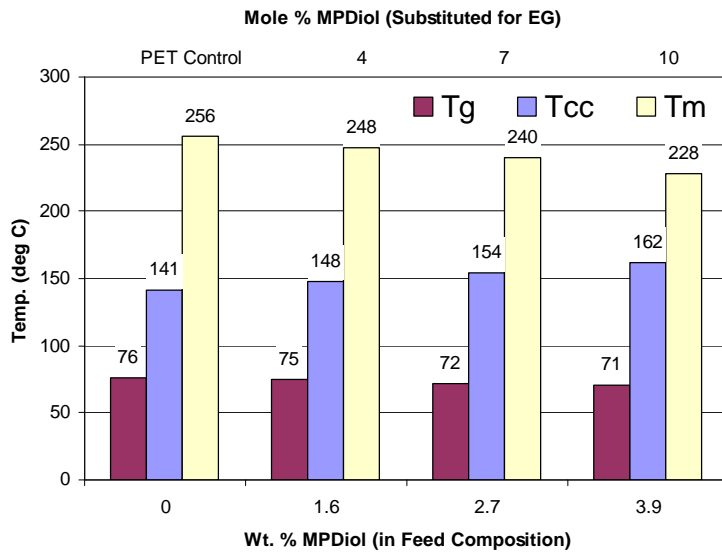
**More energy is required** for the molecular rearrangement that is required for homogeneous nucleation and crystal growth as MPDiol content increases. **Takes energy and time to sort through the polymer segments and reject MPDiol**

**T<sub>m</sub>:**

**MPDiol comonomer exclusion** ® **thinner lamellae** (than would likely result from PET homopolymer)

# Effect of MPDiol on Thermal Transitions

## Quench-Cooled Pellets



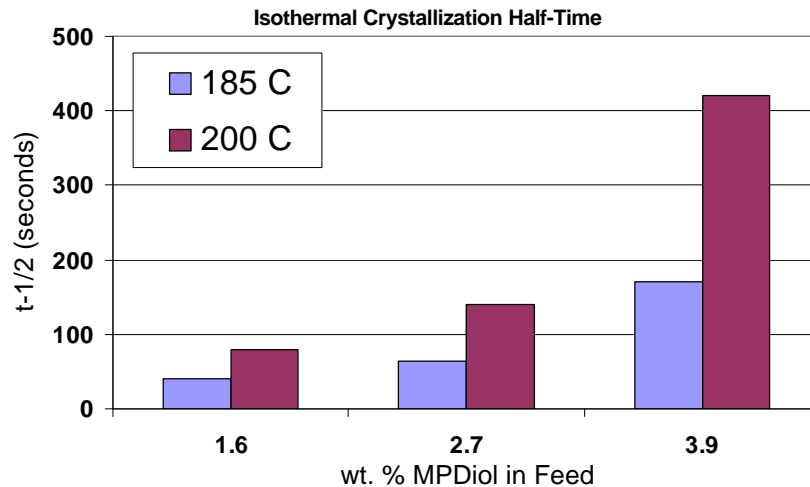
**Substantial Effect at Low MPDiol Levels**

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## Effect of MPDiol on Crystallization Kinetics

Quench-Cooled Pellets



**MPDiol Retards Crystallization  $\Rightarrow$  Broader Processing Window**  
•Melt Spinning – “Wind-Up Speed Suppression”  
•Draw-Texturization

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### Wind-Up Speed Suppression (WUSS):

Fiber spun at high speeds is **made to behave as if it is spun at a lower speed**

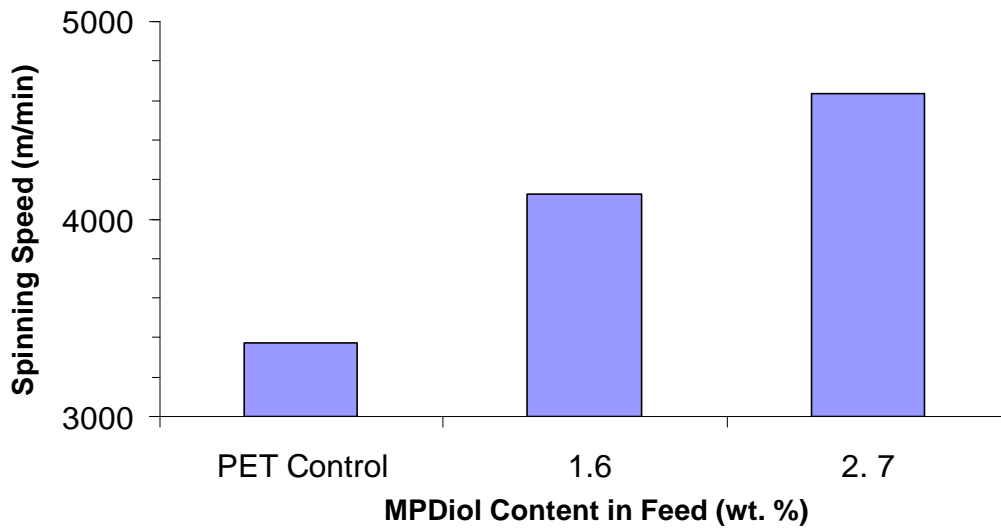
Polyester fibers, when melt spun above a certain speed (typically 3500 m/min), tend to **crystallize in the spin line itself**, which drastically changes the mechanical properties of the yarn to **render the yarn properties useless in post-processing of POY processes.**

Above a certain speed the rates of crystallization tend to become so high that the fibers tend to undergo a cohesive failure at the freeze line.

**MPDiol delays the onset of stress-induced crystallization to higher levels of stress and consequently higher speeds.** The fiber processed at higher speeds, retains a majority of the physical properties.

# MPDiol-co-PET Increased Spinning Speed

Monofilament Processing in Lab Set-up

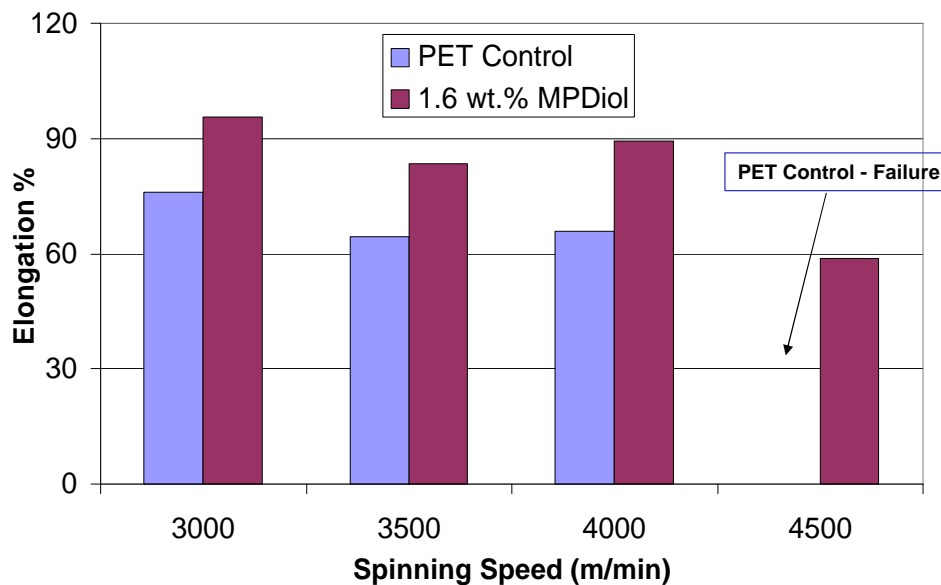


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## MPDiol-co-PET Increased POY Elongation

Elongation vs. Spinning Speed  
(12 hole spinneret, 33 denier POY)



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### Wind-Up Speed Suppression (WUSS):

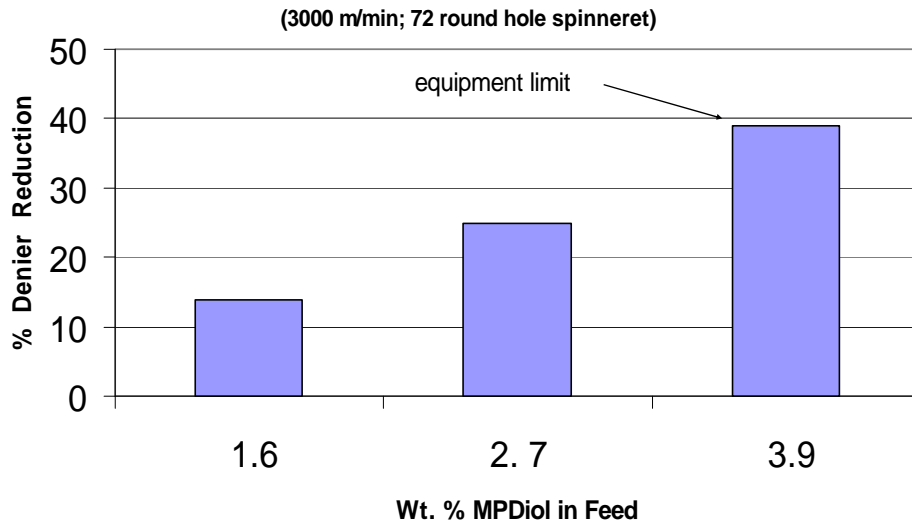
- Fiber spun at high speeds is made to behave as if it is spun at a lower speed

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- Above a certain speed the rates of crystallization tend to become so high that the fibers tend to undergo a cohesive failure at the freeze line.

- MPDiol delays the onset of stress-induced crystallization to higher levels of stress and consequently higher speeds. The fiber processed at higher speeds, retains a majority of the physical properties.

## MPDiol-co-PET Reduced Denier POY



**> 40% Finer Denier at Low MPDiol Level**

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### Wind-Up Speed Suppression (WUSS):

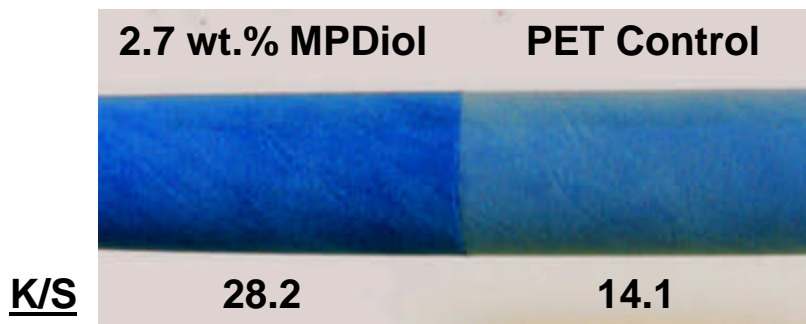
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## MPDiol-co-PET Dyeability Enhancement



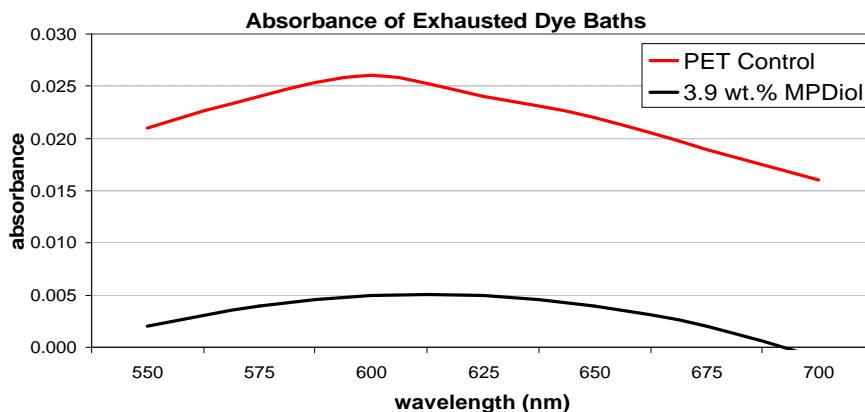
Competitive Pressure Dyebath (130°C) to Exhaustion (No Carrier)

- **Increased Dye Uptake Rate**
- **Improvement in Fabric “Hand”**

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## MPDiol-co-PET Greater Dyebath Exhaustion



Separate, Atmospheric (100°C) Dyebath to Exhaustion (No Carrier)

### **Dyeability Enhancement + Cost Reduction**

- Carrier-Free
- Low Temperature
- Open Beck

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2 wt. % (on weight of fiber) disperse dye solutions  
(Dianix Blue AD-R from Dystar)

#### Dyeing Cycle:

1. T=25°C to 100°C at 2°C/min
2. T=100°C for 45 min
3. T=100°C to 50°C at 2°C/min

## MPDiol® Glycol- Substituted PET Summary

- **Crystallization Retardation**
  - Stress-induced Crystallization at Higher Spinning Speeds and Elongation
    - Fine Denier Processability, Softer Feel
    - Wind-up Speed Suppression
- **Reduced Thermal Transitions**
  - Low Melt/High Shrinkage
    - Thermal Bonding Material in Conjugate Fibers
    - Bonding: Low Temperatures/Higher Speeds
    - Heat Texturing to Yield High Bulk Yarns – Self-Bulking/Self-Crimping
- **Improved Dyeability**
  - Carrier-Free
  - Low Temperature/Open Beck Process

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## **MPDiol® Glycol- Substituted PET Conclusions**

- Processing Efficiencies
- Innovative Yarns – Wovens and Non-Wovens
- Reduced Dyeing Costs and Energy Savings
  - Low Temperature/Low pressure
  - Environmentally Friendly (carrier-free dyeing)
- Other Potential Applications – Film, Sheet

**PRODUCT DIFFERENTIATION  
THROUGH EASILY MADE  
COPOLYMER COMPOSITIONS**

## Acknowledgements

Wellman

University of Tennessee

YKK

North Carolina State University

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