Abstract
Process Economics Program Report 128B
SYNDIOTACTIC POLYPROPYLENE
(December 1995)

As of early 1995, syndiotactic polypropylene (sPP) has been produced only in experimental quantities by Fina Oil and Chemical Company and Mitsui Toatsu.

This Report reviews the technology for sPP production and examines the process economics of a conceptual bulk loop reactor process, a conceptual bulk slurry process, and a conceptual diluent slurry process. The study also reports the industry status of sPP, including properties of some laboratory and experimental products.

This Report should be useful not only to present and future polypropylene producers but also to present and future producers of other polyolefins, such as low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE), and to producers and users of other thermoplastics, such as polyvinyl chloride (PVC).
## CONTENTS

### GLOSSARY

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>GLOSSARY</td>
<td>xiii</td>
</tr>
</tbody>
</table>

### 1 INTRODUCTION

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 INTRODUCTION</td>
<td>1-1</td>
</tr>
</tbody>
</table>

### 2 SUMMARY

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 SUMMARY</td>
<td>2-1</td>
</tr>
<tr>
<td>INDUSTRIAL ASPECTS</td>
<td>2-1</td>
</tr>
<tr>
<td>Product Properties</td>
<td>2-1</td>
</tr>
<tr>
<td>Injection Molded Articles</td>
<td>2-2</td>
</tr>
<tr>
<td>Films</td>
<td>2-2</td>
</tr>
<tr>
<td>sPP-IPP Blends</td>
<td>2-3</td>
</tr>
<tr>
<td>Molecular Structures/Morphology</td>
<td>2-3</td>
</tr>
<tr>
<td>Potential Markets</td>
<td>2-3</td>
</tr>
<tr>
<td>TECHNICAL ASPECTS</td>
<td>2-4</td>
</tr>
<tr>
<td>Transition Metal-Containing Catalysts with Cyclopentadienyl Ligands (Metallocene Catalysts)</td>
<td>2-4</td>
</tr>
<tr>
<td>Titanium Tetrabenzyl and Zirconium Tetrabenzyl</td>
<td>2-5</td>
</tr>
<tr>
<td>Vanadium-Based Catalysts</td>
<td>2-5</td>
</tr>
<tr>
<td>Process</td>
<td>2-6</td>
</tr>
<tr>
<td>Patent Review</td>
<td>2-6</td>
</tr>
<tr>
<td>PROCESS ECONOMICS</td>
<td>2-6</td>
</tr>
<tr>
<td>A Bulk Loop Reactor Process</td>
<td>2-6</td>
</tr>
<tr>
<td>A Bulk Slurry Process</td>
<td>2-7</td>
</tr>
<tr>
<td>A Diluent Slurry Process</td>
<td>2-9</td>
</tr>
<tr>
<td>Cost Comparison of the Three Conceptual sPP Processes</td>
<td>2-9</td>
</tr>
</tbody>
</table>

### 3 INDUSTRY STATUS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 INDUSTRY STATUS</td>
<td>3-1</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>3-1</td>
</tr>
<tr>
<td>EXPECTED PRODUCERS</td>
<td>3-1</td>
</tr>
<tr>
<td>PRODUCT PROPERTIES</td>
<td>3-1</td>
</tr>
<tr>
<td>Injection Molded Articles</td>
<td>3-9</td>
</tr>
<tr>
<td>Films</td>
<td>3-18</td>
</tr>
<tr>
<td>sPP-IPP Blends</td>
<td>3-23</td>
</tr>
<tr>
<td>Molecular Structures/Morphology</td>
<td>3-23</td>
</tr>
<tr>
<td>POTENTIAL MARKETS</td>
<td>3-28</td>
</tr>
<tr>
<td>PRICE</td>
<td>3-28</td>
</tr>
</tbody>
</table>
CONTENTS (Continued)

4 TECHNOLOGY REVIEW 4-1

LITERATURE REVIEW 4-1
- Transition Metal-Containing Catalysts with Cyclopentadienyl Ligands (Metallocene Catalysts) 4-1
- Titanium Tetrabenzyl and Zirconium Tetrabenzyl 4-7
- Vanadium-based Catalysts 4-7
- Process 4-10

PATENT REVIEW 4-11
- Mitsui Toatsu (68 Patents) 4-11
- Fina (14 Patents) 4-12
- Hoechst (9 Patents) 4-12
- Exxon (5 Patents) 4-12
- Shell (2 Patents) 4-12
- Chisso (1 Patent) 4-12
- EniChem (1 Patent) 4-12
- Himont (1 Patent) 4-13
- Idemitsu (1 Patent) 4-13
- Mitsubishi Petrochemical (1 Patent) 4-13
- Mitsui Petrochemical (1 Patent) 4-13
- Showa Denko (1 Patent) 4-13
- Toa Nenryo (1 Patent) 4-13

5 SYNDIOTACTIC POLYPROPYLENE BY A BULK LOOP REACTOR PROCESS 5-1

PROCESS DESCRIPTION 5-1
- Polymerization 5-1
- Product Purification 5-3
- Product Finishing 5-3

PROCESS DISCUSSION 5-9

COST ESTIMATES 5-10
- Effect of Alternate Process Schemes and Higher Single Pass Conversion 5-23
- Price of sPP 5-23
### 6 SYNDIOTACTIC POLYPROPYLENE BY A BULK SLURRY PROCESS

**PROCESS DESCRIPTION**
- Polymerization 6-1
- Product Purification 6-3
- Product Finishing 6-3

**PROCESS DISCUSSION** 6-9

**COST ESTIMATES** 6-10
- Effect of Alternate Process Schemes and Higher Single Pass Conversion 6-23
- Price of sPP 6-23

### 7 SYNDIOTACTIC POLYPROPYLENE BY A DILUENT SLURRY PROCESS

**PROCESS DESCRIPTION**
- Polymerization and Solvent Recovery 7-1
- Product Purification 7-3
- Product Finishing 7-3

**PROCESS DISCUSSION** 7-9

**COST ESTIMATES** 7-10
- Effect of Alternate Process Schemes and Higher Polymerization Temperature 7-23
- Price of sPP 7-23

### 8 COST COMPARISON OF THE THREE CONCEPTUAL SYNDIOTACTIC POLYPROPYLENE PROCESSES

**APPENDIX A: PATENT SUMMARY TABLES**

**APPENDIX B: DESIGN AND COST BASES**

**APPENDIX C: CITED REFERENCES**

**APPENDIX D: PATENT REFERENCES BY COMPANY**

**APPENDIX E: PROCESS FLOW DIAGRAMS**
ILLUSTRATIONS

3.1 Effect of Syndiotacticity on Melting Point, Crystallization Temperature, and Heat of Fusion 3-5
3.2 Effect of Shear Rate on Viscosity of Selected sPPs and iPPs 3-7
3.3 Effect of Intrinsic Viscosity on Melt Index of Selected sPPs and iPPs 3-8
3.4 Effect of Aging on Elongation of Selected sPPs, iPPs, and Copolymer 3-13
3.5 Effect of Aging on Tensile Strength of Selected sPPs, iPPs, and Copolymer 3-14
3.6 Effect of Aging on Tensile Modulus of Selected sPPs, iPPs, and Copolymer 3-15
3.7 Effect of Aging on Flexural Modulus of Selected sPPs and Copolymer 3-16
3.8 Effect of Heating on Elongation of Selected sPPs and iPPs 3-17
3.9 Effect of Heat Seal Temperature on Seal Strength of Selected sPPs and Propylene Copolymer Films 3-21
3.10 Effect of Heat Seal Temperature on Seal Strength of Selected sPPs and sPP-Propylene Copolymer Blend 3-22
3.11 Effect of sPP Content on the Haze of an sPP/iPP Random Copolymer Blend 3-24
3.12 Effect of sPP Content on the Gardner Impact of an sPP/iPP Random Copolymer Blend 3-25
3.13 Effect of sPP Content on the Izod Impact of an sPP/iPP Random Copolymer Blend 3-26
3.14 Effect of sPP Content on the Flexural Modulus of an sPP/iPP Random Copolymer Blend 3-27
5.1 Syndiotactic Polypropylene by a Bulk Loop Reactor Process Process Flow Diagram E-3
5.2 Syndiotactic Polypropylene by a Bulk Loop Reactor Process Effect of Catalyst Consumption or Price on Product Value 5-17
5.3 Syndiotactic Polypropylene by a Bulk Loop Reactor Process Effect of Propylene Price on Product Value 5-18
ILLUSTRATIONS (Concluded)

5.4 Syndiotactic Polypropylene by a Bulk Loop Reactor Process
Effect of Capital-Related Costs on Product Value 5-19

5.5 Syndiotactic Polypropylene by a Bulk Loop Reactor Process
Effect of Production Capacity on Capital Investment 5-21

5.6 Syndiotactic Polypropylene by a Bulk Loop Reactor Process
Effect of Production Capacity on Production Cost and Product Value 5-22

6.1 Syndiotactic Polypropylene by a Bulk Slurry Process
Process Flow Diagram E-7

6.2 Syndiotactic Polypropylene by a Bulk Slurry Process
Effect of Capital-Related Costs on Product Value 6-17

6.3 Syndiotactic Polypropylene by a Bulk Slurry Process
Effect of Propylene Price on Product Value 6-18

6.4 Syndiotactic Polypropylene by a Bulk Slurry Process
Effect of Catalyst Consumption or Price on Product Value 6-19

6.5 Syndiotactic Polypropylene by a Bulk Slurry Process
Effect of Production Capacity on Capital Investment 6-21

6.6 Syndiotactic Polypropylene by a Bulk Slurry Process
Effect of Production Capacity on Production Cost and Product Value 6-22

7.1 Syndiotactic Polypropylene by a Diluent Slurry Process
Process Flow Diagram E-11

7.2 Syndiotactic Polypropylene by a Diluent Slurry Process
Effect of Capital-Related Costs on Product Value 7-17

7.3 Syndiotactic Polypropylene by a Diluent Slurry Process
Effect of Propylene Price on Product Value 7-18

7.4 Syndiotactic Polypropylene by a Diluent Slurry Process
Effect of Catalyst Consumption or Price on Product Value 7-19

7.5 Syndiotactic Polypropylene by a Diluent Slurry Process
Effect of Production Capacity on Capital Investment 7-21

7.6 Syndiotactic Polypropylene by a Diluent Slurry Process
Effect of Production Capacity on Production Cost and Product Value 7-22
### TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Syndiotactic Polypropylene Production Cost Summary</td>
<td>2-8</td>
</tr>
<tr>
<td>3.1</td>
<td>Properties of Selected Laboratory or Experimental sPPs</td>
<td>3-3</td>
</tr>
<tr>
<td>3.2</td>
<td>Properties of Two Experimental sPPs</td>
<td>3-4</td>
</tr>
<tr>
<td>3.3</td>
<td>Molecular Weight and Distribution, Xylene Solubles, and Die Swell of Selected sPPs and iPPs</td>
<td>3-6</td>
</tr>
<tr>
<td>3.4</td>
<td>Effect of Nucleators on the Crystallization of Selected sPPs</td>
<td>3-10</td>
</tr>
<tr>
<td>3.5</td>
<td>Physical Properties of Selected Injection Molded sPPs, iPPs, and Copolymer</td>
<td>3-11</td>
</tr>
<tr>
<td>3.6</td>
<td>Impact, Flexural, and Optical Properties of Selected Experimental sPPs and iPPs</td>
<td>3-12</td>
</tr>
<tr>
<td>3.7</td>
<td>Effect of Melt and Chill Roll Temperatures on the Properties of Two sPP Cast Films</td>
<td>3-19</td>
</tr>
<tr>
<td>3.8</td>
<td>Clarity and Impact Strength of Selected sPP-Modified and Other Polypropylene Films</td>
<td>3-20</td>
</tr>
<tr>
<td>4.1</td>
<td>Syndiotactic Polypropylene (sPP) Patent Summary</td>
<td>A-3</td>
</tr>
<tr>
<td>5.1</td>
<td>Syndiotactic Polypropylene by a Bulk Loop Reactor Process Design Bases and Assumptions</td>
<td>5-2</td>
</tr>
<tr>
<td>5.2</td>
<td>Syndiotactic Polypropylene by a Bulk Loop Reactor Process Stream Flows</td>
<td>5-4</td>
</tr>
<tr>
<td>5.3</td>
<td>Syndiotactic Polypropylene by a Bulk Loop Reactor Process Major Equipment</td>
<td>5-6</td>
</tr>
<tr>
<td>5.4</td>
<td>Syndiotactic Polypropylene by a Bulk Loop Reactor Process Utilities Summary</td>
<td>5-8</td>
</tr>
<tr>
<td>5.5</td>
<td>Syndiotactic Polypropylene by a Bulk Loop Reactor Process Total Capital Investment</td>
<td>5-13</td>
</tr>
<tr>
<td>5.6</td>
<td>Syndiotactic Polypropylene by a Bulk Loop Reactor Process Capital Investment by Section</td>
<td>5-14</td>
</tr>
<tr>
<td>5.7</td>
<td>Syndiotactic Polypropylene by a Bulk Loop Reactor Process Production Costs</td>
<td>5-15</td>
</tr>
</tbody>
</table>
TABLES (Continued)

5.8 Syndiotactic Polypropylene by a Bulk Loop Reactor Process Direct Costs by Section ($1,000/Yr) 5-20

5.9 Syndiotactic Polypropylene by a Bulk Loop Reactor Process Production Costs of Selected Process Schemes 5-24

6.1 Syndiotactic Polypropylene by a Bulk Slurry Process Design Bases and Assumptions 6-2

6.2 Syndiotactic Polypropylene by a Bulk Slurry Process Stream Flows 6-4

6.3 Syndiotactic Polypropylene by a Bulk Slurry Process Major Equipment 6-6

6.4 Syndiotactic Polypropylene by a Bulk Slurry Process Utilities Summary 6-8

6.5 Syndiotactic Polypropylene by a Bulk Slurry Process Total Capital Investment 6-13

6.6 Syndiotactic Polypropylene by a Bulk Slurry Process Capital Investment by Section 6-14

6.7 Syndiotactic Polypropylene by a Bulk Slurry Process Production Costs 6-15

6.8 Syndiotactic Polypropylene by a Bulk Slurry Process Direct Costs by Section ($1,000/Yr) 6-20

6.9 Syndiotactic Polypropylene by a Bulk Slurry Process Production Costs of Selected Process Schemes 6-24

7.1 Syndiotactic Polypropylene by a Diluent Slurry Process Design Bases and Assumptions 7-2

7.2 Syndiotactic Polypropylene by a Diluent Slurry Process Stream Flows 7-4

7.3 Syndiotactic Polypropylene by a Diluent Slurry Process Major Equipment 7-6

7.4 Syndiotactic Polypropylene by a Diluent Slurry Process Utilities Summary 7-8

7.5 Syndiotactic Polypropylene by a Diluent Slurry Process Total Capital Investment 7-13
### TABLES (Concluded)

7.6 Syndiotactic Polypropylene by a Diluent Slurry Process  
Capital Investment by Section  
7-14

7.7 Syndiotactic Polypropylene by a Diluent Slurry Process  
Production Costs  
7-15

7.8 Syndiotactic Polypropylene by a Diluent Slurry Process  
Direct Costs by Section ($1,000/Yr)  
7-20

7.9 Syndiotactic Polypropylene by a Diluent Slurry Process  
Production Costs of Selected Process Schemes  
7-24

8.1 Syndiotactic Polypropylene Production  
Cost Summary  
8-2