



POLYOLEFINS VII

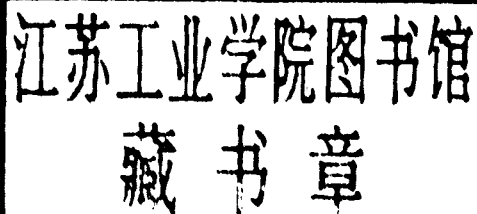
INTERNATIONAL CONFERENCE

February 24-27 1991
Houston, Texas

JOINTLY SPONSORED BY:
SOUTH TEXAS SECTION
and
THERMOPLASTIC MATERIALS & FOAMS DIVISION

PAST POLYOLEFINS CONFERENCES

POLYOLEFINS I	Houston Oaks-Houston March 1975	Herb Meyer, Chairman
POLYOLEFINS II	Westin-Houston February 1978	Corbin Aslakson, Chairman
POLYOLEFINS III	Whitehall-Houston February 1981	Corbin Aslakson, Chairman
POLYOLEFINS IV	Westchase Hilton-Houston February 1984	Corbin Aslakson, Chairman
POLYOLEFINS V	Wyndham Greenspoint Houston February 1987	Larry Holmes, Chairman
POLYOLEFINS VI	Wyndham Greenspoint Houston February 1989	Larry Holmes, Chairman
POLYOLEFINS VII	Wyndham Greenspoint Houston February 1991	Martin Husti, Chairman



NEXT CONFERENCE

POLYOLEFINS VIII	Houston February 1993
------------------	--------------------------

SPE SOUTH TEXAS SECTION

President
Martin Husti
Farrel Corporation

President-Elect
Ed Marshall
Farrel Corporation

Vice President
Gerry Burstain
Shell Development

Secretary
Allan Hartman
Dow Plastics

Treasurer
Charles Shedd
H. Muehlstein & Company

National Councilor
Max Kloesel
Bayshore Industrial, Inc.

Past President
George Reed
GE Specialty Chemicals

POLYOLEFINS VII COMMITTEE

General Chair
Martin Husti
Farrel Corporation

Program Co-Chairs
Gerry Burstain
Shell Development

Steve Polemenakos
Dow Plastics

Housing Co-Chairs
Ed Marshall
Farrel Corporation

Jack Bertotti
Bertotti & Company

Exhibit Chair
Ray Johannessen
Ethyl Corporation

Registration Chair
George Menghi
Polycomplect

Printing Chair
Jennifer Agnew Scott
Dow Plastics

Publicity Chair
Bill Diecks
Tarquin Corporation

Secretary
Larry Holmes
Advantage Polymer Systems

Treasurer
Charles Shedd
H. Muehlstein & Company

Student Chair
Allan Letton
Texas A&M University

Program Committee
George Reed
GE Specialty Chemicals

Ted Marker
Himont, Inc.

Houston Brown
Shell Development

Tom Walsh
Solvay Polymers

Harry White
Southwest Chemical Services

Rex Maugans
Dow Plastics

SPE THERMOPLASTIC MATERIALS AND FOAM DIVISION

Chair
Michael Warner
Custom Resins

Chair-Elect
Tom Butler
Dow Plastics

Secretary
Ray Shute
Huls America, Inc.

Treasurer
Hormoz Hormozi
Quantum Performance Films

STATEMENT OF POLICY

RELEASE FOR PUBLICATION OF CONFERENCE PAPERS

An SPE conference is a forum for discussion of contributions to the scientific and engineering knowledge of plastics. Conference preprints aid communications between speakers and audience, encouraging meaningful discussion. They are not a substitute for publication.

Selected conference papers and discussions are added to the literature through publication by the Society, as in *Plastics Engineering* or *Polymer Engineering and Science*. Others are released for publication elsewhere in accordance with the following policy:

1. All papers submitted to and accepted by the Society for presentation at one of its Conferences become the property of the Society of Plastics Engineers, Inc., and all publication rights are reserved by the Society.
2. By two weeks after the close of the Conference at which the papers are presented, the Society shall make known to the authors those papers selected to be considered for publication. All other papers are released to their authors with the stipulation that if they are published elsewhere, accompanying credit shall be given the Society and the Conference at which they are presented.
3. The Society shall not grant previous or simultaneous publishing rights to any of the papers it intends to publish.
4. The Society shall not be responsible for statements or opinions advanced in publications, reports, papers, or in discussion at its meetings unless specifically approved by Council.
5. An abstract not to exceed one-third the original of any paper presented at a Conference may be published without further permission from the Society provided accompanying credit is given to the Society of Plastics Engineers and the Specific Conference.

SESSIONS

TABLE OF CONTENTS

SESSION I: POLYMER MANUFACTURING - CATALYSTS AND PROCESSES

1980-2000 TWO DECADES OF PROGRESS IN POLYOLEFIN PROCESS TECHNOLOGY K.B. Sinclair, SRI International	1
ENVIRONMENTAL PERFORMANCE AND PRODUCT UNIFORMITY OF THE UNIPOL™ GAS PHASE REACTOR SYSTEM W. G. Sheard and L. McMaster, Union Carbide Chemicals and Plastics Company J. W. Stauffacher, Shell Development Company	15
THE REACTOR GRANULE -- A UNIQUE TECHNOLOGY FOR THE PRODUCTION OF A NEW GENERATION OF POLYMER BLENDS P. Galli and J. C. Haylock, HIMONT Incorporated	27
STRUCTURE/PROPERTY RELATIONSHIPS IN EXXPOL™ POLYMERS C. S. Speed, B. C. Trudell, A. K. Mehta and F. C. Stehling, Exxon Chemical Company	45
THE AMOCO/CHISSO GAS PHASE POLYPROPYLENE COPOLYMER TECHNOLOGY N. F. Brockmeier, Amoco Chemical Company	67

SESSION II: POST-REACTOR PROCESSING

LCM CONTINUOUS MIXER/GEAR PUMP SYSTEM FOR POLYOLEFIN RESINS T. Fukui and R. Minato, Kobe Steel, Ltd.	93
OPERATING CHARACTERISTICS OF 24X ROTORS FOR POLYOLEFIN CONVERSION IN THE FARREL CONTINUOUS MIXER L. N. Valsamis, E. L. Canedo and G. S. Donoian, Farrel Corporation	119
GEAR PUMPS IN COMPOUNDING APPLICATIONS T. Bartilla and R. Heller, MAAG Gear-Wheel Company, Ltd.	129
FULLY AUTOMATED EXTRUDER LINES IN THE COMPOUNDING OF POLYOLEFINS R. Munz and H. Wobbe, Werner & Pfleiderer	143
PRODUCT QUALITY BY GENTLY CONVEYING PLASTIC PELLETS R. Storf, Waeschle Maschinenfabrik	169

POLYETHYLENE DEGASSING EXPERIMENTS WITH EQUIPMENT SCALE-UP COMPARISON	185
G. Martin, Berstorff	

SESSION III: POLYMER STABILIZATION

THE EFFECT OF STABILIZERS ON THE CROSSLINKING VS. SCISSION BALANCE DURING MELT PROCESSING OF LLDPE	207
R. T. Johnston and E. J. Slone, Dow Chemical Company	
THE RELATIONSHIP OF PHOSPHITE STRUCTURE TO POLYMER STABILITY AS DETERMINED BY PHYSICAL AND ANALYTICAL METHODS	221
T. Lemmen and P. Roscoe, GE Specialty Chemicals	
STABILIZATION OF NEW GENERATION POLYPROPYLENE	223
W. O. Drake, J. R. Pauquet and R. V. Todesco, Ciba-Geigy, Ltd.	
STABILIZATION OF POLYPROPYLENE WITH HINDERED AMINE LIGHT STABILIZERS	253
George Kletecka, BF Goodrich	
HYDROQUINONE PHOSPHITES AS PROCESSING STABILIZERS FOR POLYPROPYLENES	275
H. S. Wang and G. L. Myers, Eastman Chemical Company	
FURTHER STUDIES IN THE STABILIZATION OF POLYPROPYLENE WITH FLUOROPHOSPHONITE STABILIZERS	293
G. J. Klender and K. R. Jones, Ethyl Corporation	

SESSION IV: EXTRUSION - TEXTILE AND FILM

GAS PHASE RANDOM COPOLYMERS FOR POLYPROPYLENE FILM APPLICATIONS	309
J. E. Flood, Shell Development Company	
ECONOMICS OF POLYPROPYLENE FIBER SPINNING	335
A. Wilke, Hills Research and Development	
RECENT ADVANCES IN POLYOLEFIN STABILIZATION TECHNOLOGY -- A NOVEL NON-REACTIVE HINDERED AMINE LIGHT STABILIZER	359
R. L. Gray, CIBA-GEIGY Corporation	
FLEXOMER™ POLYOLEFINS, A UNIQUE CLASS OF POLYOLEFINS FOR FILM APPLICATIONS	373
M. R. Rifi, D. C. Filotte and H. L. Batleman, Union Carbide Chemicals and Plastics Company	
INTERPRETATION OF SMALL ANGLE SCATTERING IN FIBER	393
E. S. Clark, University of Tennessee	

SESSION V: INJECTION MOLDING - AUTOMOTIVE, PACKAGING AND MEDICAL

- EFFECTS OF POLYPROPYLENE REPROCESSING ON GAMMA RADIATION TOLERANCE OF INJECTION MOLDED PARTS** 401
R. C. Portnoy and C. T. Gulla, Exxon Chemical Company
- DESIGNING FOR INJECTION MOLDED PARTS USING THERMOPLASTIC ELASTOMERIC ALLOYS** 423
P. D. Agrawal, K. E. Kear and G. K. Lawrence, Advanced Elastomer Systems, L.P.
- INJECTION MOLDING OF TPO'S: PROCESSING PARAMETERS** 439
G. Brown, Dexter Plastics
- CO-INJECTION MOLDING OF POLYOLEFINS FOR MAXIMIZING USE OF RECYCLED MATERIALS WITHOUT DAMAGING APPEARANCE AND STRENGTH OF STRUCTURAL FOAM PARTS** 441
R. Discacciati, Presma Corporation
- AN EVALUATION OF MINERAL ANTIBLOCK ADDITIVES IN POLYOLEFIN FILM** 473
W. P. Steen and E. F. McCarthy, Cyprus Industrial Minerals

SESSION VI: POLYMER CHARACTERIZATION AND QUALITY CONTROL

- THE TOTAL QUALITY SYSTEM** 485
B. Efaw, Dow Chemical Company
- AN EFFECTIVE TORQUE-RHEOMETRY METHOD FOR THE ASSESSMENT OF THE RELATIVE SUSCEPTIBILITY OF POLYOLEFINS TO THERMO-MECHANICAL, OXIDATIVE DEGRADATION DURING MELT PROCESSING** 495
P. W. Fraiss, Dow Chemical Canada, Inc.
- ACCURACY AND PRECISION OF MEASUREMENTS OF MOLECULAR WEIGHT DISTRIBUTIONS OF POLYOLEFINS** 521
S. Pang and A. Rudin, University of Waterloo
- A NEW GPC METHOD FOR CHARACTERIZING POLYOLEFINS** 537
M. Haney, Viscotek
- THE USE OF MAGNESIUM HYDROXIDE FOR FLAME RETARDANT/LOW SMOKE POLYPROPYLENE** 539
F. Molesky, Solem Industries Division of J. M. Huber

SESSION VII: FILLERS AND MODIFIERS

- THE DEVELOPMENT AND APPLICATION OF A NOVEL ENDOTHERMIC CHEMICAL BLOWING FOAMING AGENT** 541
R. A. Garcia and J. Kosin, J. M. Huber Corporation

PRACTICAL ASPECTS OF NUCLEATION OF POLYPROPYLENE WITH SODIUM BIS (PARA-T-BUTYL PHENYL) PHOSPHATE S. S. Ahluwalia, M. H. Fisch, A. Lockhart, Witco Corporation, Argus Division	553
TALC ANTI-BLOCKS FOR MAXIMIZED LLDPE BLOWN FILM PERFORMANCE J. A. Radosta, Pfizer Inc.	561
TERNARY POLYOLEFIN BLENDS WITH STYRENIC BLOCK COPOLYMERS L. A. Pottick and M. J. Modic, Shell Development Company	575
PROCESSING ADDITIVES AND ACID NEUTRALIZERS -- FORMULATION OPTIONS IN POLYOLEFINS T. J. Blong, K. J. Fronek, B. V. Johnson, D. F. Klein and J. M. Knunde, 3M Corporation	593
LONG-TERM STATIC PROTECTION OF POLYPROPYLENE USING FATTY ACID ESTERS D. A. Jervis, Eastman Chemical Company	615
SESSION VIII: RECYCLING AND ENVIRONMENTAL ISSUES	
RECYCLING PLASTICS -- LOOKING AHEAD B. Prioleau, Exxon Chemical Company	637
PLASTIC RECYCLING: WALNUT CREEK CITY CURBSIDE COLLECTION PILOT STUDY M. Li Wu, Dow Chemical Company	659
THE PHYSICAL PROPERTIES AND EFFECTS OF POLYMERIC CONTAMINATION ON POST-CONSUMER RECYCLED HIGH DENSITY POLYETHYLENE M. G. Harris, United Resource Recovery Division, Hancor, Inc.	671
FILM RECYCLING AT UNION CARBIDE E. T. Clark, Union Carbide Corporation	679
EFFECT OF CO-ADDITIVES ON THE PROCESS AND LONG-TERM THERMAL STABILITY OF POLYOLEFINS L. T. Pearson and R. Todesco, CIBA-GEIGY Ltd.	681
FORECAST FOR POLYOLEFINS SUPPLY AND DEMAND IN THE 1990'S W. C. Kuhlke and E. H. Armstrong, DeWitt & Company Incorporated	703

**1980-2000 TWO DECADES OF PROGRESS IN
POLYOLEFIN PROCESS TECHNOLOGY**

by

K. B. Sinclair

**SRI International
Menlo Park, CA**

**Society of Plastics Engineers
Polyolefins VII International Conference
February 24-27, 1991
Wyndham Greenspoint Hotel
Houston, Texas**

1980–2000: TWO DECADES OF PROGRESS IN POLYOLEFIN PROCESS TECHNOLOGY

The polyolefins industry of today evolved from the discovery in the 1930s of polyethylene (PE) produced by a high-pressure, free-radical polymerization process. In the 58 years since then, this laboratory curiosity has developed into the world's most important bulk plastic (Figure 1). Pilot plant production was followed by the first commercial production of LDPE in the early 1940s, and from the late 1940s, the technology developed into the two well known autoclave and tubular reactor processes which today to produce some 14 million tons/yr (t/y) of LDPE worldwide.

The development of low-pressure technologies for production of linear PEs (HDPE and LLDPE) began about 15–20 years behind high-pressure LDPE, but the technology has developed much more rapidly. The key ingredient in the low-pressure processes is the catalyst. Initial discoveries by Amoco and Phillips around 1950 were based on molybdenum and chromium oxide catalysts. A few years later, Ziegler's reduced titanium chloride/aluminum alkyl discoveries led to a new family of catalysts. Since then, both metal oxide and Ziegler-type catalyst systems have evolved rapidly, and today at least 50 companies have developed proprietary catalyst technologies.

The early commercial low-pressure PE processes produced polymer in solution. Catalyst residues were then removed from the solution and the polymer recovered by vaporization of the solvent. In the early 1960s, catalysts active at lower temperatures were introduced, allowing polymerization directly to solid polymer particles slurried in an inert diluent. This greatly improved process economics by permitting the use of simple mechanical separation to recover polymer from the reaction medium. In the late 1960s, catalysts of very high activity were developed, which left negligible amounts of residue in the polymer, thus further simplifying the production process and, at the same time, allowing the development of gas-phase processes, in which even the reaction diluent was eliminated. Today, modern versions of the solution-, slurry-, and gas-phase technologies for linear PEs are used worldwide on a very large scale. World production of linear PEs by these processes now exceeds 17 million tons per year.

The history of polypropylene (PP) process development has followed that of linear low-pressure PE quite closely, but has lagged it by about 5–7 years. This is hardly surprising, since PE catalysts will also usually polymerize PP and vice versa. However, in addition to being highly effective polymerization agents, PP catalysts must also be stereospecific: that is, they must assemble the chain of propylene molecules in a specific way to give the regular three-dimensional structure of crystalline, isotactic PP, rather than the irregular structure of amorphous, atactic PP. This additional requirement is the primary reason for the initial lag in development of PP technologies. Today, several very efficient slurry-phase and gas-phase processes and catalyst technologies are available for production of isotactic PP: world production now exceeds 12 million t/y.

Throughout this technology development era, engineering innovators have continually refined production processes to reduce investments and improve operating efficiency. The range of low-cost processes have evolved for both PE and PP are all closely competitive. This evolution has not ended, however, and process improvements continue to be made, and production capabilities continue to improve. Let us now take a look at how these improvements have affected the economics of the linear PE and PP industries in the past, and see if further significant improvements are possible or even likely in the coming decade.

Figure 2 shows an experience curve for HDPE developed by one of my colleagues at SRI. This curve reflects both market prices and manufacturing economics for HDPE over the 29 years from 1960 to 1989. The value-added curve is based on actual market prices in each year, and represents the selling prices in the United States (FOB), less the variable cost of production. The fixed cost curve is our estimate of HDPE manufacturing costs, less variable costs, for a "high-cost" producer in the United States over the same time frame. These fixed costs include the producer's administration, research, and selling costs, but exclude depreciation and interest charges. It is clear from this curve that the industry as a whole has made tremendous progress in improving manufacturing economics, with fixed costs being reduced by around one order of magnitude during the commercial life of the product.

Another very clear demonstration of the efficiency of the industry is given in Figure 3, which shows a supply/cost curve for linear PE in North America. This curve is based on capacities projected for 1993, when a number of new plants currently under construction will be on stream, and shows a rank ordering of estimated cash production costs for a nominal commodity HDPE grade, starting with the plant having the lowest production costs on the left hand side, and ending with the highest cost plant on the right hand side. A uniform monomer price is assumed for all plants. This must be one of the flattest supply/cost curves for any industry: the variation in ex-plant cash costs is less than $\pm 1\text{¢}$ per pound across around 9.5 million tons of production capacity. Such cost uniformity is amazing when you consider that eight different production processes are used and that the capacities of individual plants range from a low of 80,000 t/y nameplate [175 million pounds per year (lb/yr)] up to 815,000 t/y (1.8 billion lb/y).

Given that the linear PE industry is now extremely cost efficient, is there any hope for significant further improvements in manufacturing costs? Put another way, will the experience curve continue along the negative slope evidenced by the past 30 years? The answer to this question is, in our opinion, affirmative, at least for the remainder of this century. We base this opinion on an examination of the factors that have contributed to the historical reduction in manufacturing costs (Figure 4), followed by an assessment of whether the absolute limits have been reached in all of these factors. With respect to process improvements, the greater efficiencies of polymer recovery and process simplification have gone hand-in-hand throughout the development period. The biggest steps were made in the early days of development when highly active catalysts became available, thereby obviating the need for catalyst residue removal. Since then, significant improvements have been made in control systems and in mechanical equipment design, particularly in the extrusion area. These have resulted in lower utility consumptions and hence lower off-sites investment requirements, and have allowed plant design and operation to move closer to theoretical limits. Along with this has been an increase in the scale of production due to the improvement in the productivity of existing reactors and due to the ability of the market to absorb much greater volumes of commodity grades.

Improvements in catalyst technology have been extremely important to the reduction of PE production costs. Once catalyst activity had reached levels where residue removal could be avoided, the development efforts concentrated on developing catalysts capable of operation at higher temperatures and with a longer active life span to improve the thermal efficiency of production processes and to facilitate production of complex molecular structures in multistage reaction systems. Great progress was also made in the controllability of catalyst systems, such as the control over molecular weight, molecular weight distribution, comonomer inclusion, and compositional distribution. Figure 5 summarizes the performance of some of the many catalyst systems available today. The last four of these belong to a new family of metallocene/alumoxane Ziegler catalysts, which are only now entering commercial application, but which offer extremely high performance capabilities. These four also illustrate the typical stages of development in a new catalyst system: the first system showed reasonable activity, almost commercial at high monomer pressures, but at a low polymerization temperature that

would preclude its use for commodity PE grades. The second system shows activity fully competitive with other commercial catalyst systems, but still with a polymerization temperature too low for large-scale commercial application. The last two, however, show incredible activity at commercially useful polymerization temperatures. Although this family comprises basically homogeneous catalyst systems, supported variations have now been developed, showing high performance characteristics in gas-phase and slurry-phase systems, as well as supported high-temperature variations for use in solution processes and in high-pressure processes at temperatures of 180–300°C. Other variations have been demonstrated for production of isotactic PP at similar conditions to those used in modern bulk and gas-phase PP production processes.

A convenient way of tracking the development of polyolefin technologies is to plot the improvement in commercial reactor productivity over time (reactor productivity = pounds of polymer produced per hour per cubic foot of reactor volume). Productivities will be different for different reaction systems, so it is necessary to develop a plot for each of the basic polymerization processes. One such plot for the gas-phase fluid-bed PE process is shown in Figure 6. This technology was first commercialized for PE in 1968 by Union Carbide in its first production unit at Seadrift, Texas. By our estimates, the design reactor productivity for a reaction system similar to Carbide's has increased by more than 500% in the period between 1972 and 1990. Thus, a reactor with a design output of 100 million lb/y in 1972 might now be able to produce up to 540 million lb/y from the same reaction vessel. Obviously, substantial new investments would be required in the product handling area to cope with such a massive increase in output, but the complexity of the manufacturing operation, the number of process operators required, and the physical size of the reaction system would be the same as a 100 million lb/y plant designed in 1972. Some plants have been able to take full advantage of these improvements with only minimal new investment. For example, the output of Union Carbide's plant at Taft has increased from its 1980 design output of around 600 million lb/y to around 1 billion lb/y in 1990. Because this plant has neither a product extrusion system nor product storage silos, the only additional investment required has been, we presume, for the upgrading of reactor cooling systems and product handling conveyors.

In the coming decade, we believe that there is room for further improvement in the gas-phase fluid-bed process before the ultimate limits of the reaction system are reached. Possible future improvements (Figure 7) include the upgrading of the heat removal capabilities of the reactor cooling system by use of an inert diluent gas with a higher specific heat. This could have drawbacks in terms of grade change flexibility and may also result in changes in polymer properties. It may also require the development of somewhat more active catalyst systems, but there seems no reason why this could not be achieved, particularly with the latest family of Ziegler catalysts. Other ways of increasing heat removal capabilities could be to increase gas supercooling (increase the amount of condensed liquid) in the cool gas stream returned to the reactor. It may also be possible to increase the gas circulation rate, either by increasing the density or size of the polymer granules, or by using a cyclone or solids separator on the reactor outlet to return entrained solids to the bed. Some developments of this type are described in the patent literature and some may be used commercially within the next few years. We therefore conclude that design reactor productivities for the technology could approach a level 7 to 8 times the original 1972 design before the end of the decade.

What do these improvements in reactor productivity mean to PE manufacturing costs? In Figure 8, we show our estimates of production costs by the gas-phase process at various stages of technology development between 1972 and the year 2000. All costs are expressed in constant money and using 1990 values for materials, labor, energy, and other utilities. Even in 1972, this technology was highly efficient in that catalysts used did not require deashing, and the gas-phase process was inherently much simpler than the solution and slurry processes widely in use at that time. However, in the period from 1980 to 1990, the direct manufacturing costs (excluding monomer) improved by some 25% and, if depreci-

ation is included, the improvement is almost 28%. In the future, we project that these costs may be reduced by a further 7–8%. Because of the overwhelming importance of monomer cost, however, this would amount to a reduction of only about 1% in total manufacturing cost. Thus, further improvements in this PE technology will not have a major effect on the cost structure of the industry, but they will have a very large effect on future investment requirements: if all linear PE technologies improved to a similar extent, the output of existing linear PE reactors could be increased by about 3 million t/y in North America alone.

Turning now to developments in PP production technology, Figure 9 shows some of the milestones in development of stereospecific catalysts that have had major impact on the cost structure of the industry. Note that the gas-phase process was commercialized for PP slightly earlier than for PE, but because of the slower development of stereospecific catalyst technologies, process improvements in gas-phase PP have lagged well behind those of the PE technology and have only recently reached the high efficiency levels typical of PE technologies. The “fourth-generation” catalyst systems indicated for the 1990–to–2000 timeframe refer both to improvements in existing superactive third-generation systems, as well as to the likely introduction of similarly high-performance catalysts of the metallocene/alumoxane type.

Our plot of the development in PP reactor productivity since 1970 is shown in Figure 10. This plot is based on a loop reactor, bulk slurry process similar to those used by Himont, Phillips, Solvay, and others. The plot shows that a reactor designed for an output of 100 million pounds in 1970 would probably have a design output close to 450 million lb/y in 1990. Most of this improvement has occurred in the period since 1975, when the high-activity supported third-generation catalyst systems were introduced. Although this improvement is not as great as for PE over the same time frame, we believe that the future potential for PP technologies is significantly better: within the next 10 to 15 years, design reactor productivities could approach levels 8 to 11 times a typical 1970 reactor design. There are several reasons for this more optimistic outlook for PP (Figure 11). One reason is that PP has a much higher melting point than PE. Most slurry- and gas-phase PE processes currently operate at temperatures approaching the point at which either the polymer particles become sticky and dissolve in the slurry diluent, or they begin to melt and stick together to form lumps in a gas-phase system. In PP processes, however, typical reaction temperatures of current processes are around 70–80°C and could perhaps be raised by about 80°C before problems of agglomeration and melting would interfere with smooth operation. Thus, there is great potential for increasing the heat transfer capabilities of PP reaction systems by developing catalysts suitable for isotactic polymerization at high temperatures.

Another aspect limiting the output of loop reactor slurry PE technologies is the ratio of heat transfer area through the reactor wall to the reactor volume (and hence to volume productivity). By our estimates, most loop reactor slurry PE technologies are already operating close to this heat transfer area/volume limit and they are also at the upper limit of reaction temperature as determined by polymer solubility and agglomeration. PP reactors of this design, however, have at least a 30% margin before the area/volume limits are reached because of propylene's lower heat of polymerization. PP processes also currently operate at significantly lower temperatures than PE technologies, so that existing reactors already have more surface area installed than similar PE reactors. In addition to this, it seems likely that two- to fivefold improvements in PP catalyst activity and productivity are likely within the next 10 years, and this will enable producers to take advantage of some of the unused heat removal capabilities of their reactors. Thus, there seems to be a good probability that the reactor output of existing PP technologies will eventually be doubled.

The effect that these historical and projected improvements in PP technologies have on the cost structure of the industry is illustrated in Figure 12. Because of the early requirement for polymer deashing and atactic removal, the improvement in the direct nonmonomer production costs has been

very large: improvement since 1972 has been an estimated 70% compared to 55% for PE technologies. Overall improvements, including monomer costs, have been around 33% for PP compared to 15% for PE. Further improvements of around 20% by the year 2000 seem likely. As with PE, the impact on future investment requirements for PP is also very large: the indicated increase of 70% in reactor productivity over the next 10 years could potentially add 3–4 million tons to existing reaction capacity in North America alone.

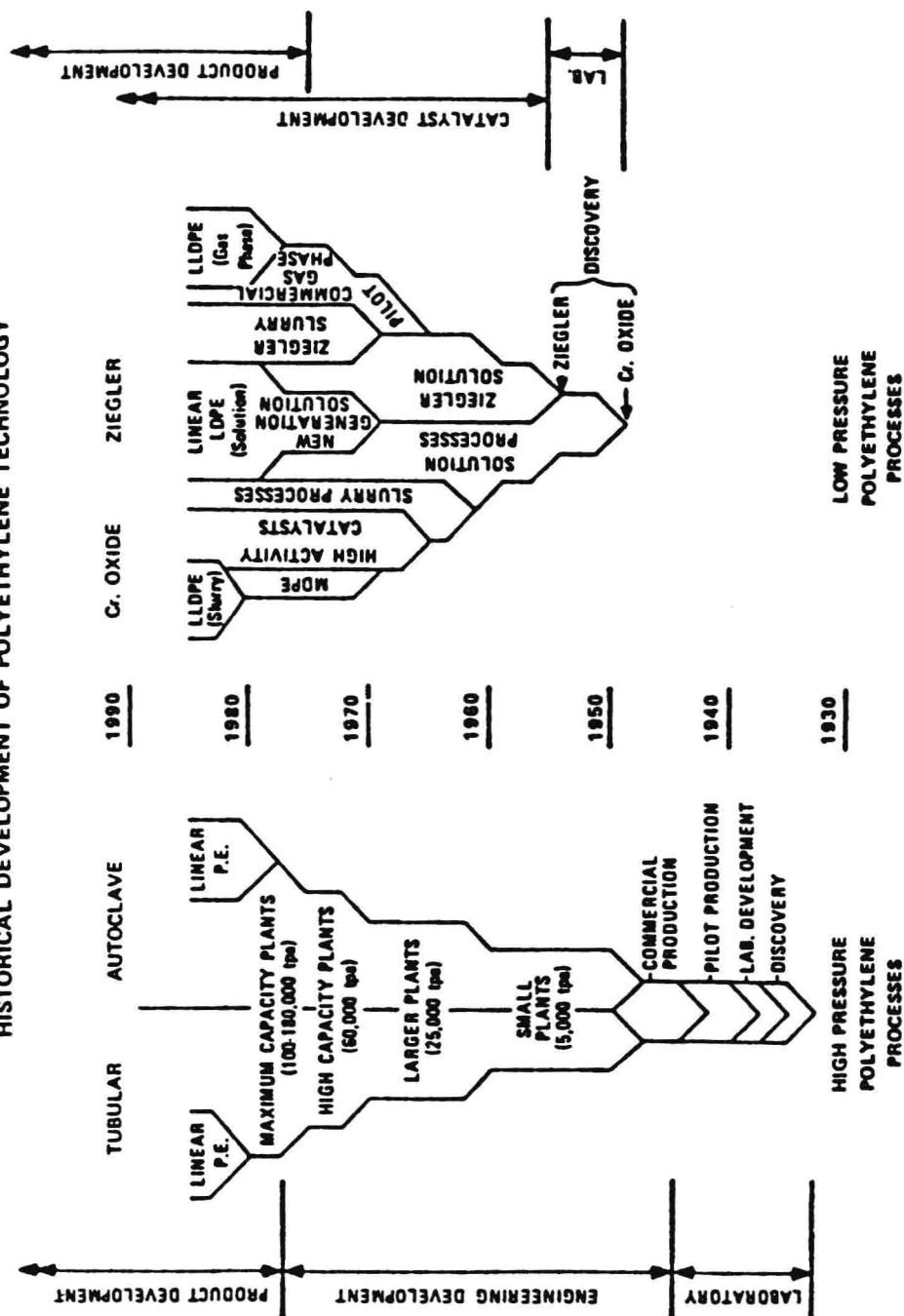
What does this teach us about the outlook for some of the new polyolefins that are only now entering the early stages of development? The most important lesson is that polyolefin catalyst and process technologies still have a lot of potential ahead of them. Thus, polymerizations that would appear to us now to be uneconomic, are quite likely to approach commercially acceptable levels within a period of 5 to 10 years. One example of a development which seems to us to be quite promising is shown in Figure 13. Significant advances have recently been made in copolymerization of ethylene with cyclic olefins such as tetracyclododecene to yield polymers with exceptional optical properties, suitable for production of optical disks in competition with polycarbonates. It appears from the patent literatures that the current stage of development of these polymerizations is similar to that of PP in 1972: catalyst deashing and polymer purification steps are required. Thus, production costs for these polymers are currently rather high, not counting the cyclic olefin cost, which is certainly much higher than ethylene and propylene. The metallocene family of catalysts, however, seem particularly suited to polymerization or copolymerization of cyclic olefins and it therefore seems likely that process efficiencies will be improved along similar lines to the improvements in PP technology. It may be, therefore, that within 5 to 10 years we will have a polyolefin with properties competitive with polycarbonates, but at prices possibly below \$1 per pound in today's money, depending on the cost of the cyclic olefin. Many other new compositions are being described in the patent literature and it seems that the polyolefins industry is entering a new and very exciting decade of development.

REFERENCES

- (1) Private communication, W. Sedriks, SRI International, Menlo Park, California (1990)
- (2) "Polyolefins Through the 80s," SRI International, Menlo Park, California (1990)
- (3) van der Ven, S., "Polypropylene and other Polyolefins," Polymerization and Characterization Studies in Polymer Science 7, Elsevier (1990)

POLYETHYLENE TECHNOLOGY FAMILY TREE

HISTORICAL DEVELOPMENT OF POLYETHYLENE TECHNOLOGY



SOURCE: SKI International

SRI International

Figure 1

figs for paper/1