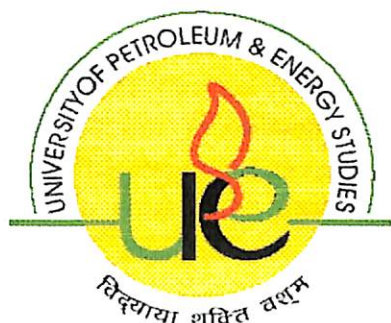


**A  
PROJECT REPORT  
ON  
Growth of Polymer Industry in India with  
special reference to Polyethylene.**



**PREPARED IN PARTIAL FULLFILMENT  
FOR THE REQUIREMENT OF THE DEGREE  
OF  
BACHELOR OF TECHNOLOGY**

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## UNIVERSITY OF PETROLEUM & ENERGY STUDIES

### CERTIFICATE

*This is to certify that the project report on “Growth of Polymer Industry with special reference to Polyethylene ” submitted to UPES, Dehradun by Mr. Amit Kalra & Mr. Summit Mittal in partial fulfillment of the requirements for the degree of Applied Petroleum Engineering & academic session (2003-2007) is a bonafide work carried out by him under my supervision & guidance of Mrs. Bhawna Lamba. This work has not been submitted anywhere else for any other degree or diploma.*

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Mrs. Bhawna Lamba

Lecturer, B.Tech. (APE)

Date:

## ACKNOWLEDGEMENT

Project on GROWTH OF POLYMER INDUSTRY WITH SPECIAL REFERENCE TO POLYETHYLENE was an enriching experience for us. It provided us with an insight into the world of health, safety and environment.

We would like to thank Mrs. BHAWNA LAMBA , Lecturer & Prof. C.K.Jain, course coordinator, for giving us the opportunity to undergo our dissertation. We were motivated by the encouragement they gave us.

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Last but not the least we thank all fellows for the information they shared and the healthy discussions they held with us.

Finally, we thank our mentor and course coordinator for the information they shared and the healthy discussions on the topic, they held with us. This enabled us to earn a lot of practical knowledge during this period. We remain indebted to UPES, Dehradun for the memorable learning experience.

THANKING YOU!  
SUMIT MITTAL  
AMIT KALRA

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## POLYMER INDUSTRY

### Overview

Basic chemical	Chemical intermediate	Synthetic fibre	Polymers	Synthetic rubber
<input type="checkbox"/> Ethylene	<input type="checkbox"/> Monoethylene glycol	<input type="checkbox"/> Acrylic fibre	<input type="checkbox"/> LDPE / LLDPE	<input type="checkbox"/> Styrene butadiene
<input type="checkbox"/> Propylene	<input type="checkbox"/> Phthalic anhydride	<input type="checkbox"/> Nylon filament yarn	<input type="checkbox"/> HDPE	<input type="checkbox"/> Poly butadiene
<input type="checkbox"/> Butadiene	<input type="checkbox"/> DMT	<input type="checkbox"/> DMT	<input type="checkbox"/> PVC	
<input type="checkbox"/> Styrene	<input type="checkbox"/> Vinyl Chloride	<input type="checkbox"/> Polyester staple fibre	<input type="checkbox"/> Polystyrene	
<input type="checkbox"/> Benzene	<input type="checkbox"/> Caprolactin	<input type="checkbox"/> Polyester filaments yarn	<input type="checkbox"/> Poly propylene	
<input type="checkbox"/> Toluene	<input type="checkbox"/> Acrylonitrile			
<input type="checkbox"/> Orthoxylene	<input type="checkbox"/> Linear Alkyl Benzene			
<input type="checkbox"/> Paraxylene				
<input type="checkbox"/> Mixed xylenes				
<input type="checkbox"/> Ethylene oxide				

Polymers are the most important constituent as they account for 70% of petrochemicals. Naphtha and natural gas are the two important feedstocks used. Basic Chemicals Considered the building blocks of the entire industry. Naphtha - a major feedstock; current (Dec 99) domestic price - naphtha around Rs 12,040 per tonne (US \$ 2800 per tonne). Naphtha prices move with international oil prices.

## **Ethylene**

Ethylene is the feedstock for the production of polyethylene commodities like HDPE, LPDE, LLDPE Polymer grade ethylene is also used to produce Vinyl chloro monomer Chemical grade ethylene is used to produce MEG More than 60% of ethylene consumed in India is for PE and around 18% for PVC

International prices of ethylene (f.o.b Korea) : US \$ 420-430 / tonne

Market around Rs. 815 crores. (US \$ 190 mn.); imports - 26.5%

Major players - Reliance Industries (RIL), Indian Petrochemical Corporation (IPCL), Hindustan Petrochemicals (HPCL), Gas Authority of India (GAIL), NOCIL and others

## **Propylene**

Used in the production of poly propylene Prices have weakened due to competition in Asian markets and from European, Latin American suppliers

Propylene imports into India not pre-dominant. 97-98 imports 50,000 MT

International prices of propylene (f.o.b Korea): US \$ 270-280 / tonne

Market around Rs. 83 crores. (US \$ 19 mn.); imports - 0.33% - does not include captive consumption

Major players - RIL, IPCL, NOCIL, GAIL and Oswal

## **Polymers**

Essentially plastic raw materials

Major products in this group are LDPE, LLDPE, HDPE, PVC, PP & PS

This segment has recorded an overall growth of 18% while capacities have recorded a 26% CAGR in the last three years

## **LDPE/LLDPE**

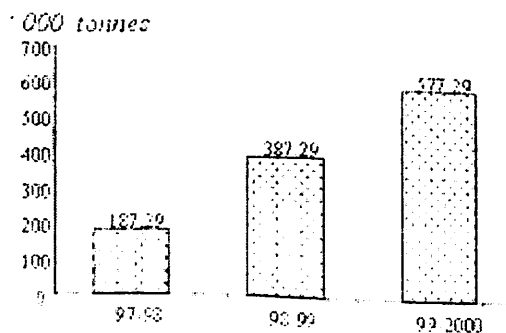
LDPE / LLDPE account for fifth of domestic polymer in India

Segment growing at the rate of 12%

50% of the polymer used in packaging industry

Prices : Rs 54.25 / kg (Aug 99) -(US \$ 1.26 )

Major players - RIL, IPCL and Oswal



## **HDPE**

Second largest polymer with 22% share

Domestic consumption value  
Rs. 2,123 crs. (US \$ 494 mn)

Segment growing at 12 to 15%

Prices : Rs 50 / kg (Aug 99) - US \$ 1.2

Used in injection moulding, paper industry, Raffia and blow moulding

Major players - RIL, IPCL and NOCIL

## **POLYPROPYLENE**

PP substituting other polymers due to light weight characteristics

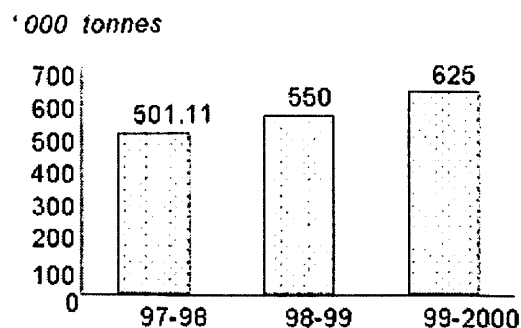
Imports were at 11,000 tonnes in 97-98

Domestic demand 595,000 tonnes, has grown by 38% over last three years

Prices : Rs 47.5 /kg (Aug 99)

Used for mainly - Woven sacks (40%), Ropes & Twines (10%), Injection moulding (30%) and BOPP & other films (20%)

Major players - RIL and IPCL



## **PVC**

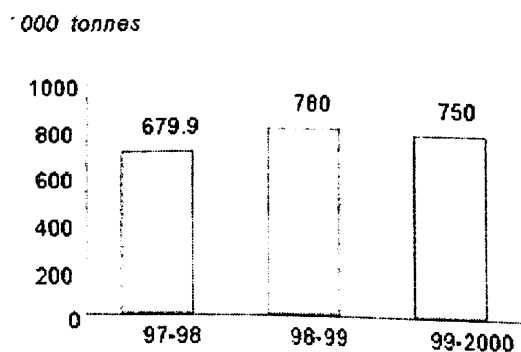
Segment has been growing at 15%.

Domestic demand estimated at 5,54,000 tpa

Prices : Rs 44.95 / kg (Aug 99)

Pipes account for 54% of PVC consumption and cable sheathing accounts for 14%

Major players - RIL and IPCL





## **FEEDSTOCK**

Chemicals are produced mainly from the petroleum feedstock. In past, and in some of the smaller plants, the agricultural feedstock mainly molasses are used for production of ethylene. The feedstock pattern varies from one country to another. In the US and It is possible to produce petrochemicals from a variety of basic raw materials. The cost of raw material is the single largest cost in production of variety of petrochemicals. In India, following the global trends, petrothe Middle East, ethane (derived from natural gas) is the prime feedstock for the production of commodity plastics, while in Japan, Western Europe and even in emerging Asia, the feedstock is predominantly naphtha. The use of a particular feedstock is governed by its availability in a region and the economics of obtaining it. The Indian petrochemicals industry has an even share of naphtha and ethane-propane (gas) based plants. Among the crackers under operation, while naphtha accounts for around 56.5% of the ethylene capacity, ethane-propane (natural gas) accounts for the rest 43.5%. Till recently, the distribution of petroleum products and natural gas was controlled by the various ministries under the Government of India. The regulations regarding natural gas distribution had led to only State-owned companies possessing gas crackers. However, in mid-2002, the major State-owned petrochemicals company, namely IPCL, was acquired by RIL, a private sector petrochemicals company.

## **Natural Gas**

The gas market in India is predominantly controlled by the State-owned companies. There are separate companies for gas production and distribution. Currently, gas pricing is based largely on the recommendations of T. L. Shankar Committee. The consumer price of gas is linked to the international price of a basket of internationally traded fuel oils. This linkage has been progressively increased in the proposed manner since the initiation of the current pricing mechanism. Till recently, the Government had fixed a price band of Rs. 2,150 per thousand cubic meters (tcm) as the lower limit and Rs. 2,850 per tcm as the ceiling. In May 2005, the Government approved increase in prices depending on sector in which gas is being consumed. While for power and fertilisers, the price is Rs 3200/tcm (thousand cubic metres), the gas prices for petrochemicals and other industries has been made market determined and the current level is around US\$3.86/MMBtu.

## **Naphtha**

· Till 1999-2000, the Indian refining sector was dominated by the state-owned companies. However, with the commissioning of refinery by Reliance Petroleum Limited (RPL, now

merged with RIL), significant production of petroleum products has started from the private sector also.

- Indian refining capacity, which was around 69 mmt as on April 1, 1999, has increased

substantially to around 127 mmt as on March 31, 2005 on account of capacity additions by new as well as the existing players.

In the past, till September 1997, the prices of naphtha were administered and controlled by government bodies, and varied with the calorific value of the feedstock. Naphtha was also supplied to fertiliser manufacturers at a subsidised rate. Since September 1997, in an effort to further decontrol naphtha, the domestic prices of naphtha were made the same for both fertiliser and non-fertiliser consumption. From April 1998, naphtha prices have been decontrolled and made market determined.

- The domestic prices of naphtha are based on landed costs (for fertiliser sector, they are

linked to export parity prices) with a revision every fortnight. Accordingly, these prices have fluctuated in line with volatile international crude prices (which determine the international naphtha prices). Currently, the prices vary according to the location and the price is matched to the landed cost from the nearest port.

Further, the fertiliser companies are charged on the basis of export parity prices (rather than import parity). Also, the fertiliser companies are charged only half of the marketing costs and margins till that point.

- Further, the companies sourcing naphtha from the local markets have to pay sales tax

which was at 20% in some states (equivalent to Rs. 2,000 per tonne at current prices) prior

to implementation of VAT. The domestic prices closely follow the trends in landed costs and international prices. With rising naphtha prices in the international market, the domestic prices have also followed the trend and increased in line with international naphtha prices. Out of the three integrated petrochemical complexes (under operation) based on naphtha, the two owned by the Reliance group, consume naphtha supplied by group refinery located at Jamnagar. The refinery enjoys sales tax exemption on products sold in the State of Gujarat. Therefore, the two plants (also located in Gujarat) enjoy sales tax exemption on naphtha purchased by them.

## **FACTS**

The word polymer is derived from the classical Greek word poly meaning "many" and meres meaning "parts." Simply stated, a polymer is a long chain molecule that is composed of a large number of repeating units of identical structure. Certain polymers, such as proteins, cellulose, and silk, are found in nature, while many others, including polystyrene, polyethylene, polypropylene, and nylon, are produced only by synthetic routes.

Petroleum chemicals or petrochemicals in short, are compounds or elements recovered or derived from petroleum or natural gas. As chemicals they do not represent any different class of compounds. They are organic chemicals, and have got the same composition, structure and properties as corresponding organic compounds derived from non-petroleum sources.

The petrochemical industry is one of the most competitive industries. New advances in catalyst development, process improvement, or even completely new routes to established chemicals from cheap raw materials are reported here more often than any other field of chemical process industries. All these have made the study of economics o petrochemicals industry important and necessary.

The major task for the petroleum refiners in the very fast developing country like us is to achieve maximum lighter distillates from gradually obtainable heavy and sour crude's maintain the various stringent environment norms from time to time specially for the transport fuels. As such the petrochemicals are literally chemicals from petroleum origin is hidden into the basic objective of the refineries along with the exploration of the heavier stocks from the bottom of the barrel. It also includes the optimum use other equivalent natural sources for eco friendly products and development of low volume high priced value added products/ chemicals.

## **CLASSIFICATION OF POLYMERS**

Thousands of polymers have been synthesized and more are likely to be produced in the future. Fortunately, all polymers can be synthesized to one of the two groups based upon their processing characteristics or type of polymerization mechanism.

More specific classification can be made on the basis of polymer structure. Such groupings are useful because they facilitate the discussion of properties.

## **THERMOPLASTICS AND THERMOSETS**

All polymers can be divided into two major groups based upon on their thermal processing behavior. Those polymers that can be heat softened in order to process into a desired form are called thermoplastics. Waste thermoplastics can be recovered and refabricated by application of heat and pressure. Polystyrene is an important example of a commercial thermoplastic. Other major examples are polyolefin's (polyethylene and polypropylene) and poly (vinyl chloride). In comparison, thermo sets are polymers whose individual chains have been chemically linked by covalent bonds during polymerization or by subsequent chemical or thermal treatment during fabrication. Once formed, these cross linked networks resist heat softening, creep, and solvent attack, but cannot be thermally processed. Such properties make thermo sets suitable materials for composites, coatings, and adhesives applications. Principal examples of thermo sets include epoxy, phenol- formaldehyde resins, and unsaturated polyesters.

## **POLYETHYLENE**

It is the most extensively used thermoplastic. The demand for polyethylene is due to abundant availability of the monomer ethylene. The processing cost is also low. It is permeable to most gases. It has two grades LDPE and HDPE .

**LDPE:**It is syndotactic or isotactic and has branched chain.It is more flexible due to branched chain, is used mostly for domestic purposes. As it is branched , it has low density and viscosity and thus high MFI( melt flow index).

**HDPE:** It is atactic and has linear chain. It is closely packed and less permeable to gases. As it is linear in nature , it has a high density and viscosity and thus low MFI( melt flow index). It has low degree of water absorption.

## **MAJOR PLAYERS:**

### **IPCL**

Expand gas cracker at Gandhar to 400,000 tonnes per annum

Create a new cracker at Vadodara of 300,000 tonnes per annum

Once achieved total ethylene capacity of IPCL would be 1 million tpa

Capacities in tpa : LDPE (160,000), LLDPE (190,000), HDPE (120,000), PP(165,000) and PVC (205,000)

Total investment planned -  
Rs 4300 crores (US \$ 1000 mn) towards facilities at Nagarhona, Vadodara and Gandhar Complex

### **Haldia Petro**

Joint sector project - WBIDC and Chatterjee Soros Group

Setting up a plants - for 420,000 tpa of ethylene

200,000 tpa of propylene

65000 tpa of Butadiene

65000 tpa of Benzene

### **NOCIL**

Setting up 450,000 tpa of ethylene which will be expanded to 600,000 tpa

Capacities (tpa) for HDPE (170,000), PP (180,000), PVC (25,000)

### **RIL**

RIL refinery at Jamnagar 27 mln tpa

Hazira complex capacities (tpa) - 750,000 (PP) & 420,000 (PVC)

Patalganga complex - facilities for PSF / PFY and LAB

Setting up expansion of 400,000 tpa of Propylene

**GAIL**

Commissioning its plants for 300,000 tpa of ethylene

Estimated capacities by FY2000 for 160,000 tpa, 100,000 tpa and 40,000 tpa

**Essar**

Setting up facilities for 100,000 tpa of propylene

**PRODUCT SPECIFICATIONS OF MAJOR PLAYER:**

RELIANCE INDUSTRIES LIMITED d			
RELENE (POLYETHYLENE)			
RELENE - B 46003 (BLOW MOULDING GRADE)			
Product Description and Applications			
Relene B 46003 is a High Density Polyethylene grade suitable for Blow Moulding applications which require high environmental stress-crack resistance (ESCR). The resin offers good melt strength, rigidity and excellent ESCR required for pesticide, chemical and detergent containers.			
Physical Characteristics			
Property	ASTM Test Method	Unit	Typical Value*.
Density	ASTM D 1505	g/cc	0.946

MFI (2.16 kg)	ASTM D 1238	g/10 min.	0.30
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#### Typical Properties

Property	ASTM Test Method	Unit	Typical Value*.
Tensile Yield Strength	ASTM D 638	MPa	20
Flexural Yield Strength	ASTM D 790	MPa	24
Elongation at Break	ASTM D 638	%	440
Flexural Modulus	ASTM D 790	MPa	645
Hardness	ASTM D 2240	Shore D	63
Vicat Softening Point	ASTM D 1525	°C	125

### RELENE (POLYETHYLENE)

#### RELENE - B 56003 (BLOW MOULDING GRADE)

##### Product Description and Applications

Relene B 56003 is a High Density Polyethylene grade suitable for general purpose blow moulding applications. Articles blown from this grade exhibit good stiffness. The resin offers good melt strength, ESCR and impact resistance.

##### Physical Characteristics

Property	ASTM Test Method	Unit	Typical Value*.
Density	ASTM D 1505	g/cc	0.956
MFI (2.16 kg)	ASTM D 1238	g/10 min.	0.30

##### Typical Properties

Property	ASTM Test Method	Unit	Typical Value*.
Tensile Yield Strength	ASTM D 638	MPa	26
Flexural Yield Strength	ASTM D 790	MPa	28.5

Flexural Modulus	ASTM D 790	MPa	900
Hardness	ASTM D 2240	Shore D	69

## RECLAIR (POLYETHYLENE)

### RECLAIR - F 18010 (BLOWN FILM GRADE)

#### Product Description and Applications

Reclair F 18010 is a Butene comonomer based Linear Low Density Polyethylene with optimum levels of Antioxidant and Polymer processing aid but without Antiblocking agent and Slip additive. The grade is designed to make lamination film applications.

#### Physical Characteristics

Property	ASTM Test Method	Unit	Typical Value*.
Density	ASTM D 1505	g/cc	0.918
MFI (2.16 kg)	ASTM D 1238	g/10 min.	0.90

#### Typical Properties

Property	ASTM Test Method	Unit	Typical Value*.
Tensile Yield Strength MD TD	ASTM D 882	MPa	12.5 12.0
Ultimate Tensile Strength MD TD	ASTM D 882	MPa	38.0 30.0
Elongation at Break MD TD	ASTM D 882	%	650 800
Dar impact Strength, F <sub>50</sub> (38 mm Dart, 66 cm height)	ASTM D 1709	g/cm	3.5
Tear Strength MD TD	ASTM D 1922	g/cm	3.3 10.3



## **RESEARCH OBJECTIVE**

- To study the Technology processes.
- To study the demand and the growth pattern.
- TO study the latex particle theory of polymers.
- To study the BACT model for emission control.
- To do a SWOT analysis of the polymer industry.
- To study the latest trends and future prospects.
- To do a comparative study of LDPE and HDPE.

## **TECHNOLOGY PROCESSES**

### **POLYETHYLENE**

**APPLICATION :** To produce linear low density polyethylene (LLDPE) to high density polyethylene (HDPE) using the low pressure, gas phase UNIPOL PE process.

**DESCRIPTION:** A wide range of polyethylene is made in a gas phase, fluidized bed reactor using proprietary solid and slurry catalyst. The product is in a dry, free flowing granular form substantially free of fines as it leaves the reactor and is converted to pellet form for sale. Melt index and molecular weight distribution are controlled by selecting the proper catalyst type and adjusting operating conditions. Polymer

Density is controlled by adjusting comonomer content of the product. High productivity of conventional and metallocene catalysts eliminates the need for catalyst removal.

The simple and direct nature of this process results in low investment and operating costs, low level of environmental pollution, minimal potential fire and explosion hazard, and easy operation and maintenance.

Gaseous ethylene, comonomer and catalyst are feed to reactor (1) containing a fluidized bed of growing polymer particles and operating near 25 kg/cm<sup>2</sup> and approximately 100°C. A conventional, single stage, centrifugal compressor (2) circulates reaction gas, which fluidizes the reaction bed, provides raw material for the polymerization reaction, and removes the heat of reaction from the bed. Circulating gas is cooled in a conventional heat exchanger (3) the granular product flows intermittently into product discharge tanks (4) where unreacted gas is separated from the product and returned to the reactor. Hydrocarbons remaining with the product are removed by purging with nitrogen. The granular product is subsequently palletized in a low energy system (5) with the appropriate additives for each application

### **PRODUCTS**

Polymer density is easily controlled from 0.915 to 0.970 g/cm. Depending on catalyst type, molecular weight distribution is either narrow or broad. Melt index may be varied from less than 0.1 to greater than 200. Grades suitable for film, blow molding, pipe, and rotomolding and extrusion applications are produced.

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## **POLYETHYLENE (COMPACT solution process)**

**APPLICATION:** TO produce polyethylene with a very wide density range from 0.900 to 0.970 using the COMPACT solution process with a single proprietary, advanced Ziegler Natta type catalyst. As comonomers, either (for high density range), butane or octane or combinations are used.

**DESCRIPTION:** Liquid or gaseous ethylene is fed, together with a solvent and required comonomers into a stirred, liquid filled, vessel type reactor(1) The reactor is operated adiabatically; thus the feed is precooled. All heat of reaction is used to raise polymerization temperature up to approximately 200<sup>0</sup>c. Hydrogen is used to control polymer molecular weight. A high activity, proprietary catalyst is prepared onsite, from commercially available components. Ethylene conversions exceeds 95% per pass are obtainable.

The latent heat of the polymer solution leaving the reactor is used to flash off the solvent, unconverted ethylene and light comonomers in flash vessel.(2) Vapors from this vessel are unconverted ethylene and light comonomers in flash vessel (3) and recycled back to the reactor feed without purification.

A killing agent (4) is added to the concentrated polymer solution which is pumped to the second flashing through a solution heater. No catalyst removal step is necessary.

In the second flash vessel (5), further concentrating to over 95% polymer is done and the product is fed into a degassing extruder (6) to remove the last traces of solvent and octene . Vapors from the second flash vessel and degassing extruder are purified in the purification section. In the degassing extruder, specified additives are added, and the polymer is palletized. After, drying the palletized resins are transported to the silos.

The COMPACT solution process is characterized by its low residence time (few minutes in the reactor and less than 30 minutes in total), thus enabling fast grade changes and wide flexibility for usage with various comonomers. Especially, the octene copolymers are the ultimate in LLDPE grades.

### **PRODUCTS**

Almost any density PE can be cost effectively produced with comonomers - propylene, butane, octene or combinations. Densities range from 0.900 to 0.970 with MFI's ranging from 0.8 to 100. Major applications are film, injections molding, rotational molding, and sheet, pipe and cross linking, where extreme mechanical properties are required.

### **ECONOMICS:**

Typical raw materials and utilities consumption per metric ton (mt) of palletized product:

Ethylene and comonomers, mt.	1,016
Electricity, Kwh	500
Steam, kg	400
Water cooling, m <sup>3</sup>	230
Steam, LP, kg , credit	330

**LICENSOR** Stamicarbon bv.

## Polyethylene

Polyethylene  $n(\text{CH}_2-\text{CH}_2)_n$ : the most extensively used thermoplastics.

### Special features:

- Low cost (Availability of Ethylene)
- Resistance to chemicals
- Flexibility

Two types of PEs are available. High density Polyethylene(HDPE) produced by low pressure methods, is used mainly for blow molded containers and injection moulded articles and pipe. HDPE density  $0.960 \text{ g/cm}^3$ .

Low Density Polyethylene (LDPE) produced by high pressure methods is used mainly for plastic films. LDPE density  $0.910-0.940 \text{ g/cm}^3$ .

The structural differences between the high and low density polyethylene are in the structure of the polymer chain.

LDPE chain is highly branched with both short and long chain branches, HDPE has very few side chains.

LDPE (Linear Low Density polyethylene) which combines the LDPE and HDPE by using a co monomer such as butene-1 (Union Carbide) Hexene-1 (Phillips) or octene-1 (Dow and Due Point).

LDPE density between  $0.918-0.940 \text{ gm/cm}^3$ .

LLDPE contains short side chains that are spaced uniformly and periodically on the long backbone chain. LLDPE has the most of the good features of both LDPE and HDPE-strength flexibility, clarity, good dielectric and high temp. Stability (for wire and cable shielding).

### Physical and chemical Properties:

- Polyethylene is permeable to most gases. HDPE is less permeable than LDPE, has low degree of water absorption and is not attacked by dilute acids and alkalis (attacked by conc. acids)

Polyethylene's are attacked by hydrocarbons and specially chlorinated hydrocarbon

- Tensile strength of PE is relatively low but impact resistance is high. The use of polyethylenes in insulation is due to its excellent electrical resistance properties.

## **Manufacturing Processes:**

Polyethylene first produced by accident in 1933. ICI-UK attempting to make Styrene at high pressure reaction of Benzaldehyde with Ethylene noticed White flakes on the reactor inside-LDPE

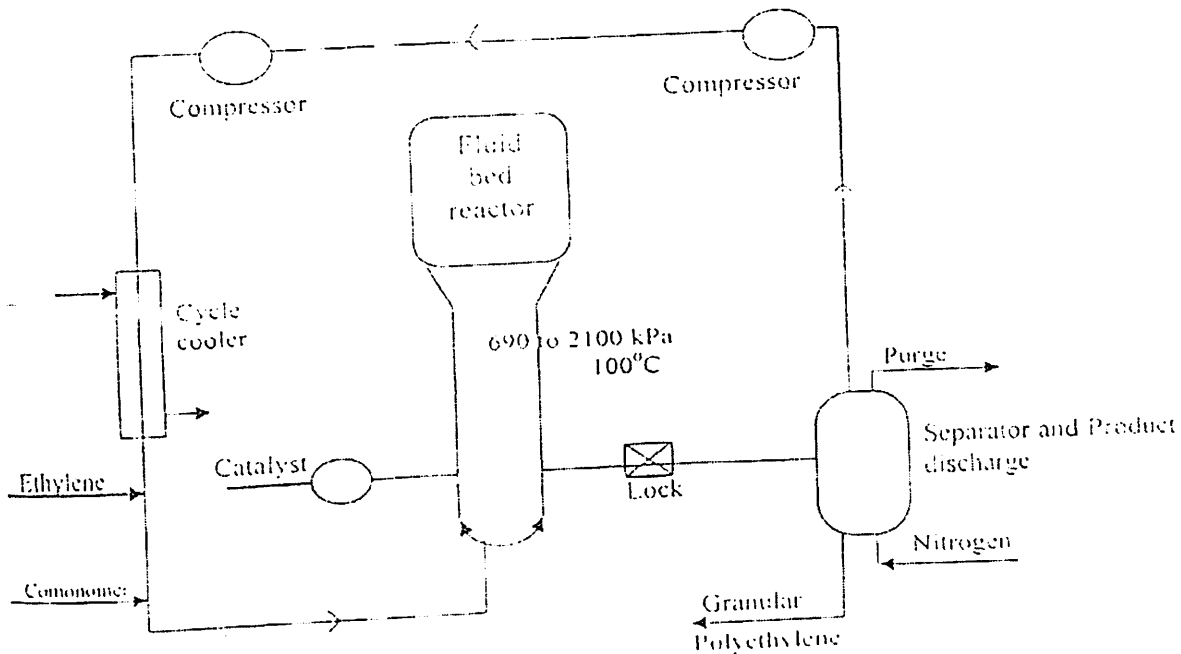
1939, German scientist Max Fischer at I.G. Farben Industries was trying to synthesize Lube oil from ethylene catalyst Aluminum Powder and Ti at low pressure used. White Wax like Material formed; HDPE.

## **HDPE:**

All high density PEs are made by a low pressure process in a fluidized bed reactor. The catalyst is either a Ziegler type catalyst which is a complex between an Aluminum Alkyl and a transition Metal Halide such Ti Cl<sub>4</sub> or a Catalyst of silica or silica alumina impregnated with a small amount of a metal oxide usually either a chromium oxide or Molybdenum oxide. The property of the polymer specially its molecular wt. may be controlled by Introducing hydrogen to the circulating gas.

The polymerization of ethylene is an exothermic reaction. It releases 850 calories/gm of ethylene. So an effective method of removal of heat is needed. Polyethylene decomposes at high temp. even in the absence of air. If not controlled explosive condition may occur.

In HDPE manufacturing plants : the heat of reaction is removed by circulating the gas through heat exchangers Then compressing it for recycling to the reactor. The polymerization may be in the gas phase as in Union Carbide Process or in the liquid phase where a hydrocarbon like hexane is added (Hoechst process). In such cases the hydrocarbon recovery system needs to be incorporated in HDPE Production Plant.



High density polyethylene by low -pressure process

In the Hoechst process, ethylene recycle and monomer recovery systems are not required because of almost complete conversion of ethylene yield > 99%.

Because of a very small amount of catalyst used; its removal from the polymer is not needed. The Polymer is usually in the form of Powder or granules.

Either solution or suspension reaction conditions are maintained. Above 130 C the hydrocarbon is a solvent: below this temp. The polymer forms suspension.

### Uses of HDPE:

- About 85% of blow moulded bottles are made from HDPE.
- HDPE is widely used in making irrigation pipes. Pipes made from HDPE are flexible, tough and corrosion resistant.
- HDPE pipes are used for carrying corrosive materials and /or abrasives or various chemicals.
- These pipes are also used in crude oil transfer and transfer of chemicals.

Typical reaction conditions of some HDPE processes:

Licensors	Union Carbide	Hoechst	
Temp.	85-105°C	80-90°C	80-100°C
Press.	Below 7 Bar	Below 10 Bar	15-30 Bar
Catalyst	Supported Cr.	-----	-----

## LDPE:

Most LDPE's are made by high pressure processes. Either tubular or Stirred. Autoclave reactors are used.

In the stirred Autoclave Reactor (cdF chemie France; DSM, the Netherlands; Union carbide, USA, Sumitomo Japan) the heat of reaction is absorbed by the cold ethylene feed which is mixed with the reacting polymer. The stirring action keeps a uniform temp. through out the reaction vessel.

LDPE production requires high purity ethylene (99.97%) A free-radical yielding catalyst such as peroxide is added to the high purity ethylene' compressed to operating pressure (1500-2000 bars) and then led to high pressure Autoclave reactor.

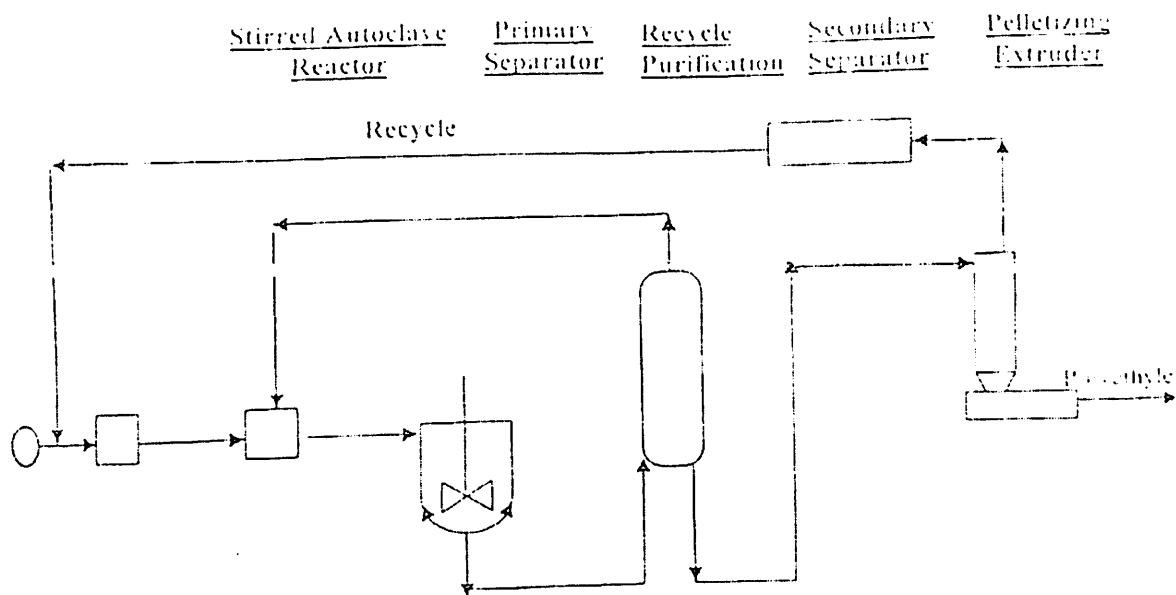
The compression is carried out in 2 or more stages.

In the first stage, highly purified ethylene (99%+) is mixed with purified ethylene from the low pressure cycle and is compressed to about 300 bars. In the intermediate pressure, recycle ethylene is introduced and the pressure raised to about 2000 bars using a secondary compressor. The free radical initiator is added in the last stage of compression. expands through a let-down valve and the unreacted ethylene is cooled, passed recycled to the secondary compressor

The product leaves the reactors, expands through a let down valve and enters the primary separator where the unreacted ethylene is cooled, passed through the through filters to remove waxes and recycled to the secondary compressor.

Molten polymer gets to a secondary separator at near atmospheric pressure' The product then fed in to the extruder to be palletized.





The Gulf process for producing LD-Polyethylene using the stirred autoclave react

### Typical reaction conditions are

Temp. 100 – 200° C  
Pressure 1500-2000 bars

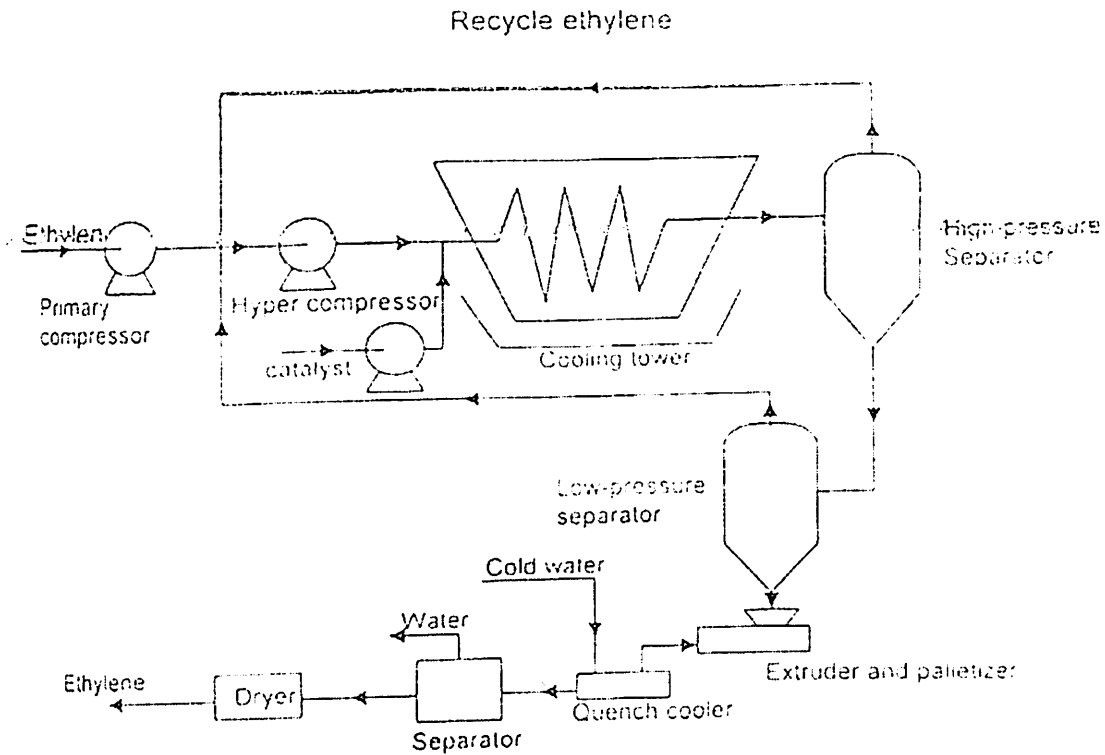
Ethylene : conversion  
Per Pass 10-25%  
Overall 95%+

IPCL ; Nagothane and Oswald Petrochemical, Mumbai have LDPE plants using Autoclave Reactors'

The Arco process uses a tubular reactor. LDPE polymers produced using tube reactors are better suited for film manufacture. Since the process operates at high pressures ;the built in safety measures in the plant are:

Explosion proof walls surrounding the tubular reactor coils and the pressure safety valves to instantly release excess pressure from the reactor to the flare when the decomposition occurs as feeds ethylene gets a small quantity of oxygen added through initiators

. IPCL, Baroda operates a tubular reactor plant'



IPEL: Baroda operates a tubular reactor

### LLDPE:

Linear low density Polyethylene process is of more recent origin.-LLDPE has economies of scale and capital cost advantage pressure LDPE manufacturing process. The process uses a catalyst to copolymerize Ethylene with alpha olefins. Ziegler-Natta catalyst systems have been used for LLDPE and now a new breed of highly selective catalysts called Metallocenes are used to produce vast range of LLDPE polymers.

The new enabling catalysts Metallocenes are used in 4 processing routed and are enabling new co monomer combinations including polymerization with styrene,VC,acrylates etc.

LLDPE has all the flexibility, clarity, good features of both LDPE and HDPE-strength, dielectric and high/low temp. Stability

## **Licensors for LLDPE process include:-**

Fluidized bed technology

- BP chemicals, UK
- Union Carbide, USA

Solution Polymerization process

- Montell, Italy
- Novacor Canada

## **USES:**

- Extrusion: Films; injection molding paint
- Cans Food Containers, Lids for glass Jars.

## **LLDPE Manufacturing Process:**

**Solution Phase Process:** Originally used to make HDPE; this process has been adapted to Copolymerization and production of LLDPE. The System runs at around 80 Bar and temp of 200<sup>o</sup> C-325<sup>o</sup>C with Ziegler Natta Catalysts. The metallocene catalysts improve the feed flexibility and range of Properties. This process has the advantage of taking a wide range of co monomers and can also use ethylene with purity as low as B5%. Novacor, Canada-Licensors.

For example if the reaction is to occur in cyclohexane medium; the reactor is filled with cyclohexane. Cyclohexane keeps the ethylene, the catalyst and Polyethylene fluid in contact with each other and also absorbs all the heat from the exothermic reaction.

The ethylene resides in the reactor about 2 minutes and as it polymerizes it remains dissolved in the cyclohexane. To keep the conc. Of PE in Cyclohexane at 35-40% the part of solution of feed, solvent and product are Continuously drawn off. Downstream the ethylene flashes off to be recycled in a flash tower

A precipitator removes the PE from cyclohexane by centrifuge. The LLDPE is stream-stripped to remove any remaining cyclohexane, dried, extruded, palletized and packaged.

## Fluidized bed reactors process

This most widely used but relatively simple wide range of copolymers. Popular comonomers include propylene, octane, process produces LLDPE with a normal hexane, isohexane and octane

The simple configuration of this process results in low level of environmental pollution, minimizes potential fire and explosion hazards and makes the process easy to operate and maintain.

Gaseous ethylene, co monomer and catalyst are fed to a reactor 1 containing a fluidized bed of growing polymer particles and operating at 20 Kg/cm<sup>3</sup> and around 100°C. A conventional single stage centrifugal Compressor 2. Circulates reaction gas, which fluidizes the reaction bed, provides raw material for the polymerization reaction and removes the heat of the reaction from the bed. The circulating gas is cooled in a conventional heat exchange (3).

The granular product flows intermittently into product discharge tanks (4) where unreacted gas is separated from the product. The separated gas is compressed and is returned to the reactor. Hydrocarbon remaining with the product are removed by purging with nitrogen

Polymer density can be controlled between 0.915-0.97 g/cm<sup>3</sup> and depending upon the catalyst type, molecular weight distribution is narrow to moderately wide

### Process Licenses-

- B.P.Chemicals, UK;
- Union carbide, USA,

## Polypropylene

PP is the most versatile among the polyolefins. PP is available as a homopolymer and a copolymer in combination with ethylene as the co monomer.

The process of polymerization essentially utilizes a Ziegler-Natta Catalysts.

## DEMAND AND SUPPLY SCENARIO

YEAR	05-06	06-07	07-08	08-09	09-10
DEMAND	1450	1595	1755	1930	2123
SUPPLY	1710	1790	1820	1920	2120
GAP	260	195	65	-10	97

YEAR	10-11	11-12	12-13	13-14	14-15
DEMAND	2335	2569	2826	3108	3419
SUPPLY	2220	2220	2220	2220	2220
GAP	-115	-349	-606	-888	-1199

ALL UNITS IN KTA

## SUPPLY FORECAST

- The Subcontinent' s conventional LDPE capacity has not increased since 2000 and no additions are planned for the forecast period. Domestic demand growth will be satisfied through imports.
- LLDPE capacity is forecast to grow at a rate of 9.0 percent per year during the forecast period. The capacity additions in the region are GAIL, adding a 120,000 metric ton swing unit in 2006, at Auraiya (60,000 metric tons are allocated to LLDPE). In 2009, Indian Oil will start up a 400,000 metric ton swing unit.
- The region' s HDPE capacity will only grow at 6.6 percent through the forecast period.
- The new HDPE capacity due to come on stream during the forecast period is a GAIL project mentioned in the LLDPE comments with 60,000 metric tons allocated to HDPE. Reliance plans to expand their 120,000 metric ton plant at Hazira, Gujarat by 40,000 metric tons in 2006. In 2009, Indian Oil will bring on stream a dedicated HDPE unit in Baroda, Gujarat.

- The region's PP capacity will increase on an average annual basis by 14.2 percent through the forecast period. Four world scale plants will be added by 2010.

- The new PP capacities coming on stream in the region are a 300,000 metric ton unit Reliance at Jamnagar, Gujarat in the first half of 2006. This unit uses Unipol gas phase technology. Reliance also plans to add three units of 300,000 tons each in 2010, also based on Unipol technology.

In 2009, Indian Oil will start up a 425,000 ton unit. Indian Oil has chosen the Basell Spheripol technology.

## **DEMAND FORECAST**

- LDPE's largest end use segment is film and sheet, representing over 70 percent of the end use demand, with extrusion coating accounting for 9 percent of the end use demand.

- In common with many other regions, LLDPE is the fastest growing polymer in the polyethylene group in the Subcontinent, in terms of industry demand.

- LLDPE film and sheet has the largest end use market share, with almost 70 percent. The next most significant sector is rotational molding with a 14 percent market share.

- We forecast domestic demand for LLDPE to grow at a rate of 8.6 percent per year through the forecast period.

- We forecast that the region's HDPE domestic demand will grow at 7.4 percent per year through the forecast period.

- The end use demand pie chart shows that HDPE has more balanced segments compared to the other polyethylenes, which are heavily dependant on film and sheet. The film segment is the largest at almost 25 percent, but blow molding and injection molding account for 18 percent each. The pipe market has the highest growth within the end use market segments and is forecast to grow at almost 11 percent through the forecast period.

- Domestic demand for PP will grow at 9.6 percent through the forecast period.
- Injection molding end use makes up over 40 percent of the regions PP demand. The fiber and raffia segments account for 30 percent. India will produce in excess of 1 million passenger cars this year. The growth of automobile production from 2005 through 2010 will be 9-10 percent per year, and as polypropylene is the most widely used polymer in car production, it explains

why despite all the new capacity additions, India remains a net importer.

## **SUMMARY FORECAST**

- Operating rates for LDPE are forecast to remain fairly stable through 2007 and then fall off in latter years, as new capacity enters the global market.
- Domestic operating rates for LLDPE will "seesaw" up & down, as new capacity starts up during the forecast period.
- Operating rates for HDPE for the forecast period are expected to remain above 90 percent.

Relatively strong PP demand growth will keep the operating rates averaging close to 90 percent early in the forecast period. The rates will drop quickly in 2009 and 2010 as the new IOC and Reliance capacity start up.

# Polymer dispersion

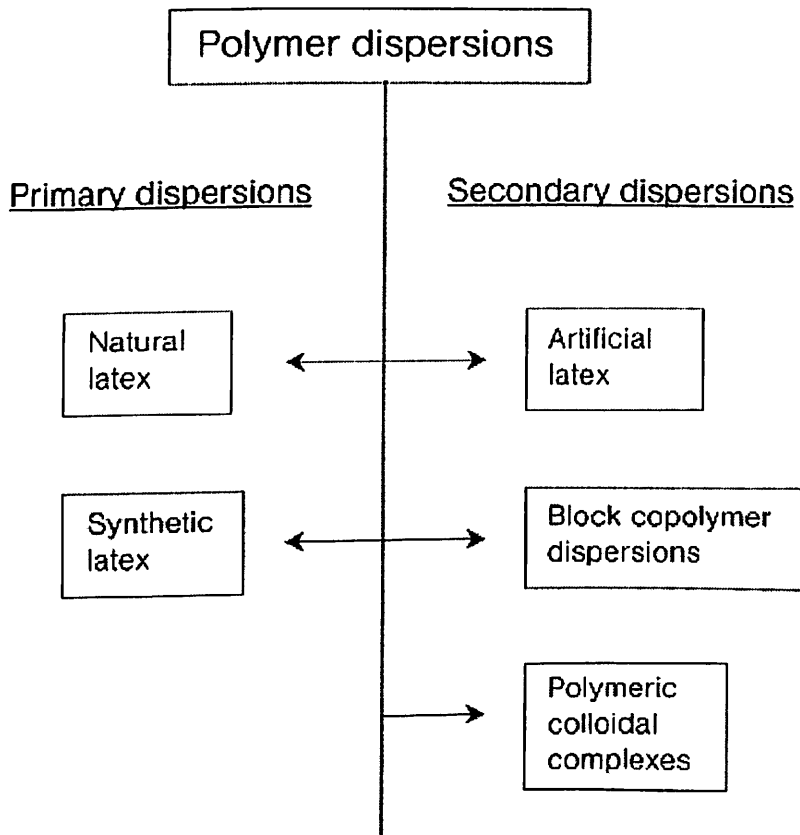


Fig. 1.1 Classification of polymer dispersions.



## **Preparation of Polymeric Latex Particles**

The technical term "polymer dispersion" describes a special state of matter and not a special chemical composition of the polymeric material. In other words, any kind of polymer can be obtained in the form of a polymer dispersion as either a primary or secondary dispersion (see Fig. 1.1). Many applications of latex particles require not only a specific chemical composition but also a specific particle size or particle size distribution. Particle size in the following always means the diameter of an equivalent sphere. Note that at a given solids content the particle size determines the interfacial area between polymer and continuous phase as well as the surface-to-volume ratio of the dispersed material. Thus, it is an important parameter determining both the preparation and the application of latex particles.

### **Secondary Polymer Dispersions**

Artificial latexes have until now never been of much industrial interest although several preparation methods have been developed. There are basically three driving forces for the development of artificial latexes. The first is of some economic importance because it is more advantageous to transport polymers as dry solid material instead of dispersions with about 50% by weight dispersion medium.

The second has to do with the superior material properties of polymers that cannot be prepared by heterophase polymerization techniques, such as polyurethanes or chlorosulfonated polyolefins, but whose application as polymer dispersions is

advantageous or desirable. The importance of composite polymer dispersions, involving combinations of different materials such as mineral substances and polymers for various potential applications, are the third reason for ongoing research on artificial latexes.

There are two principal possibilities for preparing emulsions: the disruption of a larger volume into smaller subunits (comminution) or the construction of emulsion droplets from smaller units (condensation). Both methods are of technical importance for the preparation of emulsions for polymerization processes.

Emulsification by comminution is very common and the most widely used procedure. Under the action of intense mechanical energy any combination of immiscible and mutually nonreactive liquids can be broken up into an emulsion.

Comminution can be performed either by intense stirring, with homogenizers, or by ultrasonication. The most exciting question after completion of the emulsification is that concerning the structure of the emulsion, i.e. which liquid forms the dispersed phase and which the continuous one? The result of the emulsification process is influenced not only by the energy input but by the volume ratio of the liquids, the kind of emulsifying agent, and its concentration, the last effect being strongly affected by the temperature. The most important property of the emulsifying agent is its solubility or, in the case of solid, so-called "Pickering stabilizers", the wetting behavior of the liquids, expressed by the contact angle.

Bancroft summarized the results of emulsification experiments obtained until the early twentieth century in a rule of thumb, which indicated that in order to have a kinetically stable emulsion the emulsifying agent must be soluble in the continuous phase. This rule finds its expression also in the empirical system of the HLB values (hydrophilic-lipophilic balance), which was developed in the

middle of the twentieth century in order to simplify the selection of effective emulsifiers for a particular emulsification task .

In contrast to comminution techniques the preparation of emulsions by condensation does not require mechanical energy, except sometimes gentle stirring to avoid creaming or settling. There are basically two different types of condensation methods: droplet nucleation and swelling of disperse systems. However, a combination of the two has some meaning especially for heterophase polymerizations. Note that condensation processes are mainly determined by thermodynamic principles. For a more detailed summary of the principles of preparing emulsions with regard to their application in heterophase polymerizations the reader is referred to .

The preparation of artificial latex particles by direct emulsification of polymer solutions has been reviewed . The authors distinguish between three different methods. First, direct emulsification, which means that a liquid polymer or polymer solution in a volatile, water-immiscible solvent is emulsified in a surfactant solution and at the end the solvent is removed by steam stripping. Second, inverse emulsification, which means that as a first step the polymer or polymer solution is mixed with fatty acid and in a subsequent step is slowly fed dilute aqueous base. Thus, a water-in-polymer emulsion is formed, which, with increasing amount of base solution, is finally converted into a polymer-in-water emulsion. Third, self-emulsification, which is obtained with polymers containing lyophilic groups in such amounts that dispersions are formed spontaneously upon contact with the continuous phase. Prominent examples are block copolymers in selective solvents (see above). This method is based on thermodynamic principles and hence is classed as an emulsification technique by condensation. Examples of

polymeric materials that have been successfully transformed into artificial latex particles by either of the first two principles above are: polystyrene, poly(vinyl acetate), epoxy resins, derivatives of cellulose, polyesters, alkyd resins, synthetic rubber, poly(vinyl butyral), silicones, polyurethanes, and many others. Moreover, core-shell latex particles have been prepared by seeded emulsion polymerization using artificial latex particles as seeds. For instance, by emulsification with ultrasonication of poly(styrene-*b*-butadiene-*b*-styrene) (Kraton from Shell Chemical Company) rubbery seed particles have been prepared, which were subsequently covered with a glassy shell of poly(methyl methacrylate). Another example of potentially practical importance for the application of artificial latex particles is given in . Amino-terminated telechelic polybutadiene (number average molecular weight of  $3100 \text{ g mol}^{-1}$ ) dissolved in toluene was emulsified by ultrasonication into an aqueous solution of sodium dodecyl sulfate (27.4 wt.% of emulsifier relative to the amount of polybutadiene) to get stable artificial latex particles with an average diameter of about 50 nm. These particles were used as curing agents in a blend with poly(styrene-co-*n*-butyl acrylate-co-dimethyl-*m*-isopropenylbenzyl isocyanate) primary latex particles, which were prepared by emulsion polymerization. Among the above comminution techniques ultrasonication has a special position. Ultrasonication means the application of high-frequency vibrations. In a first step larger drops are produced in such a way that instabilities of interfacial waves are enhanced, leading finally to crushing. These drops are subsequently fragmented into smaller ones by acoustic cavitation. The use of ultrasound in emulsification processes is much more efficient than the application of rotor/stator systems. Experimental results clearly show that ultrasonication leads to smaller drops, less polydisperse drop-size distribution, more stable emulsions, and less surfactant

consumption for a desired drop size. Furthermore, during ultrasonication much less energy is wasted compared to all other mechanical comminution techniques.

The preparation of artificial latex particles by condensation also requires as a first step the formation of a polymer solution. In the second step the decomposition of this solution is induced by any method that reduces the interaction between the polymer and solvent molecules. For instance temperature changes, or addition of nonsolvents, or increasing the ionic strength in polar or aqueous solutions are suitable means to induce this phase separation. Stabilization of the precipitating polymer molecules prevents the formation of a macroscopic coagulum and favors the formation of artificial latexes. The following examples should illustrate the procedure. First, solutions of sulfonated polystyrene molecules with a molecular weight of about  $3 \times 10^5 \text{ g mol}^{-1}$  and a degree of sulfonation of about 5% in tetrahydrofuran ( $2 \times 10^{-3}$  or  $2 \times 10^{-2} \text{ g ml}^{-1}$ ) were mixed with an excess of water. The precipitating polymer forms particles in a size range below 100 nm in diameter, which are stabilized by sulfonate groups. The particle size distribution does not depend on the kind of mixing (ultrasonication or stirring) but it does depend on both the concentration of the starting solution and the order of mixing, that is whether the solution is added to water or vice versa. Second, the formation of sterically stabilized particles of poly(ethylene glycol-*b*-*N*-isopropylacrylamide) particles by increasing either the temperature or the ionic strength. Third, the formation of polystyrene particles stabilized with cetyltrimethylammonium bromide as surfactant and the utilization of these particles as seed in a subsequent emulsion polymerization. Note, the first two examples belong to the above self-emulsification principle. Other examples are the forma-

tion of micelles from amphiphilic block copolymers (see above), which can be subsequently used as seed particles in emulsion polymerization . But also block copolymers themselves in selective solvents can form latex particles with unique morphologies. The utilization of block copolymers for various (potential) applications has recently been reviewed. As condensation techniques to prepare artificial latex particles are governed by thermodynamic principles the final, stable structure should be the thermodynamically favored one. However, the formation of this equilibrium structure can take quite a long period of time, depending on the chain mobility and energetic characteristics of the particular structure (especially the depth of the minimum in the free energy in relation to thermal energy). For instance, when to a solution of poly(styrene-*b*-2-cinnamoyl ethyl methacrylate) polymer in tetrahydrofuran (good solvent for both blocks) acetonitrile (nonsolvent for both blocks) is added, precipitation takes place over several weeks, depending on the amount of acetonitrile. If the acetonitrile content is 80±90% structure formation starts with simple core±shell particles then changes via more complex morphologies such as onion-like structures until the final precipitate is formed .

The few examples mentioned here illustrate that there is obviously no limitation with regard to the kind of polymer that can be used to prepare well-defined artificial latex particles. The process is easier if the polymer can be dissolved but this is no limitation as it is in principle also possible to start with a solid, although the probability of degradation due to high shear and tribochemical reactions is inherent during grinding in the presence of the continuous phase.

# Primary Polymer Dispersions via Heterophase Polymerizations

## General Remarks

Heterophase polymerization techniques offer the possibility of preparing directly almost any type of latex particles that is desired. A general rule can be formulated that any polymerization recipe that works well under homogeneous conditions can be transformed into a heterogeneous polymerization system by the proper choice of a corresponding continuous phase, which should be liquid, at leastrene (titanium complex)

Tab. 1.2 Heterophase polymerization chemistry

<i>Polymerization mechanism</i>	<i>Example</i>	<i>Ref.</i>
Enzymatic biosynthesis	cis-polyisoprene (natural rubber)	[90]
	poly-3-(hydroxyalkylalkanoates)	[14]
Condensation	polyurethanes	[91]
	silica particles (Stöber silica)	[92]
Ring opening	poly- $\epsilon$ -caprolactone	[93]
	poly(D,L-lactide-co-glycolide)	[94]
Ionic	cationic (methyl cyclosiloxanes)	[95]
	anionic (methyl/cyclosiloxanes styrene)	[96, 97]
Noble metal catalysts	polyethylene (bi-nuclear Ni-ylide)	[98]
	styrene (titanium complex)	[99]
Radical	Most often in water and organic continuous phases	[55, 100]

polymerization temperature. The continuous phase has to fulfill three basic requirements: it should be chemically inert, a nonsolvent for the polymer, and possess good heat transfer properties (for technical applications on larger scales). If,

however, the continuous phase interferes with recipe components, the transfer from homogeneous to heterogeneous polymerization conditions requires additional effort and may require exchange of one or other recipe component. Tab. 1.2 summarizes examples of the kinds of polymerization chemistry that have been applied in heterogeneous polymerizations so far. This list is by no means complete but it confirms on the one hand the above statement with respect to the universality of heterophase polymerization and on the other the ongoing research interest over almost a century.

Latex particles can be specifically designed with regard to various parameters as depicted in Fig. 1.2. The statement that basically all kinds of polymers can form latex particles already implies that there is no limit regarding the mechanical properties of latex particles. Tab. 1.3 shows that the glass transition temperatures of various homopolymers already span almost 250 degrees and thus particles are accessible at room temperature that may be either fluids or solids. A further fine-tuning of the mechanical properties is possible by copolymerization and/or controlled cross-linking. The volume properties of particles can be modified in various ways. Solid cores with desired gradients in chemical composition and physical properties can be prepared by sophisticated methods of computer-controlled semi-batch polymerizations with predetermined monomer addition protocols.



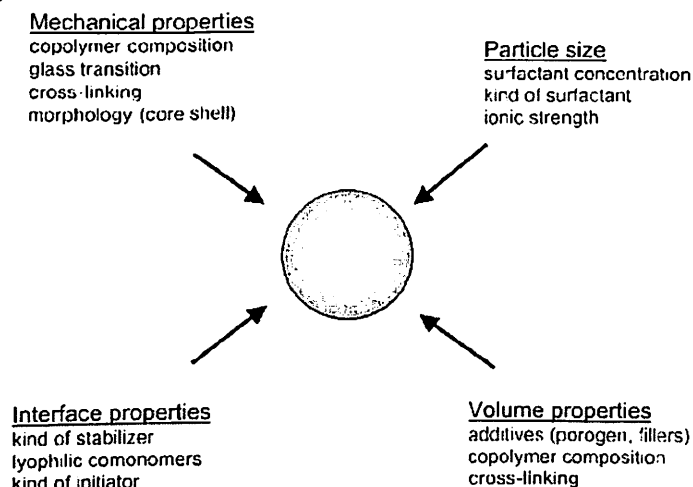
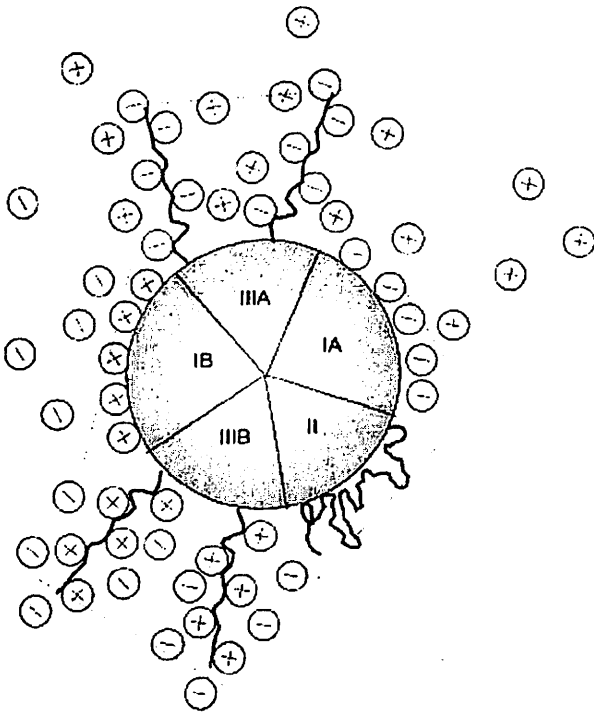


Fig. 1.2 Parameters characterizing latex particles, and the possibilities for adjustment.

Tab. 1.3 Glass transition temperatures ( $T_g$ ) for some homopolymers (Data from J. Snupek, *Progr. Org. Coat.* 1996, 29, 225–233)

Monomer	$T_g$ (°C)	Monomer	$T_g$ (°C)
Acrylamide	133	n-Butyl methacrylate	20
Methacrylic acid	130	Tetradecyl acrylate	20
o-Vinyl toluene	115–125	Cyclohexyl acrylate	16
Phenyl methacrylate	110	Methyl acrylate	5–8
t-Butyl methacrylate	107	Vinyl isopropylether	–3
Acrylonitrile	96–106	n-Hexyl methacrylate	–5
Acrylic acid	106	i-Propyl acrylate	–5
Methyl methacrylate	105	Tetradecyl methacrylate	–9
p-Vinyl toluene	101	n-Octyl methacrylate	–20
Styrene	100	Ethyl acrylate	–20 to –27
Vinyl chloride	80	Vinylidene Chloride	–23
m-Vinyl toluene	72–82	Ethyl vinyl ether	–42
Ethyl methacrylate	65	n-Propyl acrylate	–52
sec-Butyl methacrylate	60	n-Butyl acrylate	–52 to –57
2-Hydroxyethyl methacrylate	55	2-Ethylhexyl acrylate	–60 to –77
t-Butyl acrylate	41	n-Dodecyl methacrylate	–65
n-Propyl methacrylate	35	n-Decyl methacrylate	–70
n-Hexadecyl acrylate	35	Ethylene	–70 to –77
Vinyl acetate	32	Butadiene	–87
2-Hydroxypropyl methacrylate	26	Octadecyl methacrylate	–100



**Fig. 1.3** Illustration of the latex particle-continuous medium interface and the possibilities for stabilization (not to scale).

Fig. 1.3 Illustration of the latex particle-continuous medium interface and the possibilities for stabilization (not to scale).

For applications where individual latex particles are required, the interfacial properties and the particle size are the more crucial parameters. The interfacial properties can be adjusted by the choice of stabilizer, initiator, and lyophilic co-monomers. For example, by changing these recipe components four different types of polystyrene latexes have been prepared and investigated in a comprehensive study . The interface of an assumed model latex particle as sketched in Fig. 1.3 is characterized with regard to charge sign as well as concentration of charges and the extension of the interfacial layer into the continuous phase. The main function of the particle interface is to contribute to particle stabi-

lization, that is to counteract the attractive van der Waals forces. Parts IA and IB of Fig. 1.3 show the most common cases of electrostatic stabilization with anionically and cationically charged stabilizers, respectively. Part II shows steric stabilization of colloidal particles without any contribution of charges, which can be perfectly realized in nonpolar, organic continuous phases with polymeric stabilizers. In contrast, parts IIIA and IIIB sketch the case of electrosteric stabilization with anionic and cationic polyelectrolytes, respectively. The dotted lines in each section of the model particle indicate the hydrodynamic layer thickness, or corona thickness, that is the extension of the interfacial layer into the continuous phase (DR). The particles move in the continuous phase with this size, which can be measured by dynamic light scattering. In contrast, transmission electron microscopy pictures the core size of the particles, because the stabilizer layer collapses in most cases during sample preparation onto the particle with a thickness of only about 1 nm. Each of the major cases I, II, and III contributes specifically to particle stability. The stabilizers or stabilizing moieties have to fulfill only one basic requirement, which is, according to Bancroft's rule (see above), they have to be lyophilic, i.e. soluble or strongly interacting with the continuous phase. The stabilizer molecules can be either adsorbed or covalently connected with the core material, or in some special cases simply dissolved in the continuous phase. But the last case, which will be not considered further, also requires a lyophilic decoration of the particle interface. Tab. 1.4 summarizes the key features of the principal kinds (I±III) of latex particle Stabilization. Each kind of stabilization has at least one special advantage that makes this particular kind of stabilization useful, but for technical polymer dispersions application of a well-balanced mix of all stabilization possibilities is neces-

sary. This is especially so if during storage and application of water-based dispersions both the ionic strength and the temperature change considerably. The most effective way to realize electrostatic stabilization is via the application of low molecular weight ionic surfactants such as alkyl sulfates (prominent example: sodium dodecylsulfate), or alkyl sulfonates, or alkyl ammonium compounds (prominent example: cetyltrimethylammonium bromide). Depending on the charge sign of the stabilizer either anionic (most prominently peroxydisulfates) or cationic initiators (such as 2,2'-azobis(2-amidinopropane)dihydrochloride) are used. But it has been shown that nonionic, water-soluble initiators such as symmetrical poly(ethylene glycol)-azo compounds might also be advantageous. Moreover, the same investigations showed that much smaller particles were obtained with polymerization recipes containing ionic species than in completely nonionic polymerizations. These results clearly indicate that for effective stabilization some ions arising from the initiator, or ionic surfactants, or ionic co-monomers are needed at the particle surface. Furthermore, ionic emulsifiers are obviously more effective in stabilizing polymer particles than nonionic stabilizers. The drawback of purely electrostatic stabilization is the proneness to decrease with addition of electrolyte as the repulsive potential decreases exponentially with increasing ionic strength (see Tab. 1.4). In contrast, the use of nonionic stabilizers has a dramatic effect on the electrolyte stability of latex particles. For instance, the additional stabilization of negatively charged polystyrene particles with dodecyl hexaoxyethylene glycol monoether causes an increase in the critical coagulation concentration (determined with lanthanum nitrate) by an order of magnitude. Besides increased stability against electrolytes another advantage of steric stabilization is the frequently observed reversibility of the flocculation process, which occurs if the con-

ditions that have caused the flocculation are removed again. This reversibility requires that the stabilizers are strongly adsorbed or covalently bound to the particles. Also, an increase in the molecular weight of the steric stabilizer can kinetically retard the displacement of otherwise only weakly anchored stabilizers. Finally, as the name already indicates, electrosteric stabilization should combine features of the two other principles. However, the situation with regard to the structure of electrosteric stabilizers is ambiguous, as the charges may be either distributed statistically along the chain or arranged as a polyelectrolyte block. The first case leads to a so-called ringlet adsorption pattern (DR comparable with low molecular weight ionic surfactants) and the latter to so-called porcupine particles (DR up to more than 100 nm). Compared with poly(carboxylic acid) blocks as stabilizers, polyelectrolytes with strong acid groups (such as sulfonates) offer the advantage that their stabilizing action is practically independent of the pH. For strong polyelectrolytes tethered to spherical particles and forming a corona of thickness  $DR$ , Pincus derived the scaling relation given in Tab. 1.4. Note that this relation predicts extraordinary electrolyte stability compared with purely electrostatically stabilized particles, which show an exponential dependence on the ionic strength. Indeed, this was experimentally observed for various types of polyelectrolyte block copolymers such as poly(alkyl methacrylate-*b*-sulfonated glycidyl methacrylate) but also for poly(ethyl ethylene-*b*-styrene sulfonate). Moreover, in the latter case a Pincus brush behavior was observed but with clear experimental evidence that  $a$  depends on the ratio of corona thickness to particle size. Seeded polymerizations the control of the final particle size in *ab* initio polymerizations is more complicated and prone to fluctuations. The particle formation process is mainly responsible for this, because it is the least understood.

part of heterophase polymerizations and its investigation faces serious experimental problems.

Tab. 1.4 Principles of stabilization of colloidal particles

Stabilization	Acting forces	Important parameters
Electrostatic (I)	Electrostatic repulsion of equally charged particles: repulsive potential ( $V_R$ ) around charged particles at distance ( $d$ ) decays as:  $V_R \propto f \cdot \Psi \cdot \exp\left(-\frac{d}{\lambda_D}\right)$	Charge density at the interface, surface potential ( $\Psi$ ), ionic strength ( $I_S$ ); Debye screening length ( $\lambda_D$ )  $\lambda_D = \left( \frac{\epsilon \cdot \epsilon_0 \cdot k_B \cdot T}{\sum_i (z_i \cdot e)^2 \cdot C_{\text{salt}}} \right)^{0.5}$
Steric (II)	Osmotic and entropic forces between overlapping stabilizer layers of approaching particles  $V_R \propto \frac{C_{S,L}^2}{v_{e,p} \cdot \rho_{S,L}^2} \cdot (\Psi_s - Z_{S,CP}) \cdot \left[ \left( \Delta R - \frac{d}{2} \right)^2 \left( 3 \frac{D}{2} + 2 \Delta R + \frac{d}{2} \right) \right]$	Solution state of stabilizing polymer molecules (interaction parameter between stabilizing polymer and continuous phase); temperature, ionic strength as far as both influence the solution state of the lyophilic polymer
Electrosteric (III)	Competition between the osmotic pressure induced by counterion condensation inside the polyelectrolyte corona, which stretches the polyelectrolyte chain into the aqueous phase, and entropic polymer elasticity, which pulls the chains back to the surface,  $\Delta R \propto I_S^a; a = -1/5$  (Pincus brush behavior)	Ionic strength, conformation and charge density of the polyelectrolyte chain, ration corona thickness to particle diameter ( $D$ ); corona shrinks upon increasing ionic strength

Particle nucleation occurs at an extremely low conversion or solid content.

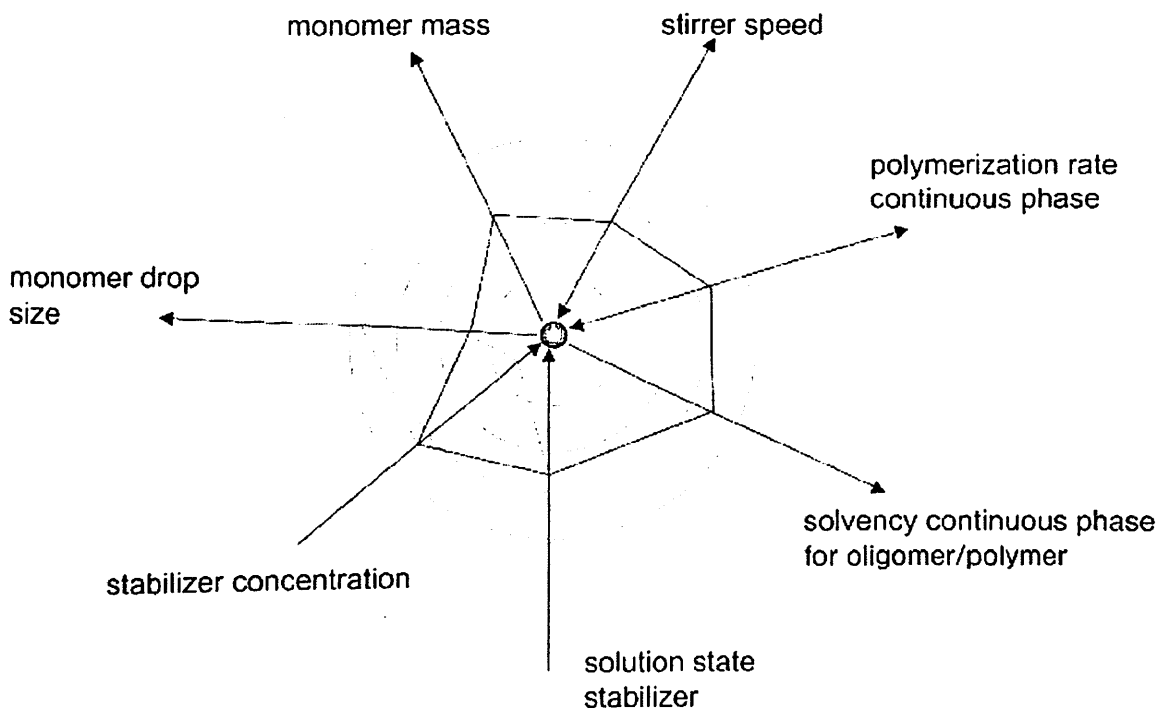
For instance, in ab initio surfactant-free styrene emulsion polymerization started with potassium peroxydisulfate, nucleation occurred at 60 °C after a pre-nucleation period - in which aqueous-phase polymerization takes place - of 431 s. At the moment of nucleation, which takes place within one second  $1.76 \times 10^{13}$  particles are formed per cm<sup>3</sup> of water with an average particle size of 13 nm. The amount of polymer, or better oligomer, formed up to this moment is  $2.13 \times 10^5$  gcm<sup>-3</sup> of water. This example of an emulsion polymerization shows that an ab initio heterophase polymerization starts in the continuous phase and that it can be carried out even in the absence of both emulsifier and free monomer phase. Thus, the nucleation process can be identified as formation of the second, polymer, phase. The straightforward conclusion is that from a thermodynamic point of view nucleation requires that the reaction system, which in this situation is a solution of oligomers in the continuous phase, be brought into a thermodynamically unstable intermediate state. From a physical point of view this corresponds exactly to a situation as described by the classical nucleation theory or the theory of spinodal decomposition. According to these theories nucleation is characterized by the necessity to surmount an energy barrier via fluctuations. Therefore a free energy of activation for such processes exists, which strongly depends on all experimental conditions such as temperature, pressure, and composition. Even minor changes in the experimental conditions can cause huge effects because the rate of the phase transition depends exponentially on the activation-free energy. This is important for carrying out heterophase polymerizations, as for instance the kind of reactor material or

even the replacement of just parts of the reactor can change reaction rate and product properties. For instance, it has been shown that emulsion polymerization of methyl methacrylate is strongly influenced by the kind of reactor material (stainless steel, Teflon, glass) especially at low emulsifier concentrations (see below). Problems with regard to reproducibility have also been observed during the initial period of dispersion polymerization of methyl methacrylate in methanol initiated with 2,2'-azobisisobutyronitrile.

Of course, the seed particles themselves have to be prepared by ab initio polymerizations but fluctuations in their properties can easily be compensated by appropriate action [varying either  $V_{seed}$  or  $V_{feed}$ , see Eq. (1)] during the seeded polymerization.

Despite all these complications during the nucleation stage of ab initio heterophase polymerizations general rules exist about how to influence the final particle size and how to move from a given starting point in a desired direction of change. For given conditions the kind of a "rule-of-thumb graph" in Fig. 1.4 can be used as a guideline for decisions with regard to kinds of monomers, initiator, stabilizer, continuous phase, and experimental setup (mainly reactor material and shape). Provided that colloidal stability is preserved throughout all variations, that graph is to be read as follows.





**Fig. 1.4** Rule-of-thumb graph for predicting tendencies in the change of average particle size during ab initio heterophase polymerizations.

The average particle size increases from the center outwards. Arrowheads indicate the direction of changes in the average particle size if the corresponding parameter is <sup>a</sup>increased<sup>o</sup> or <sup>a</sup>improved<sup>o</sup>. Double arrowheads mean the change in  $D$  is not unambiguous but depends on the level from which the changes were started. In other words the dependence of  $D$  on that parameter shows a minimum or maximum. For instance, increasing the surfactant concentration causes the average particle size to decrease whereas increasing the average size of monomer droplets in the case of suspension, microsuspension, miniemulsion, and microemulsion polymerization and proper initiation leads to an increase in  $D$ . This is indicated by the dotted lines in comparison with the starting situation depicted by full lines. In this sense the magnitude of the area

spanned by the connecting lines between each parameter is a qualitative measure of the particle size. Note that these are general considerations, which, however, can be used to modify experiments under specific conditions (recipe, reactor) in order to shift particle sizes in a desired direction. Some practical examples of how the particle size can be controlled by various recipe components and process parameters are discussed below.

For most large-scale applications of polymer dispersions a specific particle size distribution is more advantageous than monodispersity. High solids content of polymer dispersions, which is desirable in order to minimize the amount of water to be transported, requires close packing of latex particles. At the same time the viscosity should not be increased too much in order to retain ease of processing. Close packing of latex spheres depends on the potential that imparts stability to them and hence on the composition of the interface. Particles with soft potentials (that is purely electrostatic stabilization) interact over long distances and closer contact between the particles is prevented. In this sense it is not the mass fraction (solids content) but the effective volume fraction (including the hydrodynamic layer thickness) that determines viscosity. To get latexes with solids content about 70% or even higher requires polymodal particle size distributions with larger and smaller spheres (the smaller spheres have to fit in the interstices between the larger ones). This principle was successfully applied to get high solids polymer latexes up to 70% solids content and low viscosity. It was found that there is a critical ratio between the larger and smaller sphere diameters, which should be above 10 in order to get both low viscosities and high solids content. The preparation of polymodal latexes requires the occurrence of multiple nucleation events in the course of the polymerization, which can be realized either by emulsifier feeding

protocols and/or by proper choice of recipe components (co-monomers)

Monodisperse latex particles are frequently required for other than commodity applications, for example for medical applications . Moreover, monodisperse latexes are of great value for investigations elucidating the mechanism of heterophase polymerizations (especially competitive growth experiments, see below) or proving theories of colloidal stabilization, and as secondary calibration standards in electron microscopy, light scattering, sedimentation and aerosol studies, and other fractionation techniques. But they also play an important role in investigations of a variety of colloidal phenomena. Examples are: (a) as model systems for soft-matter physics especially in understanding interactions in colloids , (b) as materials to trigger new characterization methods , (c) as objects to observe directly nucleation and growth of crystals , and (d) as components in advanced material science research .

## **Practical example:**

### **Particles Prepared by Multi-step or Seeded Polymerizations**

In addition to the above methods of producing latexes on an industrial scale, tailoring of latex particles by seeded polymerizations is also a powerful tool to prepare specialty latex particles.

The first example considered here is the so-called "shot addition" or "shot Growth" technique, which has been successfully used to tailor surfaces of latex particles with lyophilic or functional monomers. The functional monomers are added during the later stages of the polymerization either all at one time (that is as a "shot") or over a longer period of time. The latter is preferred if the corresponding polymer is insoluble in the continuous phase so that secondary nucleation might occur. In this case the feed rate of the monomers has to be adjusted to fit the rate of polymerization. For instance, use of reaction calorimetry allowed the kinetically controlled synthesis of core-shell latex particles with fluid cores and cross-linked rubbery shells .

Knowledge of the reaction rate profile allowed the start of feeding of the monomer mixture for the shell (n-butyl acrylate and 1,3-diisopropylene benzene) at about 85% conversion of the first monomer batch. Feeding was continued for 90 min in order to avoid accumulation of the monomer mixture in the continuous phase and to prevent secondary nucleation. If the cross-linking density of the shell is in the correct range the fluid core polymer [(poly(2-ethylhexyl methacrylate), molecular weight regulated with tetrabromomethane as chain transfer agent]

can be extracted and thus empty shells are left.

A second example describes the preparation of cross-linked polystyrene particles with acetoxy groups at the surface by the addition of p-acetoxystyrene almost at the end of styrene/divinylbenzene emulsion polymerization. In a subsequent modification step the acetoxy groups are converted into hydroxyl groups. Finally, the poly(p-hydroxystyrene) shell of these particles is able to imbibe silver and ruthenium nanoparticles. In these composite particles the metal colloids were bound strongly to the surface and were stable in a variety of organic solvents. Another example is the preparation of monodisperse core-shell particles, which can be used to prepare three-dimensional nanocomposites as described in .

In these particles core and shell can either have different properties such as glass transition temperatures and molecular weights or can contain different functionalities such as chromophores. For instance, Kalinina and Kumacheva also describe the synthesis of particles with slightly cross-linked shells and fluid cores finally forming a porous film with a regular and controlled three-dimensional arrangement of pores. Another interesting example is the attachment of chromophores to the cores leading to polymeric nanocomposites, which can be used as three-dimensional memory storage.

Another kind of composite latex particles is polystyrene particles coated with conducting polymers such as polypyrrole, polyaniline, or poly(3,4-ethylenedioxythiophen) prepared by modification of sterically stabilized polystyrene particles as described in .

The above examples were carried out in such a way that the monomer addition to seed particles takes place during the polymerization process with very little

swelling of the first-stage particles. Two basic techniques have been developed to promote swelling of precursor particles so that polymerization finally yields monodisperse latex particles with diameters larger than 5  $\mu\text{m}$  up to several tens of micrometers, which is a size range in which a high degree of monodispersity is not accessible by a single polymerization step. Highly swollen latex particles behave much more like emulsions than like suspensions. A basic understanding of this swelling process requires consideration of both the Kelvin equation (Eq. 8) and Eq. (9), which describes the swelling behavior of latex particles as derived in .

$$\ln \frac{p'}{p_0} = \frac{4 \cdot \sigma}{D} \cdot \frac{v'}{RT} \quad (8)$$

$$\left( \frac{4 \cdot \sigma}{D} + P_{\text{sw}} \right) \cdot \frac{v_{\text{mon}}}{R \cdot T} = - \left[ \ln(1 - \phi_2) + \left( 1 - \frac{1}{j_2} \right) \cdot \phi_2 - \chi_{\text{m,p}} \cdot \phi_2^2 + \frac{v_{\text{mon}} \cdot \rho_2}{M_c} \left( \phi_2^{1/3} - \frac{\phi_2}{2} \right) \right] \quad (9)$$

The Kelvin equation indicates that larger objects, in coexistence with smaller ones, will grow in size at the expense of the smaller objects, which have a tendency to dissolve. This effect is known in colloid science as *Ostwald ripening*. Equation (8) shows the Kelvin equation for liquid droplets surrounded by vapor where  $p'$  is the vapor pressure outside the drop,  $p_0$  is the bulk vapor pressure,  $v''$  is the molar volume of the liquid, and  $RT$  is the thermal energy [204]. The smaller the drops the larger  $p'$  and hence the higher the tendency to degrade.

The term on the right hand side of Eq. (9) is the free energy of mixing between polymer and monomer where the Flory-Huggins-Rehner expression for cross-linked polymers is used.  $\sigma$  is the interfacial tension between the swollen particles and the continuous phase,  $P_{sw}$  is the swelling pressure,  $\chi_{mp}$  is the polymer monomer interaction parameter,  $\phi_2$  is the polymer volume fraction in the swollen particle,  $RT$  is the thermal energy,  $j_2$  is the average degree of polymerization of the polymer molecules,  $\rho_2$  is the polymer density, and  $\overline{M}_c$  is the average molecular weight between two cross-links in the network. If the latex particles are not cross-linked ( $\overline{M}_c \Rightarrow \infty$ ) and if  $P_{sw} \Rightarrow 0$  Eq. (9) becomes identical with the Morton-Kaizerman-Altier equation [205] as derived by Gardon [206]. Between  $\phi_1$ , the monomer volume fraction, and  $\phi_2$  the relation  $\phi_1 + \phi_2 = 1$  exists. The swollen ( $D$ ) and unswollen particle size ( $D_0$ ) are connected with  $\phi_2$  via  $(D/D_0)^3 = 1/\phi_2$  whereas  $\phi_1$  is related to the monomer concentration inside the particles ( $C_{M,p}$ ) via  $\phi_1 = C_{M,p} \cdot v_{mon} = \frac{v_{m,p}}{v_{m,p} + v_{p,p}}$  with  $v_{m,p}$  and  $v_{p,p}$  being the monomer volume and the polymer volume inside the swollen particles, respectively.

The right-hand side of Eq. (9) promotes swelling whereas the terms on the left-hand side counteract swelling. The first term on the left-hand side is the interfacial free energy, which counteracts swelling due to an increase in the particle interface. The second term on the left-hand side originates from a volume work due to attractive forces between polymer chains in concentrated solutions as has been concluded from osmotic modulus measurements.  $P_{sw}$  in Eq. (9) is comparable to the pressure known from the swelling of macroscopic gels, contributing together with the partial molar free interfacial energy to the equilibrium with the chemical potential of the swelling agent.  $\Phi_1$  increases the larger the particles, the lower both the interfacial tension and the degree of polymerization of the seed polymer, and the higher the temperature, but it decreases with increasing degree

of cross-linking and with increasing Flory-Huggins interaction parameter.

Recognizing the similarity between swollen latex particles and emulsion droplets John Ugelstad started a great deal of both theoretical and experimental work to develop new methods of monomer emulsion preparation. One of the key points is the effect that the dissolution of emulsion drops can be retarded or even prevented if the drops contain a substance (compound-2), which is insoluble in the continuous phase. In this case the decrease in size increases the chemical potential of compound-2 inside the smaller drops and generates a force counteracting Ostwald ripening. Ugelstad was able to show that compound-2 has an additional effect on swelling, because the entropy term in the swelling equation (Eq. 9), which is  $(1-1/j_2) \Phi_2$ , becomes more and more important as long as compound-2 has a low molecular weight (it could be an oligomer where  $j_2$  is in the order of about 5). Based on these two effects, Ugelstad and co-workers developed an activated two-step swelling procedure, which enabled them to prepare and commercialize large monodisperse particles for various applications.

Briefly, the procedure is as follows. In a first step an emulsion of the low molecular weight and highly water-insoluble compound-2, which may contain a solvent that is water soluble, is added to a suspension of latex seed particles. The water-soluble solvent promotes the transport of compound-2 through the aqueous phase and allows swelling, which is further facilitated if the emulsion droplets are smaller than the seed particles (action of the Kelvin equation). Then, in a second step the monomer emulsion is added. Because of the high entropy gain caused by mixing of compound-2 with the monomer inside the particles the swelling ability of the seed is activated compared to a normal seed particles that are without compound-2. For instance, using dioctyladipate as compound-2 it was possible to



swell polystyrene particles with a diameter of 1.55  $\mu\text{m}$  with chlorobenzene as model compound to a diameter of about 30  $\mu\text{m}$ , i.e. the seed particles imbibed more than seven-thousand times their own volume.

Another useful method to perform swelling was developed by Okubo and is called the dynamic swelling method. The principle of this method is a combination of nucleation and swelling. Tiny monomer droplets, which nucleate from the supersaturated continuous phase by stepwise changing its solvency for the monomer will subsequently swell the polymer particles. The following example may clarify the principle of action where the oil phase is styrene and the seed particles consist of polystyrene. In a mixture of 6 g ethanol and 4 g water as solvent are dissolved 0.4 g styrene, 0.004 g dibenzoyl peroxide, and variable amounts of poly(vinyl alcohol) stabilizer (between 3.75 and 37.5 wt.% based on styrene). Then, the slow addition of 40 g of water decreases the solvency power for styrene more and more until the conditions for droplet nucleation are met. In the absence of seed particles the nucleated droplets will form a styrene emulsion with a fairly polydisperse size distribution. However, the situation changes completely if seed particles are present which soak up the oil as soon as it is nucleated from the aqueous phase. As an example, at a water feeding rate of 2.88  $\text{ml h}^{-1}$  and in the presence of 3.75 wt.% poly(vinyl alcohol) together with 0.004 g polystyrene seed particles with a particle diameter of 1.8  $\mu\text{m}$ , which were prepared by dispersion polymerization in an ethanol±water mixture, a monodisperse styrene emulsion is formed with a diameter of 8.5  $\mu\text{m}$ . Again, as in the previously mentioned example of the activated swelling method, the presence of monodisperse polymeric seed particles leads to the formation of an emulsion with a monodisperse size distribution. Note, in the latter case no swelling promoter is necessary. The driv-

ing force for the enhanced swelling is the high Kelvin pressure inside the small styrene droplets after nucleation compared to the seed particles and the swelling proceeds via Ostwald ripening. Additionally, the freshly nucleated droplets are relatively unstable owing to the high dynamic interfacial tension of the poly(vinyl alcohol), which as a polymer only slowly adsorbs and equilibrates. Further examples of the application of the dynamic swelling methods to tailor monodisperse polymer particles including particles with various non-spherical morphologies as well as the formation of hollow particles by application of a porogen can be found in

To summarize this section: methods are available that allow latex particles to be swollen to stable emulsion droplets. The swelling agent can be a monomer, an inert solvent, or a mixture of both. During subsequent polymerization precautions are necessary to avoid nucleation of new particles. But in any case, control of swelling enables the preparation of polymer particles with specifically tailored properties.

## Best available control technology for controlling emissions

This section provides the BACT requirements for polymer units. It also describes how emissions are measured to estimate emission rates in the permit application and to verify compliance with the emission limits. The pollutants requiring control at polyethylene and polypropylene facilities include VOCs and particulates. Both VOC and particulate emissions are a function of the process technology used to manufacture the polymer. For example, a high pressure process will have a much higher residual monomer content in the polymer exiting the reactor than will a low pressure process. VOCs make up the bulk of the emissions from these units and are discussed. Emissions such as NOx and CO from auxiliary units associated with a permit application (boilers, for example) are not discussed.

The permit applicant should refer to the appropriate guidance document if these emissions are included in a permit application.

### VOC Sources

Since all types of polymer facilities produce polymer with some level of residual VOC in the fluff or pellet, BACT for these units is based, in part, on the residual VOC in the polymer for the particular process. BACT for all types of processes includes a closed loop step before the polymer is vented directly to atmosphere (without additional VOC emission control on the vent stream) to remove and recover as much residual VOC as possible. This point in the process is generally at the extruder or after the production of fluff polymer products and must be clearly identified in the permit application.

The VOC concentration in the vent streams downstream of the extruder generally is too low (<100 ppm) to be controlled without incurring a high cost. The following table provides the maximum allowable residual VOC in the polymer at the first uncontrolled vent from the unit:

\*use product

Process Type	ppmw VOC in polymer*
polyethylene - high pressure	case by case**
polyethylene - solution	case by case***
polyethylene - slurry	< 100
polyethylene - gas	< 100
polypropylene - slurry	< 100
polypropylene - gas	< 100

\* - The total non-fugitive emissions (including the residual VOC) from the processes should generally be less than 200 to 250 lb./MMlb. product.

\*\* - These units generally have residual VOC concentrations much greater than those observed in the other processes after the extruder, and would likely require additional control of the vent streams after that point in the process. The permit applicant should control these emissions until the residual in the pellet is less than 100 ppm or provide a cost estimate for control of these vent streams for use in a tier 3 BACT review.

\*\*\* - Process and cost information will be required to allow for emission rates above those shown in the table for other polyethylene processes.

Permit applicants may submit control cost estimates for use in a tier 3 (case by case) BACT review of their process if they feel the above levels are too restrictive for their facility. The residual VOCs should be determined by use of the VOC head space test or equivalent.

The VOC head space test involves taking a polymer sample and placing it in a sealed container so that any residual VOCs in the polymer may evolve from the sample over a period. The VOC in the container is measured using a gas chromatograph and the fraction of VOCs in the sample determined.

The test is done to approximate the worst case emissions from the site (longest storage time, highest temperature, etc.). This sample will be taken at or before the first vent to atmosphere and at subsequent emission points if necessary. Sampling will generally be required with each change in product type and/or weekly. Sampling frequency may be reduced based on frequency of product changes and unit operating experience.

Dryers and other emission points should be designed with single emission stacks where practical to facilitate any stack sampling and monitoring required. Stack sampling will be required when specified by NSPS Subpart DDD (if applicable) and may be required to validate the VOC head space test

method, especially where a higher molecular weight solvent (such as a C5 or greater) is used in the process.

All other emissions from the process are expected to be controlled with the devices and monitoring programs detailed below by emission type:

### **Process Vents**

VOC vent streams are expected to be recycled for use in the process if possible. All VOC waste streams not recycled are generally expected to be controlled by combustion - flare, incinerator, boiler, heater, etc. Other control devices may be used (the control efficiency for ethylene and propylene is expected to be at least 99 percent) and must be able to process streams that may contain particulate matter. Refer to the appropriate technical guidance package for the control device when considering controls.

The appropriate TNRCC table must be filled out and submitted for the control device;

### **Fugitive Emissions**

A 28VHP fugitive monitoring program is considered BACT for this type of facility. Fugitive emissions from all components (accessible and inaccessible, monitored and unmonitored) must be determined and included in the emission estimate. Credit for fugitive emission control can only be taken for those components that are accessible and monitored during operation. Refer to the Equipment Leak Fugitives Technical Guidance Package for detailed calculational guidance. Streams containing ethylene are required to use different emission factors than other VOC streams when determining fugitive emissions.

### **Cooling Water**

If cooling water is used in the process, VOC emissions from the cooling water must be estimated unless the tubes and the tube sheets in the heat exchangers are welded, or the cooling water pressure in the heat exchangers is greater than the process-side pressure so that VOCs leaking to the cooling water is not possible. These emissions should be estimated using test results from the facility, if available. If no test results are available, the cooling water emissions should be estimated using AP- 42 refinery cooling water emission factors unless better data is obtained. BACT and emissions calculations are covered in more detail in the Cooling Tower Technical Guidance Package.

### **Abnormal/Maintenance Emissions**

Abnormal and maintenance emissions are not normally shown on the MAERT, but must be identified as accurately as possible in the permit application. These emission estimates are not considered maximum allowables. They are reviewed as part of the BACT determination and for potential nuisance and health impacts. These emissions are expected to be routed to a control device (generally a flare) unless it is shown that it is technically infeasible or the cost is prohibitive. In those cases, the potential release would be evaluated for off-site impacts (see Section V). There are cases, such as a fire or a decomposition reaction in a high pressure process, where it is not technically practicable to route to a control device. In these cases, the applicant should demonstrate how such releases will be minimized. The applicant is expected to provide the emission point (and release characteristics), and an estimate of the quantity and the frequency of release in all cases.

### **Loading**

Due to the low residual VOC concentration in the polymer at this point in the process and the relatively small amount of time spent loading the polymer, these emissions might be considered negligible. This must be documented by data showing the low residual monomer additive, or solvent concentration in the polymer at that point in time and the proposed loading time. Otherwise estimate using the VOC head space test referenced earlier. The BACT for uncontrolled VOC emissions is set by the maximums shown in the table at the start of the BACT section.

## **Particulates**

These emissions can occur from the following operations: extrusion, silo storage, additive feed, additive tanks, blending, and loading. Control of these emissions is generally obtained by cyclones and baghouses and is expected to be greater than 99.9 percent or have an exhaust particulate concentration of less than 0.01 grain/scf. A table must be filled out and submitted for each particulate control device used. Other particulate control devices may be used if equivalent control efficiency is shown. If classifying the particulate by size is not possible, it should be assumed to be PM10 (diameter less than 10 microns). Loading must be done so that all particulate emissions are directed to a control device.

## **MODELING/IMPACTS REVIEW**

An impacts review must be done in accordance with the document Modeling and Effects Review Applicability Guidance Document for Non-Criteria Pollutants when processing any permit action.

Propylene is exempt from the health effects review because it is considered a simple asphyxiant.

Ethylene, other comonomers, solvents, and additives will be considered in the review. If the facility is already in operation, the applicant is encouraged to provide current, actual and allowable emissions for the facility as these are often necessary to do this review. If other information or air dispersion modeling is required for the project as part of this review, it will be requested by the permit engineer.

Air dispersion modeling also may be required by federal New Source Review (PSD or nonattainment) or to verify compliance with the NAAQS. This modeling may be submitted with the application.

However, delaying the modeling may be preferable until the permit engineer has verified how accurate and complete the emission rates are at the unit. This will ensure correct inputs to the model and reduce the possibility of having to do the modeling run again. A pre-modeling meeting also may be held to ensure that correct modeling protocol is followed.

The maintenance and upset emissions identified by the applicant will be considered by the permit engineer for their potential to cause nuisance conditions or health hazards off site. The permit applicant must submit the best estimate of the discharge parameters (quantity emitted, temperature of discharge, height of discharge, velocity of discharge, location on the site, diameter of valve or stack) for each type of emission or emission point. It is not necessary for the applicant to include every possible discharge but to identify those with the greatest quantity released or those most likely to cause health hazards off site. The permit engineer will review these emissions, which may include air dispersion screen modeling, and request additional modeling or controls on the emissions if needed, though not usually required for these types of facilities.

## **SAMPLE CALCULATIONS**

For control using combustion devices, the VOC emissions are determined using the control efficiency of the unit on the stream being controlled with the uncombusted fuel source (VOC fraction) also included. Emissions of the other products of combustion (CO, NO<sub>x</sub>, particulate, and SO<sub>2</sub> if the fuel source contains sulfur) are calculated using test or vendor data. If these sources are unavailable, AP- 42 natural gas combustion factors or TNRCC flare factors may be used, as applicable. Calculations for VOC emissions from the control device, fugitive emissions, cooling

water emissions, and tank emissions are not included here; these can be found in the technical guidance packages cited earlier in this document.

Emissions from streams with low concentrations of VOC that do not allow for accurate continuous monitoring may be estimated by using the "VOC head space" (or equivalent) test to determine the amount of residual VOC in the polymer at that point in the. For example, if the product polymer has a residence time of 24 hours in the storage silos, the emissions from each pound of polymer may be determined using this test. The emissions then can be stated as the production rate times the VOCs emitted per pound of polymer as determined by the test. A similar method may be used for other emission points. It is likely that any permits issued will require periodic testing of this type to ensure that the differing product types do not violate the maximum allowable emission rate in the permit.

An example is shown below:

### Example 1

VOC head space sampling (annual average) from an existing polyethylene unit showed the following results (samples taken just before each emission point.

at extruder/dryer -	72 ppmw VOC
at silo	51 ppmw VOC
before loading	8 ppmw VOC

The existing and proposed facility (500 MMlb./yr) are similar and only three emission points are

venting to atmosphere (extruder, silo, loading). The annual VOC emissions are estimated to be:

extruder/dryer:

$$500 \text{ MMlb./yr} * (72-51) \text{ ppm} * (1/1,000,000) * (\text{ton}/2,000 \text{ lb.}) = 5.25 \text{ TPY}$$

silo:

$$500 \text{ MMlb./yr} * (51-8) \text{ ppm} * (1/1,000,000) * (\text{ton}/2,000 \text{ lb.}) = 10.75 \text{ TPY}$$

loading

$$500 \text{ MMlb./yr} * (8) \text{ ppm} * (1/1,000,000) * (\text{ton}/2,000 \text{ lb.}) = 2 \text{ TPY}$$

The loading estimate is very conservative as it assumes that the vessel being loaded vents to the atmosphere at the plant site for a prolonged period. The VOC emissions could also be speciated, if off-site impacts are a concern, with the diluent and monomer expected to be the major species.



Sampling on the existing unit showed the maximums of VOC concentration measured throughout the year for each sample point were as much as 30 percent higher than the figures above. In addition, the maximum hourly production rate for the proposed unit could be up to 20 percent greater than the annualized average. The maximum hourly emissions are therefore:

extruder/dryer:

$$5.25 \text{ TPY} * (2000 \text{ lb./ton}) * (\text{year}/8760 \text{ hr}) * (1.3) * (1.2) = 1.87 \text{ lb./hr}$$

The silo and loading emissions would be 3.83 and 0.71 lb./hr respectively.

## **Example 2**

The loading particulate emissions are controlled by fabric filters guaranteed to reduce the particulate emissions to less than 0.01 grain/scf. The vent gas to the control device during loading is expected to be a maximum of 6800 scfm. Hourly particulate emissions are determined to be:

$$6800 \text{ scfm} * (60 \text{ min/hr}) * (0.01 \text{ grain/scf}) * (\text{lb./7000 grain}) = 0.58 \text{ lb./hr}$$

Loading at this spot will occur no more than eight hours per day so the annual emissions are:

$$0.58 \text{ lb./hr} * (\text{ton}/2000 \text{ lb.}) * (8760 \text{ hr/yr}) * (8/24) = 0.85 \text{ TPY}$$

## **OBSERVATION AND FINDINGS**

### **SWOT ANALYSIS**

#### **Strengths**

**Consolidation:** The Indian petrochemicals industry has witnessed consolidation over the last few years and nearly 85% of the polymer capacity in the domestic market is with the top three participants (Reliance, IPCL and Haldia Petrochemicals (HPL)). Of the three companies mentioned, IPCL forms a part of the Reliance stable while GAIL is set to pick up stake in HPL. Such high concentration is likely to benefit these players, as this would help reduce duplication of production.

**Synergies:** Most of the petrochemical players have integrated facilities, thereby reducing external dependence to a large extent. To put things in perspective, Reliance Industries uses naphtha from its own Jamnagar refinery as a feedstock for the petrochemicals production. IPCL uses Reliance's vast and widespread marketing network to reach out to global consumers. On the other hand, GAIL utilizes natural gas for its petrochemicals capacity. Rich natural gas is evacuated into the pipelines and after separation of the hydrocarbons such as ethane, propane and butane, the lean gas is transmitted to consumers such as power and fertilizer industry. Further, petrochemicals business being a high value add, would add further to the profitability of these integrated companies.

#### **Weaknesses**

**Low bargaining power vis-à-vis the suppliers:** Input costs form nearly 50% to 60% of the raw material costs. Further, gas prices are regulated but in short supply, while naphtha is an expensive source of feedstock. Refineries realize the import parity prices on naphtha produced and in case of high feedstock prices, petrochemical players have little bargaining power against the suppliers. These players are therefore vulnerable to raw material prices.

**Low Bargaining power vis-à-vis customers:** In case of increase in input costs, the companies might not be able to pass on the rise to the consumers as the prices of products is highly influenced by factors such as international prices and supply.

#### **Opportunities**

**Low per capita consumption:** Currently, domestic per capita polymer consumption is nearly 4 kgs while the global average is nearly 20 kgs. This underlines the fact that there is immense scope of capacity expansion in the country as the market to be tapped is huge. Further, spending on R&D activities is around 2% of sales as compared to an international average of 18%. This leaves enough room for product development. Also, currently, India has a chemicals trade deficit of about US\$ 1.5 bn a year, which leaves enough investment opportunities in the industry.

**Increased economic activity:**The government has set aside nearly Rs 400 bn for infrastructure projects such as roadways, airports and convention centers and also towards rural housing augur well for the petrochemicals industry as this is likely to increase demand for various products (high density polyethylene, low density polyethylene among others) for the purpose of road development, packaging, cables and wiring. Also sustained growth in the auto sector is likely to keep the demand for petrochemical products high. As per our estimates, the auto sector is likely to grow at nearly 12% over the next few years.

## **Threats**

**Customs duties:** Historically, the domestic industry has been protected from overseas competition by high import duties imposed by the government. However, of late, Import duty on polymers has been steadily reduced and is currently at 20%. As part of its commitment to various multilateral and bilateral trade agreements, the government is likely to reduce duties going forward and this is likely to reduce the cushion enjoyed by the domestic players as against the landed cost of imported products.

**Growing competition:** The domestic industry is likely to witness immense competition going forward with IOC all set to enter the segment with its Rs 64 bn project in FY06. Further, ONGC is also venturing into petrochemicals business. With commitments to reduce and eliminate tariff and non-tariff barriers, India, with huge market potential, might witness entry of global majors such as ExxonMobil, Dow Chemicals and Shell into the business. These global majors with deep pockets can actually lead into a pricing war, which could result in squeezing margins.

Taking a cue from their global counterparts, Indian majors such as IOC and ONGC are entering into this value add business in a huge way and is likely to change the entire business dynamics of the companies, not only in India but Asia as Asia is fast becoming the largest petrochemicals manufacturing hub.

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