

Environmental, Health and Safety Guidelines for Petroleum-based Polymers Manufacturing

Introduction

The Environmental, Health, and Safety (EHS) Guidelines are technical reference documents with general and industry-specific examples of Good International Industry Practice (GIIP)¹. When one or more members of the World Bank Group are involved in a project, these EHS Guidelines are applied as required by their respective policies and standards. These industry sector EHS guidelines are designed to be used together with the **General EHS Guidelines** document, which provides guidance to users on common EHS issues potentially applicable to all industry sectors. For complex projects, use of multiple industry-sector guidelines may be necessary. A complete list of industry-sector guidelines can be found at: www.ifc.org/ifcext/enviro.nsf/Content/EnvironmentalGuidelines

The EHS Guidelines contain the performance levels and measures that are generally considered to be achievable in new facilities by existing technology at reasonable costs. Application of the EHS Guidelines to existing facilities may involve the establishment of site-specific targets, with an appropriate timetable for achieving them.

The applicability of the EHS Guidelines should be tailored to the hazards and risks established for each project on the basis of the results of an environmental assessment in which site-

¹ Defined as the exercise of professional skill, diligence, prudence and foresight that would be reasonably expected from skilled and experienced professionals engaged in the same type of undertaking under the same or similar circumstances globally. The circumstances that skilled and experienced professionals may find when evaluating the range of pollution prevention and control techniques available to a project may include, but are not limited to, varying levels of environmental degradation and environmental assimilative capacity as well as varying levels of financial and technical feasibility.

specific variables, such as host country context, assimilative capacity of the environment, and other project factors, are taken into account. The applicability of specific technical recommendations should be based on the professional opinion of qualified and experienced persons.

When host country regulations differ from the levels and measures presented in the EHS Guidelines, projects are expected to achieve whichever is more stringent. If less stringent levels or measures than those provided in these EHS Guidelines are appropriate, in view of specific project circumstances, a full and detailed justification for any proposed alternatives is needed as part of the site-specific environmental assessment. This justification should demonstrate that the choice for any alternate performance levels is protective of human health and the environment

Applicability

These guidelines are applicable to petroleum-based polymer manufacturing where monomers are polymerized and finished into pellets or granules for subsequent industrial use.²

This document is organized according to the following sections:

- Section 1.0 — Industry-Specific Impacts and Management
- Section 2.0 — Performance Indicators and Monitoring
- Section 3.0 — References and Additional Sources
- Annex A — General Description of Industry Activities

² Elastomer manufacturing plants and fiber manufacturing plants are not included in the scope of this Guideline.

1.0 Industry-Specific Impacts and Management

The following section provides a summary of EHS issues associated with polymer manufacturing, along with recommendations for their management. Recommendations for the management of EHS issues common to most large industrial facilities during the construction and decommissioning phase(s) are provided in the **General EHS Guidelines**.

1.1 Environmental

Potential environmental issues associated with polymer manufacturing projects include:

- Air emissions
- Wastewater
- Hazardous materials
- Wastes
- Noise

Air Emissions

Volatile Organic Compounds (VOCs) from Drying and Finishing

The most typical air emissions from polymer plants are volatile organic compound (VOC) emissions from drying and finishing, and purging. Recommended measures to control VOC in drying and finishing operations include the following:

- Separation and purification of the polymer downstream to the reactor;³
- Flash separation of solvents and monomers;
- Steam or hot nitrogen stripping;
- Degassing stages in extruders, possibly under vacuum;

³ The removal effectiveness is dependent on various factors including the volatility of the VOC, the properties of the polymer, and the type of polymerization process.

- Condensing VOCs at low temperature or in adsorption beds, before venting exhaust air. Drying should recycle exhaust air or nitrogen, with VOC condensation;
- Use of closed-loop nitrogen purge systems, use of degassing extruders, and collection of off-gases from extrusion in polyolefin plants due to the fire hazard related to the flammability of the hydrocarbons and to the high temperatures involved;
- Vent gases emitted from reactors, blow-down tanks, and strippers containing significant levels of VCM should be collected and purified prior to emission to atmosphere. Water that has significant levels of VCM, for example water used for the cleaning of reactors containing VCM, transfer lines, and suspension or latex stock tanks, should be passed through a stripping column to remove VCM in polyvinyl chloride manufacturing using the suspension process;
- Use of stripping columns specifically designed to strip suspensions in polyvinyl chloride manufacturing using the suspension process;
- Production of stable latexes and use of appropriate stripping technologies in emulsion polyvinyl chloride plants, which combine emulsion polymerization and open cycle spray drying;
- Multistage vacuum devolatilization of molten polymer to reduce the residual monomer at low levels^{4,5} in polystyrene and generally in styrenic polymers manufacturing;⁶
- Spill and leak prevention in acrylic monomer emulsion polymerization, due to the very strong, pungent, low-threshold odor of all acrylic monomers⁷;

⁴ EU Commission Directive 2002/72/EC and following amendments.

⁵ Food, Drug and Cosmetic Act as amended under Food Additive Regulation 21 CFR §.

⁶ This situation may occur due to the relatively low volatility of the monomer (styrene) or solvent (ethylbenzene) compared to the low concentrations required in the process (e.g. for food application products).

⁷ US EPA Technology Transfer Network, Air Toxics Website, Ethyl acrylate

- Treatment of waste gases by catalytic oxidation or equivalent techniques in polyethylene terephthalate manufacturing;
 - Wet scrubbing of vents in polyamide manufacturing;
 - Catalytic or thermal treatment of gaseous and liquid wastes in all thermoset polymer manufacturing;
 - Installation of closed systems, with vapor condensation and vent purification, in phenol-formaldehyde resins manufacturing, due to the high toxicity of both main monomers; and
 - VOCs from the finishing sections and reactor vents should be treated through thermal and catalytic incineration techniques before being discharged to the atmosphere. For chlorinated VOCs, incineration technology should ensure the emission levels of dioxins / furans meet the limit stated in Table 1.
- accepted standards, or by thermic/catalytic oxidation, prior to emission to the atmosphere;
 - In High Impact Polystyrene Sheets (HIPS) manufacture, air emissions from polybutadiene dissolution systems should be minimized by use of continuous systems, vapor balance lines, and vent treatment;
 - In unsaturated polyester and alkyd resins units, waste gas streams generated from process equipment should be treated by thermal oxidation or, if emissions concentrations permit, by activated carbon adsorption;
 - Use glycol scrubbers or sublimation boxes for anhydride vapor recovery from unsaturated polyester and alkyd resins storage tank vents;
 - In phenolic resins production, VOC contaminated process emissions, especially from reactor vents, should be recovered or incinerated;
 - In aliphatic polyamide manufacturing, use wet scrubbers, condensers, activated carbon adsorbers, together with thermal oxidation.

VOCs from Process Purges

Process purges are associated with purification of raw materials, filling and emptying of reactors and other equipment, removal of reaction byproducts in polycondensation, vacuum pumps, and depressurization of vessels. Recommended pollution prevention and control measures include the following:

- Process vapors purges should be recovered by compression or refrigeration and condensation of liquefiable components or sent to a high efficiency flare system that can ensure efficient destruction;
- The incondensable gases should be fed to a waste-gas burning system specifically designed to ensure a complete combustion with low emissions and prevention of dioxins and furans formation;
- In polyvinyl chloride (PVC) plants, VCM-polluted gases (air and nitrogen) coming from VCM recovery section should be collected and treated by VCM absorption or adsorption, by incineration techniques following internationally

VOCs from Fugitive Emissions

Fugitive emissions in polymer manufacturing facilities are mainly associated with the release of VOCs from leaking piping, valves, connections, flanges, packings, open-ended lines, floating roof storage tanks and seals, pump seals, gas conveyance systems, compressor seals (e.g. ethylene and propylene compressors), pressure relief valves, loading and unloading operations of raw materials and chemicals (e.g. cone roof tanks), preparing and blending of chemicals (e.g. preparation of solutions of polymerization aids and polymer additives), and waste water treatment units (WWTUs). The process system should be designed to minimize fugitive emissions of toxic and hydrocarbon gases. General VOC and fugitive emissions guidance is provided in the **General EHS Guidelines**. Recommended industry-specific measures include:

- In polyethylene manufacturing, monomer leakages from reciprocating compressors used in high-pressure polyethylene plants should be recovered and recycled to the low pressure suction stage;
- In polyvinyl chloride manufacture, opening of reactors for maintenance should be minimized and automatic cleaning systems should be adopted.

Particulate Matter

Emissions of particulate matter (i.e. polymer fines and/or additives as antistick agents, etc.) are associated with polymer drying and packaging operations. Other sources of particulate matter include pellet conveyance, transfer, and dedusting. Recommended particulate matter management measures include:

- Optimization of dryer design;
- Use of gas closed loop;
- Reduction at source (e.g. granulation transfer systems) and capture via elutriation facilities;
- Installation of electrostatic precipitators, bag filters or wet scrubbing;
- Installation of automatic bagging systems and efficient ventilation in packaging operations;
- Good housekeeping.

Venting and Flaring

Venting and flaring are important safety measures used in polymer manufacturing facilities to ensure all process gases, coming from storage as well from process units, are safely disposed off in the event of a safety disk or valve opening, emergency, power or equipment failure, or other plant upset conditions. Emergency discharges from reactors and other critical process equipment should be conveyed to blow-down tanks, where the reactants are recovered (e.g. by steam or vacuum stripping) before discharging the treated wastes, or

through scrubbing and high-efficiency flaring. Industry-specific measures include the following:

- Ethylene vented from high-pressure low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) plants, cannot be conveyed to the flare due to opening of the reactor safety disks at high pressures, but should be vented to the atmosphere through a stack, after having been diluted with steam and cooled by water scrubbing to minimize risks of explosive clouds. Specifically designed systems operated by detonation sensors should be used;
- Pressure Safety Valves (PSV) should be used in polymerization plants to reduce the amount of chemicals released from an overpressure/relief device activation, where release is directly to the atmosphere;
- Because of the possibility of pipe plugging by polymer formation, redundant safety systems are recommended, with frequent and proper inspection. PSV lines should be protected upstream by PSDs, to avoid losses and plugging. Fittings should be provided to enable check of safety systems during plant operation;
- In polyvinyl chloride manufacturing, the occurrence of emergency venting from the polymerization reactors to atmosphere due to runaway reaction should be minimized by one or more of the following techniques:
 - Specific control instrumentation for reactor feed and operational conditions,
 - Chemical inhibitor system to stop the reaction,
 - Emergency reactor cooling capacity,
 - Emergency power for reactor stirring, and
 - Controlled emergency venting to VCM recovery system.⁸

⁸ EIPPCB BREF (2006)

- Where foaming occurs during emergency venting, it should be reduced by antifoam addition, to avoid plugging of venting system;
- During emergency venting, the content of the reactor should be discharged to a blow-down tank and steam stripped before disposal;
- In acrylic latexes manufacturing, emergency venting to flare system from reactors due to runaway polymerization should be prevented by one or more of the following:
 - Continuous computer controlled addition of reactants to the reactor, based on actual polymerization kinetics,
 - Chemical inhibitor system to stop the reaction,
 - Emergency reactor cooling capacity,
 - Emergency power for reactor stirring, and
 - Discharge of reactor content to a blow-down tank.

Combustion Sources and Energy Efficiency

Polymerization plants consume large quantities of energy and steam, which are typically produced on site in cogeneration facilities. Emissions related to the operation of power sources should be minimized through the adoption of a combined strategy which includes a reduction in energy demand, use of cleaner fuels, and application of emissions controls where required. Recommendations on energy efficiency are addressed in the **General EHS Guidelines**.

Polymerization plants operate in a wide range of conditions (temperature and pressure) and it is usually possible and useful to include a temperature or energy cascade in their design to recover heat (e.g. low pressure steam for stripping or heating purposes) and compression energy. The correct choice and design of the purification operations according to their thermodynamic efficiency is a major component in reduction of energy requirements. Drying and finishing of polymers are important aspects to consider, because of their energy demand and because polymers are sensitive to heat and mechanical

stress. Additional areas with potential opportunities for reduction in energy consumption include dewatering systems, closed loop cooling water systems, inert gas close loop drying, use of low shear extruders for compounding, increase of polymer concentration, and gear pumps for pelletizing.

Acid Gases

Hydrogen chloride (HCl) traces, originated from the hydrolysis of chlorinated organic compounds by the catalyst, can be present in exhaust air from drying of polymers produced by ionic catalysis. Although acid is usually present at low level, gas stream testing is recommended and pollution control measures, such as wet scrubbing, should be considered if levels become significant.

Dioxins and Furans

Gaseous, liquid, and solid waste incineration plants are typically present as one of the auxiliary facilities in polymer manufacturing plants. The incineration of chlorinated organic compounds (e.g. chlorophenols) could generate dioxins and furans. Certain catalysts in the form of transition metal compounds (e.g. copper) also facilitate the formations of dioxins and furans. Recommended prevention and control strategies include:

- Operation of incineration facilities according to internationally recognized technical standards;⁹
- Maintaining proper operational conditions, such as sufficiently high incineration and flue gas temperatures, to prevent the formation of dioxins and furans;
- Ensuring emissions levels meet the guideline values presented in Table 2.

⁹ For example, Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste.

Wastewater

Industrial Process Wastewater

Process wastewater from plant units may contain hydrocarbons, monomers and other chemicals, polymers and other solids (either suspended or emulsified), surfactants and emulsifiers, oxygenated compounds, acids, inorganic salts, and heavy metals.

Recommended wastewater management strategies include the following:

- Wastewater containing volatile monomers (e.g., VCM, styrene, acrylonitrile, acrylic esters, vinyl acetate, caprolactam) and/or polymerization solvents (e.g., condensate from steam stripping of suspensions or latexes, condensate from solvent elimination, or wastewater from equipment maintenance) should be recycled to the process where possible, or otherwise treated by flash distillation or equivalent separation to remove VOC, prior to conveying it to the facility's wastewater treatment system;
- Organics should be separated and recycled to the process, when possible, or incinerated;
- Non-recyclable contaminated streams, such as wastewater originated from polyester or from thermoset polymer manufacturing, should be catalytically or thermally incinerated;
- Emulsion and suspension polymerization aids should be selected with consideration of their biodegradability, as they enter the wastewater stream during polymer recovery;
- Whenever less biodegradable or non-biodegradable polymerization aids are used, a specifically designed water pre-treatment unit should be installed prior to discharge to the facility's wastewater treatment system;
- Wastewater originated from polymer recovery after ionic polymerization and containing metal ions from

polymerization catalysts (e.g., Li, Ni, Co, V, etc) should be pre-treated as needed prior to discharge to the facility's wastewater treatment system;

- Spent reactant solutions should be sent to specialized treatment for disposal;
- Acidic and caustic effluents from demineralized water preparation should be treated by neutralization prior to discharge to the facility's wastewater treatment system;
- Contaminated water from periodic cleaning activities during facility turn-arounds should be tested and treated in the facility's wastewater treatment system;
- Oily effluents, such as process leakages, should be collected in closed drains, decanted and discharged to the facility's wastewater treatment system;
- Facilities should prepare and implement hazardous materials management program, including specific spill prevention and control plans, according to the recommendations provided in the **General EHS Guidelines**;
- Sufficient process fluids let-down capacity should be provided to avoid process liquid discharge into the oily water drain system and to maximize recovery into the process.

Process Wastewater Treatment

Techniques for treating industrial process wastewater in this sector include source segregation and pretreatment of concentrated wastewater streams. Typical wastewater treatment steps include: grease traps, skimmers, dissolved air floatation or oil water separators for separation of oils and floatable solids; filtration for separation of filterable solids; flow and load equalization; sedimentation for suspended solids reduction using clarifiers; biological treatment, typically aerobic treatment, for reduction of soluble organic matter (BOD); chlorination of effluent when disinfection is required; dewatering and disposal of residuals in designated hazardous waste landfills.

Additional engineering controls may be required for (i) containment and treatment of volatile organics stripped from various unit operations in the wastewater treatment system, (ii) advanced metals removal using membrane filtration or other physical/chemical treatment technologies, (iii) removal of recalcitrant organics and non biodegradable COD using activated carbon or advanced chemical oxidation, (iii) reduction in effluent toxicity using appropriate technology (such as reverse osmosis, ion exchange, activated carbon, etc.), and (iv) containment and neutralization of nuisance odors.

Management of industrial wastewater and examples of treatment approaches are discussed in the **General EHS Guidelines**. Through use of these technologies and good practice techniques for wastewater management, facilities should meet the Guideline Values for wastewater discharge as indicated in the relevant table of Section 2 of this industry sector document.

Other Wastewater Streams & Water Consumption

Guidance on the management of non-contaminated wastewater from utility operations, non-contaminated stormwater, and sanitary sewage is provided in the **General EHS Guidelines**. Contaminated streams should be routed to the treatment system for industrial process wastewater. Stormwater collection and treatment may usually entail collection of runoff from paved areas and treatment through a skimmer pit to recover spilled resin. Recommendations to reduce water consumption, especially where it may be a limited natural resource, are provided in the **General EHS Guidelines**.

Hazardous Materials

Polymer manufacturing facilities use and store significant amounts of hazardous materials, including intermediate / final products and by-products. Recommended practices for hazardous material management, including handling, storage,

and transport, as well as issues associated with Ozone Depleting Substances (ODSs) are presented in the **General EHS Guidelines**.

Wastes

Storage and handling of hazardous and non-hazardous wastes should be conducted in a way consistent with good EHS practice for waste management, as described in the **General EHS Guideline**. Industry-specific hazardous wastes include waste solvents and waste oil spent catalysts, saturated filtering beds, and solid polymer wastes from polymerization plants.¹⁰

Spent Catalysts

Spent catalysts are originated from catalyst bed replacement in scheduled turnarounds of monomer purification reactors (e.g. hydrogenation of impurities in lower olefins) or less frequently, in heterogeneous polymerization catalysis. Spent catalysts can contain nickel, platinum, palladium, and copper, depending on the process. Recommended management strategies for spent catalysts include the following:

- Appropriate on-site management, including submerging pyrophoric spent catalysts in water during temporary storage and transport until they can reach the final point of treatment to avoid uncontrolled exothermic reactions;
- Return to the manufacturer for regeneration, or off-site management by specialized companies that can either recover the heavy or precious metals, through recovery and recycling processes whenever possible, or manage spent catalysts according to hazardous and non-hazardous waste management recommendations presented in the **General EHS Guidelines**. Catalysts that contain platinum or palladium should be sent to a noble metals recovery facility.

¹⁰ Refer to section on dioxins and furans for emissions-related guidance applicable to incineration of chlorinated organic wastes.

Saturated Filtering Beds

Saturated filtering beds originate from solution polymerization processes, for example, from removal of spent polymerization catalysts from the polymer solution or in a number of deodorization or clarification operations. Recommended management strategies for saturated filtering beds include minimizing purification agents through online regeneration and extended lifetime, proper containment during temporary storage and transport, and off-site management by specialized companies.

Solid Polymer Wastes

Polymer wastes are produced during normal plant operation (e.g., latex filtering and sieving, powder screening and granule grinding); campaign changes; start-up; and maintenance and emergency shutdowns of polymer processing equipment.

Recommended pollution prevention and control measures include the following:

- Recycling or re-use of waste streams where possible instead of disposal. Possible recycling options include sale of waxes to wax industry;
- Treatment as necessary to remove and separately recover VOCs (e.g. by steam stripping);
- Segregation and storage in a safe location. Some polymer wastes (e.g. heat or shear stressed polymers produced during start or stop operations of drying and finishing equipment, oxidized polymer recovered during dryer maintenance, process plant crusts without antioxidants, and aged polymer wastes) might be unstable and prone to self-heating and self-ignition. Such waste should be stored in a safe manner and disposed of (e.g., incinerated) as soon as practical.

Noise

Significant noise sources in polymer manufacturing facilities include activities involving physical processing of polymers (e.g., screening, grinding, pneumatic conveying), as well as large rotating machines, such as extruders, compressors and turbines, pumps, electric motors, fans, air coolers. During emergency depressurization, high noise levels can be generated due to high pressure gases to flare and/or steam release into the atmosphere. Recommendations for noise management are provided in the **General EHS Guidelines**.

1.2 Occupational Health and Safety

The occupational health and safety issues that may occur during the construction and decommissioning of polymer manufacturing facilities are similar to those of other industrial facilities, and their management is discussed in the **General EHS Guidelines**.

Facility-specific occupational health and safety issues should be identified based on job safety analysis or comprehensive hazard or risk assessment, using established methodologies such as a hazard identification study [HAZID], hazard and operability study [HAZOP], or a quantitative risk assessment [QRA]. As a general approach, health and safety management planning should include the adoption of a systematic and structured approach for prevention and control of physical, chemical, biological, and radiological health and safety hazards described in the **General EHS Guidelines**. The most significant occupational health and safety hazards occur during the operational phase of polymer manufacturing and primarily include:

- Process Safety
- Fires and Explosions
- Other chemical hazards
- Confined spaces

Process Safety

Process safety programs should be implemented due to industry-specific characteristics, including complex chemical reactions, use of hazardous materials (e.g., toxic and reactive materials and flammable or explosive compounds), and multi-step reactions. Process safety management includes the following actions:

- Physical hazard testing of materials and reactions;
- Hazard analysis studies to review the process chemistry and engineering practices, including thermodynamics and kinetics;
- Examination of preventive maintenance and mechanical integrity of the process equipment and utilities;
- Worker training; and
- Development of operating instructions and emergency response procedures.

Process safety recommendations applicable to specific manufacturing processes are presented below.

Polyethylene Manufacturing

In polyethylene manufacturing, a specific process hazard is related to the possible release of large amounts of hot ethylene to the atmosphere and subsequent cloud explosion. Accidental events are mainly related to leaks from gaskets or during maintenance operations. For LDPE production units in particular, accidental events can include opening of the safety disk of the reactor and explosion of the high pressure separator. Specific safety management measures include the following:

- Ethylene vented due to opening of the reactor safety disks at high pressure cannot be conveyed to the flare, but should be vented to the atmosphere by a short stack, after dilution with steam and cooling with water scrubbing to minimize risks of explosive clouds;

- Product decomposition in tubular reactors should be prevented through heat transfer, temperature profile control, high speed flow and good pressure control;
- Explosion of high pressure separators should be prevented by vessel reactors design measures, careful dosing of peroxides, control of polymerization temperature, rapid detection of uncontrolled exothermic reactions and rapid isolation / depressurizing, and good maintenance of reactors and separators.

With the High Density Polyethylene (HDPE) and Linear Low Density Polyethylene (LLDPE) solution process, fire hazards originate from high-pressure and high-temperature conditions in the polymerization reactor and desolventizer operating at a temperature close to self-ignition temperature of the solvent, together with high flow rates of hydrocarbon solvent. In HDPE slurry process and in iPP bulk process, a spill from the reactor can result in an explosive cloud due to flash evaporation of isobutane and propylene. The prevention of spills and explosive clouds should be based on the application of internationally recognized engineering standards for equipment and piping design, maintenance, plant lay-out, and location / frequency of emergency shut-off valves.

PVC Manufacturing

Accidental venting to the atmosphere of VCM with a subsequent formation of an explosive and toxic cloud can be caused by opening of Pressure Safety Valves (PSVs) of a reactor due to runaway polymerization. Management actions include degassing and steam flushing of reactor before opening.

VCM is easily oxidized by air to polyperoxides during recovery operations after polymerization. After recovery, VCM is held in a holding tank under pressure or refrigeration. A chemical inhibitor, such as a hindered phenol, is sometimes added to prevent polyperoxide formation. Normally any polyperoxide

formed is kept dissolved in VCM, where it reacts slowly and safely to form PVC. However, if liquid VCM containing polyperoxides is evaporated, polyperoxides may precipitate and decompose exothermically with the risk of explosion and consequent toxic cloud.¹¹

Batch Polymerization Process

Batch polymerization can generate a hazard of runaway polymerization and reactor explosion in the event of improper dosing of reactants or failure in the stirring or heat exchange systems. Recommended process safety management practices include limiting the practice of batch polymerization and the application of process controls, including the provision of backup emergency power, cooling, inhibitor addition systems, and blow-down tanks.

Compounding, Finishing and Packaging Processes

Compounding, finishing, and packaging operations present risks of fire in blenders and in extruders (if the polymer is overheated), and in equipment involving mixtures of polymer powders and air, such as dryers, pneumatic conveyors, and grinding equipment. Use of internationally recognized electric installation standards, including grounding of all equipment, and installation of specific fire fighting systems are recommended.

Fires and Explosions

Vinyl Chloride Monomer (VCM)

VCM is classified as a toxic and carcinogen (IARC group 1)¹². It is gas under normal conditions (boiling point = -13.9°C), and is potentially explosive when in contact with air. VCM is stored as a liquid in pressurized or refrigerated tanks. Transportation of VCM, including pipeline transportation, should be conducted in a manner consistent with good international practice for transport of hazardous materials. Evaluations for the location of new PVC

facilities should include consideration of distances to monomer plants, in order to minimize storage times and to reduce potential hazards from monomer transport.¹³

Styrene

Styrene polymerizes readily and should be stored at cool temperatures, with adequate levels of 4-tert-butylcatechol (TBC) used as an inhibitor, in tanks designed and built according to international standards.

Acrylic Acid and Esters^{14,15}

Acrylic acid is a liquid freezing at 13 °C, and is extremely reactive by runaway polymerization if uninhibited. Accidents originated in acrylic acid storages are relatively frequent.

It is sold inhibited with hydroquinone mono methyl ether, which is active in the presence of air. It is easy flammable when overheated and it should be stored in stainless steel tanks. Overheating or freezing should be avoided because thawing of frozen acrylic acid is an operation involving runaway polymerization risks. Acrylic esters behave in a similar way, but they don't present risks related to freezing.

Phenol

Phenol melts at 40.7°C and it is usually received, stored and handled in molten state. Tanks should be fitted with a vapor recovery system and fitted with heating coils; nitrogen blanket is also recommended. Lines and fittings should be steam-traced and should be purged with nitrogen before and after product transfer.

¹¹ EIPPCB BREF (2006)

¹² IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Volume 19 <http://monographs.iarc.fr/ENG/Monographs/vol19/volume19.pdf>

¹³ The cost of transportation may be a significant contributing factor to the co-location of new facilities in proximity to sources of VCM.

¹⁴ Acrylic acid - A summary of safety and handling, 3rd Edition, 2002; Intercompany Committee for the Safety and Handling of Acrylic Monomers, ICSHAM

¹⁵ Acrylate esters - A summary of safety and handling, 3rd Edition, 2002; Intercompany Committee for the Safety and Handling of Acrylic Monomers, ICSHAM

Formaldehyde

Formaldehyde is used as an aqueous solution at concentrations of 37 – 50 percent, usually stabilized with low amounts of methanol (<1 percent). Formaldehyde is a confirmed carcinogenic for humans (IARC Group 1)¹⁶ Formaldehyde releases flammable vapors to air, so it should be kept under an inert gas blanket during storage.

Metal alkyls (Al, Li, Zn, Na, K, etc.)

The most widely used metal alkyls are aluminum and magnesium alkyls in Z-N polymerization of olefins, and lithium alkyls in anionic polymerization of styrene and dienes.

Recommended management practices include:

- Preparation of a specific fire prevention and control plan to address the fire and other hazards associated with metal alkyls;¹⁷
- Respecting safety distances within and outside of the facility;¹⁸
- Shipping in tank cars, tank trailers, portable tanks, or ISO tanks according to internationally recognized standards;¹⁹
- Transfer should be made to bunkerized storage facilities through specially designed valves, fittings, and pumps;
- Storage tanks should be kept under a nitrogen blanket and connected to the atmosphere by one or more oil hydraulic seals. The product levels and flows should be monitored with high reliability instrumentation and alarms;
- Metal alkyl storage facilities should be equipped with containment walls, and the area within the containment

should be sloped to facilitate drainage to an emergency burning pit.

Peroxides

Organic and inorganic peroxides, as well as diazo compounds, are widely used as radical polymerization initiators. Inorganic peroxides, like hydrogen peroxide and peroxydisulfates, are capable of violent reaction with organic substrates. Inorganic peroxides are classified as oxidizers. Oxidizer hazards include increase in the burning rate of combustible materials; spontaneous ignition of combustible materials; rapid and self-sustained decomposition, which can result in explosion; generation of hazardous gases; and explosion hazards if mixed with incompatible compounds or exposure to fires.

Recommended management practices include:

- Peroxide formulations should be transported and handled according to manufacturer recommendations and applicable international standards^{20,21,22},
- Storage should be segregated facilities designed and built according to internationally accepted standards (e.g. NFPA Codes^{23,24}). Organic peroxides should be stored in dedicated refrigerated or air conditioned explosion proof buildings;²⁵
- Preparation of a specific fire prevention and control plan to address the peculiarities of strong inorganic oxidizers.²⁶

¹⁶ IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Volume 88 <http://monographs.iarc.fr/ENG/Monographs/vol88/volume88.pdf>

¹⁷ Fog spray may be used to deactivate pyrophoric alkyls. Larger amounts of water or foam should not normally be used as fire extinguishing agents due to their violent reactivity with aluminum alkyls. Water may be used to cool adjacent objects directly or as a water screen to shield any objects from heat radiation. Other agents such as CO₂ or other chemical powders are needed in large amounts to control the fire and prevent re-ignition.

¹⁸ E.J Major, H.G. Wissink, J.J. de Groot, (Akzo Nobel), Aluminum Alkyl Fires

¹⁹ UN Recommendations on the Transport of Dangerous Goods. Model Regulations. Thirteenth revised edition (2003)

²⁰ UN Recommendations on the Transport of Dangerous Goods. Model Regulations. Thirteenth revised edition (2003)

²¹ Safety and handling of organic peroxides: A Guide Prepared by the Organic peroxide producers safety division of the Society of the plastics industry, Inc. Publication # AS-109

²² NFPA 432, Code for the Storage of Organic Peroxide Formulations, 2002 Edition

²³ NFPA 430, Code for the Storage of Liquid and Solid Oxidizers, 2004 Edition

²⁴ NFPA 432, Code for the Storage of Organic Peroxide Formulations, 2002 Edition

²⁵ Class 3 peroxides may require less stringent storage standards.

²⁶ For example, the most appropriate fire extinguishing agent for organic peroxides is liquid nitrogen applied with remotely operable fire fighting equipment.

Polymers

Fires in polymer storage warehouses may be difficult to control due to the very high combustion heat of most polymers.

Polymers combustion in fires also produces toxic clouds.

Recommended management practices include:

- Storage buildings should be designed in accordance with internationally accepted standards including, for example, appropriate ventilation, air temperature control, and protection from direct sunlight;
- Effective fire prevention and control systems should be adopted, including for example, smoke detectors, IR hot spot detectors, and distributed water sprinklers designed for the very high thermal load of a polymer fire;
- Because most polymers are subjected to slow oxidative aging by heat or light, they should be kept in closed packaging;
- “First In First Out” (FIFO) management procedure for the products together with frequent inspections and good housekeeping. Aged materials should be traced, evaluated for safety, and separated for disposal.

Chemicals

Potential inhalation and dermal contact exposures to chemicals during routine plant operations should be managed based on the results of a job safety analysis and industrial hygiene survey and according to the occupational health and safety guidance provided in the **General EHS Guidelines**. Protection measures include worker training, work permit systems, use of personal protective equipment (PPE), and toxic gas detection systems with alarms.

Confined Spaces

Confined space hazards, as in any other industry sector, can, in the worse case scenario, potentially lead to fatalities if not properly managed. Confined space entry by workers and the

potential for accidents may vary among facilities depending on design, on-site equipment, and infrastructure. Confined spaces in polymer manufacturing facilities may include reactors which must be accessed during maintenance activities. Facilities should develop and implement confined space entry procedures as described in the **General EHS Guidelines**.

1.3 Community Health and Safety

Community health and safety impacts during the construction and decommissioning of polymer manufacturing facilities are common to those of most other industrial facilities and are discussed in the **General EHS Guidelines**. The most significant community health and safety hazards associated with polymer manufacturing facilities occur during the operation phase and include the threat from major accidents related to potential fires and explosions or accidental releases of finished products within the facility or during transportation outside the processing facility. Guidance for the management of these issues is presented above under the environmental and occupational health and safety sections of this document. Major hazards should be managed according to international regulations and best practices (e.g., OECD Recommendations,²⁷ EU Seveso II Directive,²⁸ and USA EPA Risk Management Program Rule).²⁹

Additional guidance on the management of hazardous materials is provided in relevant sections of the **General EHS Guidelines** including: Hazardous Materials Management (including Major Hazards); Traffic Safety; Transport of Hazardous Materials; and Emergency Preparedness and Response. Additional relevant guidance applicable to transport by sea and rail as well as shore-based facilities can be found in the EHS Guidelines for

²⁷ OECD, *Guiding Principles for Chemical Accident Prevention, Preparedness and Response, Second Edition*, 2003

²⁸ EU Council Directive 96/82/EC, Seveso II Directive, extended by the Directive 2003/105/EC.

²⁹ EPA, *40 CFR Part 68, 1996 — Chemical accident prevention provisions*

Shipping; Railways; Ports and Harbors; and Crude Oil and Petroleum Products Terminals.

2.0 Performance Indicators and Monitoring

2.1 Environment

Emissions and Effluent Guidelines

Tables 1 and 2 present emission and effluent guidelines for this sector. Guideline values for process emissions and effluents in this sector are indicative of good international industry practice as reflected in relevant standards of countries with recognized regulatory frameworks. These guidelines are achievable under normal operating conditions in appropriately designed and operated facilities through the application of pollution prevention and control techniques discussed in the preceding sections of this document.

Emissions guidelines are applicable to process emissions. Combustion source emissions guidelines associated with steam- and power-generation activities from sources with a capacity equal to or lower than 50 MWth are addressed in the **General EHS Guidelines** with larger power source emissions addressed in the **EHS Guidelines for Thermal Power**. Guidance on ambient considerations based on the total load of emissions is provided in the **General EHS Guidelines**.

Effluent guidelines are applicable for direct discharges of treated effluents to surface waters for general use. Site-specific discharge levels may be established based on the availability and conditions in the use of publicly operated sewage collection and treatment systems or, if discharged directly to surface waters, on the receiving water use classification as described in the **General EHS Guideline**. These levels should be achieved, without dilution, at least 95 percent of the time that the plant or unit is operating, to be calculated as a proportion of annual

operating hours. Deviation from these levels due to specific local project conditions should be justified in the environmental assessment.

Table 1. Air Emissions Guidelines

Pollutant	Unit	Guideline Value
Particulate Matter (PM)	mg/Nm ³	20
Nitrogen Oxides	mg/Nm ³	300
Hydrogen Chloride	mg/Nm ³	10
Sulfur Oxides	mg/Nm ³	500
Vinyl Chloride (VCM)	g/t s-PVC g/t e-PVC	80 500
Acrylonitrile	mg/Nm ³	5 (15 from dryers)
Ammonia	mg/Nm ³	15
VOCs	mg/Nm ³	20
Heavy Metals (total)	mg/Nm ³	1.5
Hg	mg/Nm ³	0.2
Formaldehyde	mg/m ³	0.15
Dioxins / Furans	ng TEQ/Nm ³	0.1

Resource Use, Energy Consumption, Emission and Waste Generation

Table 3 (below) provides examples of resource consumption indicators for energy and water as well as relevant indicators of emissions and wastes. Industry benchmark values are provided for comparative purposes only and individual projects should target continual improvement in these areas.

Environmental Monitoring

Environmental monitoring programs for this sector should be implemented to address all activities that have been identified to have potentially significant impacts on the environment, during normal operations and upset conditions. Environmental monitoring activities should be based on direct or indirect indicators of emissions, effluents, and resource use applicable to the particular project. Monitoring frequency should be sufficient to provide representative data for the parameter being monitored. Monitoring should be conducted by trained individuals following monitoring and record-keeping procedures and using properly calibrated and maintained equipment. Monitoring data should be analyzed and reviewed at regular intervals and compared with the operating standards so that any necessary corrective actions can be taken. Additional guidance on applicable sampling and analytical methods for emissions and effluents is provided in the **General EHS Guidelines**.

Table 2. Effluents Guidelines

Pollutant	Unit	Guideline Value
pH	S.U.	6 - 9
Temperature Increase	°C	=3
BOD ₅	mg/L	25
COD	mg/L	150
Total Nitrogen	mg/L	10
Total Phosphorous	mg/L	2
Sulfide	mg/L	1
Oil and Grease	mg/L	10
TSS	mg/L	30
Cadmium	mg/L	0.1
Chromium (total)	mg/L	0.5
Chromium (hexavalent)	mg/L	0.1
Copper	mg/L	0.5
Zinc	mg/L	2
Lead	mg/L	0.5
Nickel	mg/L	0.5
Mercury	mg/L	0.01
Phenol	mg/L	0.5
Benzene	mg/L	0.05
Vinyl Chloride	mg/L	0.05
Adsorbable Organic Halogens	mg/L	0.3
Toxicity	To be determined on a case specific basis	

Table 3. Resource, Energy Consumption, Emission and Waste Benchmarks

Parameter	Unit	Industry Benchmark (EU, 1999, Average best 50%)					
		LDPE ²⁰	HDPE ¹⁴	LLDPE	GPPS	HIPS	EPS
Direct energy consumption ¹²	kWh/t	720	570	580	300 ²	410 ²	500 ²
Primary energy consumption ¹³	kWh/t	2,070	1,180	810	--	--	--
Water consumption ³	m ³ /t	1.7	1.9	1.1	0.8	0.8	5.0
Dust emission	g/t	17	56	11	2	2	30
VOC emission ¹⁰	g/t	700 – 1,100	650	180 – 500 ¹	85	85	450 - 700 ⁴
COD emission	g/t	19	17	39	30	--	--
Inert waste	kg/t	0.5	0.5	1.1	2.0	3.0	6.0
Hazardous waste	kg/t	1.8	3.1	0.8	0.5	0.5	3.0
Product		S-PVC	E-PVC	PET^{15, 19}	PA 6^{15, 17}		PA 66^{15, 16}
Direct energy consumption	kWh/t	750–1,100	2,000-3,000	850 – 1,500	1,800 – 2,000		1,600 – 2,100
Primary energy consumption	kWh/t	1,100-1,600	2,800-4,300	--	--		--
Water to waste	m ³ /t	4.0 ⁹	--	0.6 - 25	1 - 3		1.5 – 3.0
Dust emission	g/t	40 ^{6,9}	200 ^{6,9}	--	--		--
Monomer emission to air ^{5, 9, 10}	g/t	18 - 43	245-813	--	6 – 10		--
VOC emission ¹⁰	g/t	--	--	5 ¹⁸	--		10 - 30
Monomer emission to water ^{7,9}	g/t	3.5	10	--	--		--
COD emission	g/t	480 ^{8,9}	340 ^{8,9}	2,000 – 16,000	4,300 – 5,700 ¹⁶		4,500 – 6,000 ¹⁶
Inert waste	kg/t	--	--	0.8 – 18	3.0 – 3.5		3.0 – 3.5
Hazardous waste ¹⁷	kg/t	55 ⁹	74 ⁹	< 0.45	0.2 – 0.5		0.2 – 0.5
Product		UPES					
Direct energy consumption	kWh/t	< 1,000					
Primary energy consumption	kWh/t	--					
Water to waste	m ³ /t	1 – 5					
Dust emission	g/t	5 – 30					
Monomer emission to air	g/t	--					
VOC emission ¹⁰	g/t	40 – 100					
Monomer emission to water	g/t	--					
COD emission	g/t	--					
Inert waste	kg/t	--					
Hazardous waste	kg/t	< 7					

Source: EU IPPC BREF (2006)

Notes: 1) According to type of comonomer (C4 or C8); 2) European average; 3) Not including cooling water purge; 4) 60% is pentane; not including storage; 5) Average best 25%; 6) PVC dust; 7) After stripping, before WWT; 8) After final WWT; 9) Median value; 10) Inclusive of diffuse emissions; 11) Direct energy is the total energy consumption as delivered; 12) Primary energy is energy calculated back to fossil fuel. For the primary energy calculation the following efficiencies were used: electricity: 40 % and steam: 90 %; 13) Good practice industry values; 14) IPP values can be considered more or less equivalent; 15) Before WWT; 16) Continuous process; 17) Solid waste containing > 1,000 ppm VCM; 18) Using catalytic oxidation (only point sources); 19) TPA process plus continuous post-condensation; 20) Based on tubular reactor

2.2 Occupational Health and Safety Performance

Occupational Health and Safety Guidelines

Occupational health and safety performance should be evaluated against internationally published exposure guidelines, of which examples include the Threshold Limit Value (TLV[®]) occupational exposure guidelines and Biological Exposure Indices (BEIs[®]) published by American Conference of Governmental Industrial Hygienists (ACGIH),³⁰ the Pocket Guide to Chemical Hazards published by the United States National Institute for Occupational Health and Safety (NIOSH),³¹ Permissible Exposure Limits (PELs) published by the Occupational Safety and Health Administration of the United States (OSHA),³² Indicative Occupational Exposure Limit Values published by European Union member states,³³ or other similar sources.

Accident and Fatality Rates

Projects should try to reduce the number of accidents among project workers (whether directly employed or subcontracted) to a rate of zero, especially accidents that could result in lost work time, different levels of disability, or even fatalities. Facility rates may be benchmarked against the performance of facilities in this sector in developed countries through consultation with published sources (e.g. US Bureau of Labor Statistics and UK Health and Safety Executive)³⁴.

Occupational Health and Safety Monitoring

The working environment should be monitored for occupational hazards relevant to the specific project. Monitoring should be designed and implemented by accredited professionals³⁵ as part of an occupational health and safety monitoring program. Facilities should also maintain a record of occupational accidents and diseases and dangerous occurrences and accidents. Additional guidance on occupational health and safety monitoring programs is provided in the **General EHS Guidelines**.

³⁰ Available at: <http://www.acgih.org/TLV/> and <http://www.acgih.org/store/>

³¹ Available at: <http://www.cdc.gov/niosh/hpg/>

³² Available at:
http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDAR DS&p_id=9992

³³ Available at: http://europe.osha.eu.int/good_practice/risks/ds/oel/

³⁴ Available at: <http://www.bls.gov/iif/> and <http://www.hse.gov.uk/statistics/index.htm>

³⁵ Accredited professionals may include Certified Industrial Hygienists, Registered Occupational Hygienists, or Certified Safety Professionals or their equivalent.

3.0 References and Additional Sources

Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste

European Commission. 2006. Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques for Polymers. October 2006. Sevilla, Spain

European Council of Vinyl Manufacturers (ECVM). 1994. Industry Charter for the Production of VCM and PVC (Suspension Process). Brussels, Belgium

European Council of Vinyl Manufacturers (ECVM). 1998. Industry Charter for the Production of Emulsion PVC. Brussels, Belgium

EU Council Directive 96/82/EC, so-called Seveso II Directive, extended by the Directive 2003/105/EC

German Federal Government. 2002. First General Administrative Regulation Pertaining to the Federal Emission Control Act (Technical Instructions on Air Quality Control – TA Luft). Berlin, Germany.

German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety. 2004. Promulgation of the New Version of the Ordinance on Requirements for the Discharge of Waste Water into Waters (Waste Water Ordinance - AbwV) of 17. June 2004. Berlin, Germany.

Intercompany Committee for the Safety and Handling of Acrylic Monomers, ICSHAM. 2002. Acrylate Esters – A Summary of Safety and Handling. 3rd Edition, 2002

Intercompany Committee for the Safety and Handling of Acrylic Monomers, ICSHAM. 2002. Acrylic acid - A summary of safety and handling. 3rd Edition, 2002
IARC Monographs on the Evaluation of Carcinogenic Risks to Humans

Kirk-Othmer, R.E. 2006. Encyclopedia of Chemical Technology. 5th Edition. John Wiley and Sons Ltd., New York, NY.

Organic Peroxide Producers Safety Division of the Society of the Plastics Industry. 1999. Safety and Handling of Organic Peroxides. Publication # AS-109. Washington, DC

National Fire Protection Association (NFPA). Standard 430, Code for the Storage of Liquid and Solid Oxidizers. 2004 Edition. Quincy, MA.

NFPA. Standard 432, Code for the Storage of Organic Peroxide Formulations. 2002 Edition. Quincy, MA.

NFPA Standard 654: Standard for the Prevention of Fire and Dust Explosions from the Manufacturing, Processing, and Handling of Combustible Particulate Solids

OECD, Guiding Principles for Chemical Accident Prevention, Preparedness and Response, Second Edition, 2003

Oslo and Paris Commission (OSPAR). 2006. Recommendation 2000/3 for Emission and Discharge Limit Values for E-PVC, as amended by OSPAR Recommendation 2006/1. Oslo, Norway and Paris, France.

Oslo and Paris Commission (OSPAR). 1999. Recommendation 99/1 on BAT for the Manufacture of Emulsion PVC (e-PVC). Oslo, Norway and Paris, France.

Oslo and Paris Commission (OSPAR). 1998. Decision 98/5 for Emission and Discharge Limit Values for the Vinyl Chloride Sector, Applying to the Manufacture of Suspension PVC (S-PVC) from Vinyl Chloride Monomer (VCM). Oslo, Norway and Paris, France.

UN Recommendations on the Transport of Dangerous Goods. Model Regulations. Thirteenth revised edition, 2003.

US EPA. 2000. 40 CFR Part 63 National Emission Standards for Hazardous Air Pollutants for Amino/ Phenolic Resins Production. Washington, DC

US EPA. 1996. 40 CFR Parts 9 and 63 National Emission Standards for Hazardous Air Pollutant Emissions: Group IV Polymers and Resins. Washington, DC

US EPA. 40 CFR Part 63 — National emission standards for hazardous air pollutants, Subpart F—National Emission Standard for Vinyl Chloride. Washington, DC

US EPA 40 CFR Part 60 — Standards of performance for new stationary sources, Subpart DDD — Standards of Performance for Volatile Organic Compound (VOC) Emissions from the Polymer Manufacturing Industry. Washington, DC

Annex A: General Description of Industry Activities

Polymers

Polymers are generally classified according to their physical properties at service temperature including:

- Resins: rigid, with high Young modulus³⁶ and low elongation to failure³⁷;
- Rubbers (or 'elastomers'), with low Young modulus and high elongation to failure.

They are also classified according to the types of manufacturing technologies used, including:

- **Thermoplastics** or thermoplasts: Soften and melt reversibly when heated (harden when cooled). They are fabricated by molding or extrusion, or by smearing or dipping, diluted in solutions or in emulsions, as in the cases of coatings and adhesives; they can be easily recycled, though with a general degradation of their properties;
- **Thermosets**: After curing, they harden permanently and decompose when heated to high temperatures. They cannot be recycled after use. Thermosets are harder, more dimensionally stable, and more brittle than thermoplastics.

Polymer Manufacturing Phases

Monomer and Solvent Purification

Polymerization reactions need high purity raw materials and chemicals because impurities can affect the catalyst or negatively influence the product properties including changes in the structure and reduction of the chain length.

³⁶ Measure of the stiffness of a given material. Defined as the ratio, for small strains, of the rate of change of stress with strain

³⁷ Measure of the ductility of a materials, it is the amount of strain it can experience before failure in tensile testing.

Polymerization Processes

Polymerization processes vary according to the properties of monomers and polymers and their polymerization mechanisms. Polymerization reactors are either continuous or discontinuous (batch). In general, batch polymerization is chosen when the production capacity is small and/or the product range is broad, leading to frequent campaign changes. Continuous polymerization is chosen for large scale production of a small number of polymer grades.

Batch reactors are usually STR (Stirred Tank Reactor) type, equipped for heat exchange (internal coils, jacket, and reflux condensers) according to process needs; stirring is optimized according to process needs. Continuous reactors are designed on the basis of the process requirement and they can be of very different types. Depending on the polymerization media, processes can be classified as follows:

- Solution polymerization: applied to monomers and polymers that are soluble in organic solvents or water; used for manufacturing HDPE, LLDPE, several acrylic polymers for coating and adhesive markets, step-growth polymerizations, etc.
- Suspension polymerization: applied to insoluble monomers, polymers, and initiators or catalysts; used for manufacturing PVC and EPS. The monomer is suspended in the solvent in small drops (facilitated by stirring and addition of a colloid), and the initiator, or catalyst, is dissolved in the monomer.
- Emulsion polymerization: the monomers, insoluble or sparingly soluble in water, are emulsified by soaps and other surfactants in droplets and are partly dissolved in micelles by the excess soap. A water-soluble initiator starts the polymerization in the micelles, which grow as

polymer particles. Monomers and other reactants, as well as new radicals, are fed to polymer particles by diffusion through the water. The final product from the reactor is a stable dispersion of polymer in water (latex). Inverse emulsion (water-in-oil) polymerization is used for water-soluble monomers. Typical products obtained via emulsion polymerization are ABS, emulsion PVC, polyvinyl acetate, and acrylic latexes;

- Bulk (or mass) polymerization: monomer is directly polymerized, after addition of initiator or catalyst or by effect of heat or light. Typical products obtained by bulk polymerization are LDPE, GPPS and HIPS, iPP, PMMA sheets, nylons, and PET;
- Slurry polymerization: the polymer is insoluble in the reaction medium, generally due to its crystalline properties. The polymer precipitates from the solution of monomer in solvent or from monomer itself and is maintained in suspension ("slurry") by stirring or from flow turbulence. Polymer recovery is obtained by decantation (settler or decanting centrifuge). Active monomer solution can be recirculated directly to the reactor. Batch and continuous polymerizations are both feasible. Typical products obtained by slurry polymerization are polyolefins (HDPE, iPP);
- Gas phase polymerization: Gas phase polymerization is operated in a fluidized-bed reactor, where the catalyst is added in fine dust form and polymerization is performed in the growing polymer particles, fluidized from the upward flow of monomer. Stirred reactors are also used to this purpose. Typical products obtained by gas-phase polymerization are polyolefins (HDPE and iPP).

Polymer Recovery

After polymerization, catalysts or initiators have to be destroyed and polymers have to be separated from residual monomers

and polymerization medium. These operations are often integrated with finishing operations. Flash evaporation, steam stripping, and wet nitrogen stripping are the most commonly used unit operations for recovery of unreacted monomers and solvents.

Finishing

Finishing of the polymers may include addition of additives, drying, extrusion and pelletization, and packaging. Typical product additives include antioxidants, UV absorbers, extension oils, lubricants, and various kinds of stabilizers and pigments.

Polymers are usually produced for sale as a powder (e.g. PVC), in granules (e.g. HDPE, EPS), in pellets (e.g. polyolefins, polystyrene, PET, polyamides, PMMA), in sheets (e.g. PMMA), or in liquid emulsions or solutions.

Specific Processes and Products

Thermoplastics

Polyethylene

Three main types of polyethylene are produced: LDPE, HDPE and LLDPE.

Low Density Polyethylene (LDPE) is produced in high pressure continuous process: ethylene is compressed up to 3,000 bar (tubular reactor) or 2,000 bar (vessel reactor), and fed to the reactor, where oxygen or organic peroxide are injected to initiate the radical polymerization at 140 – 180 °C. Temperature of the reaction is high, peaking to more than 300 °C. The ethylene – polymer blend is continuously discharged to a high pressure (250 bar) separator, where polymer precipitates and most of the unreacted ethylene is recovered, recompressed, and recycled to the reactor. Polymer is then fed to a low pressure separator, where degassing is completed. The molten polyethylene is then finished by extrusion and pelletizing.

High Density Polyethylene (HDPE) and Linear Low Density Polyethylene (LLDPE, linear copolymers with 1-butene, 1-hexene or 1-octene) are produced by Ziegler-Natta or, recently by metallocene catalysis, with mostly the same processes and in many instances in the same plants. Processes employed include:

- Gas phase polymerization: Large (> 500 m³) fluidized bed reactors are used, operating at relatively high pressure (20 – 30 bar), with high ethylene recycle through a gas cooler, to remove heat of polymerization. One or two reactors in series may be used.
- Slurry process: HDPE can be produced in slurry continuous reactors (one or more reactors in series, in some cases (BORSTAR) coupled with gas phase reactors), using as diluent isobutane in tubular loop reactors and hexane or heptane in CSTR reactors.
- Solution process: In the solution reactor, the polymer is dissolved in a solvent/comonomer system. Typically, the polymer content in a solution reactor is controlled at between 10 and 30 wt-%. The reactor pressure is controlled between 30 and 200 bar, while the reactor temperature is typically maintained between 150 and 250 °C. A hydrocarbon in the range of C₆ to C₉ is typically used as the solvent
- High pressure process: LLDPE, VLDPE and ULDPE based on butene-1 copolymerization can be industrially produced with Z-N catalysts by high pressure process, both tubular and vessel."

Polypropylene

Two different kinds of processes are applied in the production of polypropylene:

- Gas phase process at 70 – 90 °C, 20 – 40 bar. Fluidized bed reactors are used, as well as stirred vessel reactors, both vertical and horizontal.
- Slurry process in liquid monomer at 60 – 80 °C, 20 – 50 bar, also known as "bulk" or "liquid" phase process. A tubular loop reactor is used.

One or more reactors in series are used to produce a wide range of polymers, including toughened isotactic Polypropylene (iPP)³⁸, containing copolymers with ethylene. The two types of reactors can be combined for better process optimization (e.g. Spheripol® process).

Polyvinyl Chloride (PVC)

Polyvinyl chloride (PVC) is produced by the polymerization of vinyl chloride monomer (VCM). There are three different processes used in the manufacture of PVC:

- Suspension process;
- Emulsion process; and
- Mass (bulk) process.

Suspension PVC (S-PVC) is produced batchwise in a STR. The monomer is dispersed in demineralized water by the combination of mechanical stirring, colloids and surfactants. The polymerization takes place inside the VCM droplets under the influence of VCM soluble initiators. The PVC suspension is then degassed to remove the bulk of unconverted VCM, and fed to a steam stripping tower, where traces of unconverted VCM are removed. The product is subsequently sent to a centrifuge/rinsing system for the removal of impurities and for dewatering, and eventually to a drier. The dry polymer can then

³⁸ Isotactic polymers refer to those polymers formed by branched monomers that have the characteristic of having all the branch groups on the same side of the polymeric chain.

be sieved and grinded as needed. The final step is packaging or storing in silos for bulk shipping.

In emulsion processes, PVC latex is produced. E-PVC is manufactured by three polymerization processes: batch emulsion, continuous emulsion and microsuspension. The VCM is dispersed using an emulsifier, usually a sodium alkyl or aryl sulphonate or alkyl sulphate. The polymerization takes place at the VCM water interface using initiators, such as an alkali metal peroxydisulphate. Residual VCM is removed by stripping the latex. Latex is usually dried in a spray dryer and the derived exhausts are a critical point for VCM emissions to the atmosphere.

Polystyrene

Three different types of polystyrene are produced: a transparent and brittle polymer called General Purpose Polystyrene (GPPS), a white, non-shiny but relatively tough, rubber modified polystyrene called High Impact Polystyrene (HIPS), and the Expandable Polystyrene (EPS).

GPPS and HIPS are produced by continuous bulk polymerization where the monomer is polymerized by radical polymerization, initiated by heat, with or without an organic peroxide. The main difference is that in HIPS manufacturing, medium- or high- cis-polybutadiene dissolved in styrene is added to improve polymer toughness.

The process may include the addition of solvent, initiator (optional), and chain transfer agents into the reactors under well-defined conditions. Styrene itself acts as the solvent of the reaction, although up to 10 % ethyl benzene may be added to ensure better reaction control.

To remove unconverted monomers and solvents, the crude product is heated to about 220 - 260 °C and led through a high

vacuum. This operation is called devolatilization. Water injection (steam stripping) can be added to improve monomer removal. Unreacted styrene and ethyl benzene are condensed and recycled to the feed line. The molten polymer is then pelletized (dry or under water) and dried for storing and packaging.

Expandable polystyrene beads are produced by suspension polymerization of styrene initiated by organic peroxides with the addition of pentane as blowing agent. The beads are separated by centrifugation, washed, and then dried for packaging.

Acrylates

Acrylic polymers are a wide class of polymers produced by radical polymerization of acrylic monomers (acrylic acid and its derivatives) and their copolymerization with other vinyl monomers (e.g. vinyl acetate or styrene). The main acrylic monomers are acrylic acid itself, acrylamide, and a large range of acrylic esters, from methyl acrylate to fatty alcohol esters. Water-soluble monomers, as acrylic acid and acrylamide, are usually polymerized in water solution or in inverse emulsion polymerization. Acrylic esters polymers and copolymers are produced in emulsion or in solution, according with their final use.

Emulsion polymerization is the most diffused technology. Solvents used in solution polymerization are alcohols, esters, chlorinated hydrocarbons, aromatics, according to the solubility properties of the polymer. Initiators are organic or inorganic peroxides. Polymerization is usually performed in batches, in stirred tank reactors, equipped with steam/water heat exchange systems.

Polyethylene Terephthalate (PET)

PET is produced by polycondensation of terephthalic acid or its dimethyl ester (dimethyl terephthalate, DMT) with ethylene

glycol (EG). The reaction is conducted in two steps, the first step leading to a prepolymer of relatively low molecular weight (raw polymer), the second leading to the final, high molecular weight polymer. The DMT process has largely been superseded by terephthalic acid (TPA) as the preferred industrial route to polyester production.

Solid state polymerization can be operated in continuous, with various reactor designs, and hot nitrogen flow for heat exchange and volatile reaction product removal, or in batch in a solids mixer/drier operating under vacuum.

Polyamides (Aliphatic)

Polyamides have a macromolecular structure with the amide group (-NH-CO-) as a recurring functional unit that gives the specific chemical properties to the final products. Linear polyamides, widely known as 'nylons', from the original DuPont trademark name, are the most common category of the family. The family of polyamides is wide, with the number of carbon atoms in the monomers ranging from 4 to 12.

For example, the monomer of polyamide 6 is ϵ -caprolactam, polymerizing by step-growth polymerization. The main raw material for the production of polyamide 66 is an aqueous solution of the organic salt (called AH salt, 66 salt or nylon salt) obtained by the reaction of 1,6-hexamethylene diamine and 1,6-hexane dicarboxylic acid (adipic acid).

Polyamides can be produced both by batch or continuous polymerization. After polymerization, the polymer melt he polymer melt is extruded and cut, yielding chips. An extraction phase with hot water allows removes residual oligomers and monomers, and is followed by a drying phase. An extract waste processing phase is then needed to reuse the oligomers and monomers.

Thermosets

Thermosetting polymers fabrication processes include chemical crosslinking (networking) of their molecular structure, leading to a material that does not melt, but decomposes on heating. The reactive solid or liquid intermediate is transformed into the final product at the customer site by curing with hardeners or catalysts.

Phenolics

Phenolic resins are a family of polymers and oligomers, based on the reaction products of phenols with formaldehyde. Other raw materials include amines (hexamethylenetetramine [HEXA]). Phenolic resins can be classified in:

- Novolaks (solid polymers by acid catalysts);
- High ortho novolaks (fast cure polymers by neutral catalysts);
- Resoles (high formaldehyde-to-phenol molar ratio, liquids or solids, by alkaline catalysis).

Phenolic resins are produced in batch processes in STR reactors.

Unsaturated Polyesters

Unsaturated polyester (UPE) is the generic name for a variety of thermoset products, mainly prepared by polycondensation of an anhydride or a diacid (e.g., maleic anhydride, fumaric acid, phthalic anhydride, orthophthalic acid, isophthalic acid and terephthalic acid) with a diol, (e.g., ethylene glycol, diethylene glycol, propylene glycol, butanediol, hexanediol, dipropylene glycol, neopentyl glycol and dicyclopentadiene). These condensation products are dissolved in a reactive monomer, which is usually styrene, but methyl methacrylate, t-butyl acetate or diallyl phthalate are also used. When this mixture is cured by the customer, a three-dimensional network is formed. Several

hardeners, accelerators, inhibitors, additives and fillers are used in the manufacturing process.

The core of a resin plant usually consists of a number of batch reactors, served by storage and dosing of raw materials and blending tanks for finishing of products, and equipped with heat exchange systems and distillation columns, nitrogen, vacuum.

Alkyds

Alkyd coatings are a class of polyester coatings derived from the reaction of an alcohol and an acid or acid anhydride and are the dominant resin or "binder" in most "oil-based" coatings. Alkyd coatings are typically manufactured from acid anhydrides (e.g., phthalic anhydride or maleic anhydride) and polyols (e.g., glycerin or pentaerythritol). They are modified with unsaturated fatty acids (from plant and vegetable oils) to give them air drying properties. The drying speed of the coatings depends on the amount and type of drying oil employed and use of organic metal salts or "driers" which catalyze cross-linking. Based on their content of drying oil, alkyd resins are classified in "long oil", "medium oil" and "short oil"

Alkyd coatings are produced through two processes: fatty acid process and alcoholysis or glyceride process. In both cases the resulting product is a polyester resin to which drying oil groups are attached. At the conclusion of both processes the resin is purified and diluted in solvent.

Polyurethanes

The petrochemical industry produces the main polyurethane (PU) raw materials; polymerization is integrated in the process of fabrication of the final articles. Blending and compounding companies, named "system houses", prepare and sell tailor-made systems to the final users.

The main polyurethane producing reaction is between a diisocyanate (either aromatic or aliphatic) and a polyol (e.g., polyethylene glycol or polyester polyol), in the presence of catalysts, pigments, fillers, and materials for controlling the cell structure, and foaming agents and surfactants in the case of foams.