Appendix A: Report S1

Thermoplastic and thermosetting polymers –
Synthesis, chemical substances used and
initial hazard assessments

Supplementary material for journal article and supportive data for
Table S1 “Hazard classifications and scores for chemicals per polymer”

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**Introduction**

This report is provided as Supplementary material to the journal article *Environmental and health hazard ranking and assessment of plastic polymers based on chemical composition*. Together with Table S1 “Hazard classifications and scores for chemicals per polymer” (also provided as supplementary material), it includes the data on which the article is based.

In this report thermoplastic and thermosetting polymers are described with regard to the chemical substances associated with the different polymers. These plastic polymers can, often with addition of other chemical substances (additives) be used to make plastic products, synthetic fibres, coatings, adhesives, sealants, and some elastomers. The additives that are blended with the polymers are not included in this report, with a few exceptions.

For each plastic polymer family/type there is data on global annual production, concise descriptions of polymer synthesis and which chemical substances that are used for producing the polymers, figures on how much of each monomer that is needed to produce each polymer monomer synthesis, and examples of applications. This data has been collected from the polymer literature. The figures on monomer concentrations have all been recalculated into weight percentages.

All data on chemical substances (ingredients) from the polymer synthesis parts as well as figures of monomer weight percentages have been put into the hazard ranking model in Table S1, together with hazard classifications for the substances. These hazard classifications are taken from Annex VI in the EU classification, labelling and packaging (CLP) regulation adapted to the Globally Harmonized System (GHS) and includes the 1st Adaptation to Technical Progress (European Parliament and Council, 2008; European Commission, 2009).

In addition a short initial assessment part for each polymer is included. This is mainly based on assessments made on the CLP classification data derived from Table S1 (Appendix A). The Roman numerals (I-V) are used for showing the five levels of environmental and health hazards (presented in Table 1 in the journal article). Level V is the most hazardous of the hazard levels. For each polymer the results (based on monomer classifications) are presented in a small table. This includes a hazard score for the polymer, the highest hazard level for the monomer(s), and an assessment statement with a matching hazard point. The hazard score is taken from Table S1 (Appendix A). The assessment statement for the polymer is based on the hazard classifications and the polymer hazard score, and is made in accordance to Table A.

**Table A. Description assessment statements and hazard points presented for each polymer.**

<table>
<thead>
<tr>
<th>Hazard level</th>
<th>Assessment statement</th>
<th>Polymer hazard score</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Very high hazard</td>
<td>Close to 10.000</td>
</tr>
<tr>
<td>4</td>
<td>High hazard</td>
<td>Close to 1000</td>
</tr>
<tr>
<td>3</td>
<td>Medium hazard</td>
<td>Close to 100</td>
</tr>
<tr>
<td>2</td>
<td>Low hazard</td>
<td>Close to 10</td>
</tr>
<tr>
<td>1</td>
<td>Very low hazard</td>
<td>Close to 1</td>
</tr>
<tr>
<td>(1?) or (2?)</td>
<td>Hazard uncertain, but possibly low</td>
<td>-</td>
</tr>
<tr>
<td>(+?)</td>
<td>Hazard may be underestimated</td>
<td>-</td>
</tr>
<tr>
<td>(?)</td>
<td>Hazard unknown</td>
<td>-</td>
</tr>
</tbody>
</table>

3
**Polymer and plastic related concepts**

**Glossary**

**Capital letters (A), (B), (C):** are used to separate the different alternatives of processing within a polymer family/type, which affects which substances and shares that are used.

**Additive:** a substance that is added to a material to improve or change its properties or to function as diluents, e.g. fillers, to reduce cost (Harper and Petrie, 2003). Examples of additive functions are: adhesion promoters, antiblocking agents, antifogging agents, antimicrobials, antioxidants, antistatic agents, acid scavengers, blowing and foaming agents, coupling agents, crosslinking agents, curing agents, defoamers, dispersants, fillers, flame retardants, heat stabilisers, impact modifiers, low-profile additives, lubricants, pigments, plasticisers, processing aids, release agents, slip agents, thickeners (viscosity regulators), UV-stabilisers, and wetting agents (Harper and Petrie, 2003; Flick, 2004; Zweifel, 2009).

**Adhesives:** are substances that are used to join two surfaces together (Carraher, 2000). Many different plastic polymers can be used to make adhesives.

**Blowing agent:** a substance that can produce gas, and is added to a polymer melt where it forms a foam or cellular structure (expanded polymer) (Alger, 1997).

**Catalyst:** a chemical substance that either speeds up the polymerisation or curing process, or cures a resin. It does not become a part of the polymer (Harper and Petrie, 2003).

**Chain transfer agent:** a substance used in chain polymerisation to cause a chain transfer reaction (Alger, 1997).

**Coatings:** are highly viscous polymers (often plastic polymers) that are applied to a surface, and adheres to it, to protect and/or to decorate (Carraher, 2000).

**Comonomer:** a monomer that is mixed with another monomer or monomers and undergoes polymerisation producing a copolymer (Alger, 1997).

**Compound:** a mixture of plastic polymers and additives, before processing.

**Copolymer:** a polymer that is made by polymerising more than one type of monomer.

**Crosslinking:** a process that causes chemical bonds between polymer chains. In thermosets these bonds form large molecules (Harper and Petrie, 2003).

**Crosslinking agent:** a chemical that promotes or regulates the linking of polymer chains (Harper and Petrie, 2003).

**Curing:** is the solidification or hardening process of thermosets by a chemical reaction. The curing can be either heat activated (e.g. for phenolics, unsaturated polyester), mixture activated (e.g. epoxy resins and polyurethane), or activated by absorption of humidity or radiation (Osswald et al, 2008). This reaction is irreversible and creates molecule structures that are more or less cross-linked (Osswald et al, 2008).

**Curing agent (or hardener):** a chemical that is used to harden (cure) thermoset resins (Harper and Petrie, 2003). The curing agent becomes a part of the polymer, in opposite to catalysts, promoters and accelerators (Harper and Petrie, 2003).
**Elastomer (or rubber):** A macromolecular material that after deformation by weak stress rapidly approximately regains its initial shape and dimensions (Harper and Petrie, 2003). This material group includes thermoplastic elastomers, thermoplastic vulcanizate, and rubbers (melt-processable, synthetic and natural) (Harper and Petrie, 2003).

**Emulsifier (or surfactant):** A substance that lowers the surface tension and enables two immiscible liquids (e.g. monomer and water) to mix (disperse) in the form of droplets (Gowariker, 2003; Harper and Petrie, 2003).

**Homopolymer:** A polymer that is made by polymerising one single monomer.

**Inhibitor:** A substance that reacts with the initiators to prevent or delay the free radical polymerisation (Alger, 1997). It is consumed in the reaction (Alger, 1997).

**Initiator:** A substance that starts and speeds up the polymerisation of monomers by a chain reaction mechanism (Alger, 1997). The initiator reacts with the monomer and becomes a component of the polymer (Alger, 1997; Harper and Petrie, 2003). In ionic polymerisation reactions where the initiator is not consumed it is often called a catalyst (Alger, 1997).

**Monomer:** Is the main building block for polymers. It is a small molecule that can react with similar molecules or other molecules to form polymers, which are chainlike macromolecules (Harper and Petrie, 2003).

**Polymer:** A substance composed of organic high molecular weight molecules that are made up of small building blocks (monomers) to create a chain. It can be either natural (e.g. cellulose), or synthetic (e.g. plastic polymers).

**Polyol:** An alcohol with many hydroxyl groups (Harper and Petrie, 2003).

**Plastic polymers:** Polymers used to make plastic products, synthetic fibres, coatings, adhesives and thermoplastic elastomers.

**Plastics:** Are plastic polymers to which additives are usually added to enable processing or give the plastic its desired properties in a certain application (OECD, 2004).

**Plastic products:** Are plastic materials that are moulded into shapes and forms for a specific application.

**Polymerisation:** (see below)

**Prepolymer:** A polymer that is in a stage between the monomer(s) and the final polymer (Harper and Petrie, 2003).

**Promoters (or accelerators):** A chemical added to activate the initiators, e.g. organic peroxides, into free radicals (Strong, 2008). Activation can also be done by heat (Strong, 2008).

**Sealants:** A substance that is used to e.g. provide a barrier against gases, liquids, solids lower strength, and maintain differences in pressure (Carraher, 2000). They can join surfaces together like adhesives, but are lower in strength, but have better flexibility (Harper and Petrie, 2003).
Suspending agents: are used in suspension polymerisation to prevent the particles to form one big mass (Ravve, 2000).

Synthetic fibres: are (according to ISO) fibres manufactured from polymers made from chemical elements or compounds, in contrast to fibres made from fibre-forming polymers, e.g. cellulose and cotton (McIntyre, 2005).

Thermoplastics: are polymeric plastic materials which soften or melts when heated and can be remoulded. A thermoplastic material can have either a linear or a branched structure (Harper and Petrie, 2003).

Thermosetting plastics (or thermosets): are polymeric plastic materials which are crosslinked and can, therefore, neither soften while heated, nor be remoulded.

Polymerisation

Plastic polymers are made by polymerising monomers and thereby forming macromolecular chains. Besides the monomers many other chemicals substances may be needed during the polymerisation process, e.g. initiators, catalysts, chain transfer agents, emulsifying agents and solvents.

The chemical process for the chain formation may be divided into chain-growth polymerisations (mainly addition polymerisation), and step-growth polymerisation (mainly condensation polymerisation, but also addition polymerisation) (Braun et al, 2005; McIntyre, 2005). In addition polymerisation the monomers are reacted by opening a double bond, but with no molecules being split out (Harper and Petrie, 2003). In condensation polymerisation water or other simple molecules, e.g. ammonia, carbon dioxide, hydrochloric acid, ethanol and hydrogen chloride, are split out during the reaction Peacock and Calhoun, 2006; Alger, 1997).

Chain growth polymerisation

In chain growth polymerisation initiators or catalysts are often needed to start polymerisation (Braun et al, 2005). The initiator, or a species produced from the initiator, activates the the monomer molecule by reacting with it (Alger, 1997). The activated monomer then adds on other monomer molecules forming macromolecular chains (Alger, 1997; Gnanou and Fontanille, 2008). There are four different types of chain-growth polymerisations:

1. Free radical (free radical initiator: mainly organic peroxides and azo compounds)
2. Anionic (initiator: negatively charged ion reacts)
3. Cationic (initiator: positively charged ion reacts)
4. Coordination (coordination catalyst: e.g. Ziegler-Natta, metallocene) (Gnanou and Fontanille, 2008).

The four largest plastics, i.e. polyethylene, polypropylene, polyvinyl chloride and polystyrene are made by chain growth polymerisation (Peacock and Calhoun, 2006).

Step growth polymerisation

In step growth polymerisation catalysts are often not needed (Braun et al, 2005). The polymers grow by condensation or addition with a monomer, an oligomer, another polymer chain, or a species that carries an antagonist functional group (Gnanou and Fontanille, 2008). Examples of polymers produced by step growth polymerisation are polyamides (e.g. nylon 66 and nylon 610), polyesters, polyurethanes and epoxy resins (Peacock and Calhoun, 2006; Braun et al, 2005).
**Polymerisation techniques**
Three main techniques for manufacturing the polymers exist (Braun et al, 2005):

- bulk (or mass)
- solution
- dispersion (suspension or emulsion).

The bulk process (also called mass process) is carried out without solvents in either a liquid, solid or gas phase (Braun et al, 2005). This technique gives the purest polymers since, nothing except than trace amounts of catalysts or initiators, and maybe chain transfer agents are used besides the monomers (Nicholson, 2006). Due to technical problems with this process, such as to high viscosity, overheating, degradation of polymer, it is for many polymers not possible to use this technique is on an industrial scale (Nicholson, 2006).

The solution process is carried out in organic solvents or water (Braun et al, 2005), and the polymer has to be removed from the solvent by evaporation or precipitation in a non-solvent (Gowariker et al, 2003).

In the dispersion process the liquid monomer is stirred into small droplets in a liquid in which it is insoluble, either in suspension or in emulsion (Braun et al, 2005). The suspension contains water or aliphatic hydrocarbons, initiator and suspension aids (dispersants), e.g. protective colloids and emulsifiers, and the monomers are polymerised into beads or pearls (Braun et al, 2005; Gowariker et al, 2003). These are isolated by filtration and are washed clean from surfactants and protective colloids by water (Gowariker et al, 2003). The emulsion contains water, initiator, emulsifier (i.e. surfactant) and sometimes a chain transfer agent (Braun et al, 2005; Gowariker et al, 2003). The polymers formed are dispersed in the aqueous phase, which can either be used directly for adhesives or paints, or can be isolated by drying or freezing (Gowariker et al, 2003).

There are some environmental drawbacks with the solution and dispersion techniques associated with the use of solvents. The organic solvent may be toxic and flammable, it has to be removed from the polymer (the last traces may be very difficult to remove) and it needs to bee recycled and purified (Braun et al, 2005; Nicholson, 2006). Even when the polymerisation occurs in an aqueous phase disposal of the liquid wastes poses problems (Braun et al, 2005).

**Crosslinking or curing**
In thermosetting plastics the polymer chains are chemically bound to one another with crosslinks (Peacock and Calhoun, 2006; Nicholson, 2006). These can be promoted or regulated by adding a crosslinking agent (Harper and Petrie, 2003) or a curing agent (hardener). Curing may also be done by heat, humidity or radiation (Osswald et al, 2008). Crosslinking can either take place in the polymerisation step, or in a separate step after the macromolecules (prepolymers) have been formed (Nicholson, 2006) when the plastic product is going to be shaped.

Copolymers are made by incorporating one or more monomers into a polymer either by step or chain growth (Peacock and Calhoun, 2006).

**Additives for polymerisation**
Some polymerisation additives may be needed during the polymerisation process, depending on factors such as monomers, the chemical process, polymerisation technique, and desired properties. Examples include initiators and/or catalysts, inhibitors, promoters (or accelerators), retarders (retards of suppress the rate of polymerisation), chain transfer agents (terminating the chains), curing agents, crosslinking agents, solvents, and suspending agents. In table A common polymerisation additives are presented. Some additives become a part of the polymer while others do not.
Table B. Fate of additives used for polymerisation

<table>
<thead>
<tr>
<th>Additive</th>
<th>Becomes part of polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>no</td>
</tr>
<tr>
<td>Crosslinking agent</td>
<td>yes</td>
</tr>
<tr>
<td>Curing agent (hardener)</td>
<td>yes</td>
</tr>
<tr>
<td>Inhibitor</td>
<td>yes</td>
</tr>
<tr>
<td>Initiator</td>
<td>yes</td>
</tr>
<tr>
<td>Promotor</td>
<td>no</td>
</tr>
</tbody>
</table>

Other additives that are not needed in the polymerisation, but that are needed to make characteristics that determine a plastic type such as blowing agents for expandable polystyrene, plasticisers for soft PVC and, or additives that are crucial for processing (e.g. heat stabilisers for PVC) are included in this survey.

The remaining types of additives are not included in the survey, e.g.: antiblock agents, antioxidants, antislip agents, antistatic agents, bactericidal agents, brighteners and whiteners, colorants, flame retardants lubricants, light stabilisers, melt strength improvers, mould release agents, slip additives, uv-protective agents etc.

Monomer raw materials

Most of the monomers that are used in plastic polymers are derived from raw material molecules as methane, ethylene, acetylene, propylene, benzene, xylene and butadiene (Table B) which in turn are formed by cracking of fractionated crude (raw) oil (petroleum) (Carraher Jr, 2007) or natural gas. The use of these has implications for the environment in several ways. They are derived from fossil sources and therefore contribute to global warming, and the environmental risks and effects that arise from crude oil and natural gas extraction and refining. In addition several of them are hazardous for human health and the environment, for instance naphtha, benzene and butadiene.

Efforts are being made trying to replace some of these fossil-based raw materials with raw materials based on renewable resources. The share of plastic polymers made from renewable resources (bio-based) is today very small, but growing. Examples of renewable raw materials are; starch from corn, potatoes and cassava; oil from castor beans, soy beans and rapeseed; and cellulose from wood, cotton and hemp) (British Plastic Federation, 2010). Bio-based polymers in this study only include polylactic acid (PLA) and polyamide 11, but it is possible to make e.g. other starch based, cellulose based plastics, and bio-based polyethylene.

Table C. Raw material molecules for monomer synthesis

<table>
<thead>
<tr>
<th>Raw material substances</th>
<th>Monomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>Hexamethylene tetramine, melamine, vinyl acetate, ethylene, ethylene glycol, methyl metacrylate, phosgene, formaldehyde</td>
</tr>
<tr>
<td>Ethylene</td>
<td>Acrylic acid, vinyl chloride, styrene, vinyl acetate, acrylonitrile, ethylene glycol</td>
</tr>
<tr>
<td>Acetylene</td>
<td>1,3-Butadiene, vinyl chloride, acrylonitrile, vinyl fluoride, vinyl acetate</td>
</tr>
<tr>
<td>Propylene</td>
<td>Acrylonitrile, acrylic acid, epichlorohydrin, glycerol, methylmetacrylate, bisphenol A, phenol</td>
</tr>
<tr>
<td>Benzene</td>
<td>Styrene, adipic acid, phenol, bisphenol A</td>
</tr>
<tr>
<td>Xylene</td>
<td>Dimethyl terephthalate, terephthalic acid</td>
</tr>
<tr>
<td>Butadiene</td>
<td>Hexamethylene diamine, sebacic acid, lauryl lactam, polybutadiene</td>
</tr>
</tbody>
</table>

Data from: (Carraher Jr, 2007; OECD SIDS IAR, 2001; Fourné, 1999; Richards, 2005; Gnanou and Fontanille, 2008; Sheldon, 1983).
Thermoplastic polymers

Thermoplastics are plastic materials which soften or melt when heated and can be remoulded. They are by far the largest division of plastics both by means of annual production and diversity. The five largest plastic families polyethylenes (HDPE, LLDPE, LDPE), polypropylene (PP), polyvinylchloride (PVC), polystyrenes (PS, EPS) and polyethylene terephthalate (PET) alone account for approximately 75% of the European plastics demand (PlasticsEurope, 2009).

ACRYLIC RESINS

Acrylic resins are made of either acrylic or metacrylic esters (Fink, 2005). There are both thermoplastic and thermosetting acrylic resins. Polyacrylonitrile and polymethyl metacrylate are the most important thermoplastic ones (Gnanou and Fontanille, 2008). A non-thermoplastic member of the acrylic resin family is polyacrylic acid, which is a superabsorbent polymer (also called a hydrogel) (Kabiri et al, 2009) described after thermosetting polymers.

The thermosetting acrylic resins are e.g. used in dental fillers (Fink, 2005), most commonly Bisphenol A-Glycidyl Methacrylate (BIS-GMA), which is the addition reaction product of bisphenol A and glycidyl methacrylate often blended with lesser amounts of e.g. triethylene glycol dimethacrylate (TEGDMA) (Fleisch et al, 2010; Björkner et al, 1984). Bisphenol A and glycidyl methacrylate are i.a. skin sensitising (cat. 1; IV), and bisphenol A is in addition also suspected of damaging fertility (cat. 2; III) and causes serious eye damage (III). Triethylene glycol dimethacrylate (TEGDMA) is not classified. These thermosetting acrylic resins are not described further in this report.

1. Polyacrylonitrile (PAN) and copolymers

Global annual production
3 million tons of polymers mainly constituted of acrylonitrile (Gnanou and Fontanille, 2008).

Polymer synthesis and composition
Polyacrylonitrile is most commonly made by free radical dispersion polymerisation (A) of acrylonitrile in an aqueous solution of the monomer with e.g. potassium persulfate and sodium bisulfite as an initiator system and ferric or ferrous iron as a catalyst (Cox, 2005).

Solution polymerisation (B) is another widely used method in which the polymer is formed in a highly polar solvent, most commonly dimethylformamide (DMF), dimethylsulphoxide (DMSO) or aqueous sodium thiocyanate (45-55% solution) (Cox, 2005; Frushour, 2007 ). Azo compounds, e.g. azobisisobutyronitrile, or organic peroxides, e.g. benzoyl peroxide can be used as initiators (Cox, 2005).

Emulsion polymerisation (C) is mainly used to prepare copolymers (modacrylics) (Cox, 2005).

Polyacrylonitrile is commonly copolymerised with comonomers (Cox, 2005). Over 200 comonomers are listed, but vinyl acetate, methyl acrylate, methyl methacrylate, acrylamide, vinylidene chloride, vinyl bromide and vinyl chloride are the major ones (Cox, 2005; Frushour and Knorr, 2007).

Monomer concentrations
Acrylic fibres contain 85-100 wt% acrylonitrile (Cox, 2005). Typically 90-94 wt% acrylonitrile is mixed with a neutral comonomer of mainly either vinyl acetate, methyl acrylate, methyl methacrylate or acrylamide (usually 6-9 wt%), and a acid comonomer such as sodium styrene sulphonate, sodium methallyl sulphonate, or sodium 2-methyl-2-acrylamidopropyl sulphonate (0-1wt%) (Cox, 2005).
Modacrylic fibres contain less than 85 wt% acrylonitrile but more than 35 wt% comonomer, typically around 40 wt% (Cox, 2005). The most common comonomers are vinylidene chloride, vinyl bromide and vinyl chloride (Frushour and Knorr, 2007).

**Monomer synthesis**

Main monomer: Acrylonitrile (and hydrogen cyanide & acetonitrile (by-products)) \(\leftrightarrow\) propylene (oxidation in the presence of ammonia) (Cox, 2005; European Commission JRC, 2004).

**Fibre production**

All acrylic fibre polymers are spun from solvents, most commonly dimethylformamide, dimethlyacetamide, aq. sodium thiocyanate, aq. zink chloride, dimethyl sulphoxide, nitric acid and ethylene carbonato (Cox, 2005). Approximately 85% of the fibre is produced by wet spinning, in which the spinning dope (25 wt% polymer in solvent) is immersed in a coagulation bath which contains a nonsolvent, and is thereafter washed in hot water (Frushour and Knorr, 2007; Cox, 2005). The remaining 15% is produced by dry spinning where the solvent is removed by evaporation in hot air or inert gas (Frushour and Knorr, 2007; Cox, 2005).

**Applications**

PAN homopolymer fibres are used for industrial or high-performance end-end uses, e.g. used to produce carbon fibres used in composite materials (Cox, 2005; Gnanou and Fontanille, 2008). PAN comonomers are used as textile fibres mainly in the apparel and home furnishings sector (Gnanou and Fontanille, 2008; Frushour and Knorr, 2007).

**Initial assessment**

Results for PAN polymers, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard scores</th>
<th>6957-12739</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>V</td>
</tr>
<tr>
<td>Assessment</td>
<td>Very high hazard (5).</td>
</tr>
</tbody>
</table>

Acrylonitrile, which is the main component in polyacrylonitrile and its copolymers, is hazardous and i.a. classified as carcinogenic (cat. 1B; V), skin sensitising (cat. 1; IV), toxic if inhaled (III), if swallowed (III) or in contact with skin (III).

Of the comonomers acrylamide is the most toxic, (i.a. carcinogenic and mutagenic cat. 1B; V), followed by vinyl chloride and vinyl bromide (carcinogenic cat. 1B; V), methyl acrylate and methyl methacrylate (i.a skin sensitising cat. 1; IV), and vinylidene chloride (i.a suspected of causing cancer; III). Vinyl acetate is the least toxic option, only classified as highly flammable and liquid vapour (I).

For modacrylics, which have a higher percentage of comonomers, a less hazardous comonomer such as vinylidene chloride gives a polymer with a lower hazard score.

Dimethylformamide, which is commonly both used as a solvent in the common solution polymerisation process, and in fibre spinning, may damage the unborn child (V) and ought to be substituted with the less hazardous alternatives. Another hazardous and common solvent for the fibre spinning is aqueous zinc chloride, which i.a is very toxic to aquatic life with long lasting effects (IV).

The most hazardous initiator example is potassium persulphate, i.a. skin and respiratory sensitising (IV; cat. 1).

The halogenated comonomers (vinylidene chloride, vinyl bromide and vinyl chloride) used in modacrylics give the fibres flame resistance (Frushour and Knorr, 2007), so no flame retardants are needed for these types.

The global annual production is large.
2. Polymethyl methacrylate (PMMA)

**Global annual production**
1.8 million tons PMMA (2007) (calculated from PlasticsEurope MRG, 2008).

**Polymer synthesis and composition**
Poly(methyl methacrylate) is most commonly made by free radical polymerisation of methyl methacrylate in bulk (A), using peroxide or azo initiators, e.g. benzoyl peroxide or 2,2'-azobisisobutyronitrile (Ravve, 2000; Shi, 2006).

Suspension polymerisation (B), in water with protective colloids (magnesium carbonate or aluminium carbonate) and peroxides as initiators, is also used (Sinha, 2004). The slurry is treated with sulphuric acid, washed with water, filtered or centrifuged and dried (Sinha, 2004).

Solution polymerisation (C) where e.g. benzene or toluene is used as solvent is not used so frequently, but is used for surface coatings (Feldman and Barbalata, 1996; Ravve, 2000).

**Monomer concentrations**
Only one monomer (methyl methacrylate) is used.

**Monomer synthesis**
Methyl methacrylate (many methods exists) (Edshammar, 2002).
Ex 1: ↔ propylene and methanol (oxidative carbonylation) (Carraher Jr, 2007).
Ex 2: ↔ methacrylamide sulphate (reaction with methanol and water) ↔ cyanoxydine (reaction with sulphur acid) ↔ acetone and hydrogen cyanide (Edshammar, 2002).

**Applications**
Can be used as a substitute for glass, e.g. for sign boards, lenses for automobile lighting (Gowariker, 2003). It is commonly known as acrylic glass or plexiglass.

**Initial assessment**
Results for PMMA polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard score</th>
<th>1021</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>IV</td>
</tr>
<tr>
<td>Assessment</td>
<td>High hazard (4).</td>
</tr>
</tbody>
</table>

The only monomer methyl metacrylate is hazardous, i.a. skin sensitising (cat. 1; IV).

Solution polymerisation with benzene (carcinogenic and mutagenic cat. 1A and 1B; V) should be substituted with the less hazardous alternatives.

In some cases plasticisers are added (Feldman and Barbalata, 1996).

The global annual production is large.
3. Polytetrafluoroethylene (PTFE)

Global annual production
98,000 tons (figures for 2006) (Drobny, 2008).

Polymer synthesis and composition
Polytetrafluoroethylene is mainly polymerised from gaseous tetrafluoroethylene (PTFE) by free radical suspension and emulsion polymerisation methods in aqueous media with water soluble initiators, e.g. ammonium peroxodisulfate, sodium peroxodisulfate, potassium peroxodisulfate, hydrogen peroxide, benzoyl peroxide, disuccinic acid peroxide, or oxygen (Nuyken et al, 2005; Drobny, 2008). Two main methods exist. One method (A) uses little or no dispersing agents, and produces a granular resin (Drobny, 2008). The other method (B) uses dispersing agents e.g. perfluoro- or ω-hydroperfluoro alkanoic acid salts for instance ammonium perfluorooctanoate (which is the salt of perfluorooctanoic acid (PFOA), and perfluorotributylamine, and produces aqueous PTFE dispersions or a fine powder resin (Drobny, 2008; Nuyken et al, 2005; van der Putte, 2010).

Monomer concentrations
Only one monomer (tetrafluoroethylene) is used.

Monomer synthesis
Tetrafluoroethylene $\rightarrow$ tetrafluoroethylene and HCl (by-product) and halogenated substances (by-products) $\rightarrow$ chlorodifluoromethane (dihydrochlorination) $\rightarrow$ chloroform and hydrogen fluoride (reaction) (Carraher Jr, 2007; Edshammar, 2002).

Applications
PTFE is used in different applications for its exceptional chemical, mechanical, electrical, thermal and surface properties (Chanda and Roy, 2008). Due to its non-stick properties it is used as coating of metals, e.g. for non-stick cookware. Due to its chemical resistance it is used for seals, gaskets, packings, valve and pump parts and laboratory equipment. Due to its electrical insulation and heat resistance it is used in wire and cable insulation, molded electrical components, insulated transformers, hermetic seals for condensers, and laminates for printed circuitry (due to electrical insulation and heat resistance) (Chanda and Roy, 2008).

Initial assessment
Results for PTFE polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard score</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>Not classified*</td>
</tr>
<tr>
<td>Assessment</td>
<td>Hazard unknown (?), because the only monomer is not classified.</td>
</tr>
</tbody>
</table>

The only monomer, tetrafluoroethylene, is neither classified nor has an SIDS Initial Assessment Report, so this monomer can not be assessed.

The surfactant PFOA is yet not classified in the CLP, but according report on PFOA, reviewing the results from SIDS Initial Assessment Report and later studies, PFOA are persistent and toxic, and will probably be classified as reprotoxicant category 2 (van der Putte et al, 2010). Uncertainties regarding human health and bioaccumulating properties remain and carcinogenic properties are under evaluation (van der Putte et al, 2010). Perfluorooctane sulfonic acid, its salts, and perfluorooctane sulfonyl fluoride are listed under the Stockholm convention of persistent organic pollutants (POPs).
The manufacture of tetrafluoroethylene yields many by-products, mainly HCl, but also a large number of halogenated products are formed. Of these hexafluoropropylene (harmful if inhaled (III), and respiratory irritation III)), perfluorocyclobutane, 1-chloro-1,1,2,2-tetrafluoroethane (HCFC-124a) with some (0.022) ozone depleting potential, are the most significant (Drobny, 2001; European parliament and council, 2009, p21). Perfluoroisobutylene is formed in small amounts (Ebnesajjad, 2003).

The global annual production is of medium size.

4. Polyvinylidene fluoride (PVDF)

Global annual production
20.000 tons (figures for 2006) (Drobny, 2008).

Polymer synthesis and composition
PVDF is produced by free radical polymerization of vinylidene fluoride under elevated temperature and pressure (Yen and Amin-Sanayei, 2005; Lokensgard, 2004). Hydrogen and chlorine atoms are removed in the polymerisation (Lokensgard and Richardson, 2004). Aqueous emulsion or suspension techniques are used (Ebnesajjad, 2003).

In emulsion polymerisation (A) the initiators can be either organic peroxides, e.g. cumene hydroperoxide, diisopropyl benzene hydroperoxide, and tert-butyl hydroperoxide, or inorganic peroxides, e.g. ammonium persulfates, zinc peroxide and hydrogen peroxide (Ebnesajjad, 2003). The most commonly used surfactants are fluorine containing salts of a fluoralkanoic acid (PFAS) (Ebnesajjad, 2003). Usually ammonium perfluorooctanoic acid (APFO) which is the salt of perfluorooctanoic acid (PFOA) is used, or a perfluorinated carboxylate mixture mainly composed of ammonium perfluoronanoate (APFN) (70-80 wt%) and ammonium C-11 perfluoroundecanoate (15-20 wt%) ammonium C-13 perfluorotridecanoate (5 wt%), and APFO (< 1wt%) (Järnberg et al, 2006; van der Putte, 2010). However an alternative to APFO, has recently been found.

In suspension polymerisation (B) suspending agents, e.g. cellulose derivates (e.g. methyl hydroxyalkyl cellulose) or polyvinyl alcohol are added (0.01-0.5 wt%) (Ebnesajjad, 2003). Organic peroxides, e.g. diisopropylperoxydicarbonate, tert-butyl peracetate are used as initiators (0.05-0.5 wt%) (Ebnesajjad, 2003).

Monomer concentrations
Only one monomer (vinylidene fluoride) is used.

Monomer synthesis
Vinylidene fluoride (many methods exist)
Ex 1: ← 1-chloro-1,1-difluoroethane (HCl removal) ← trichloroethylene (chlorination by hydrofluorination)← acetylene (hydrofluorination),

Applications
Chemical processing of pipes and components, semiconductor, architectural finishes and coatings, electrical plenum, cable jacketing, offshore/petrochemical flexible piping, binders for lithium ion batteries, fuel cell membrane, polymer processing additives, decorative films and sheets (Yen and Amin-Sanayei, 2005) coatings, impellers, and chemical tubing (Lokensgard, 2004).
Initial assessment
Results for PVDF polymer, based on monomer classifications.

Hazard score -
<table>
<thead>
<tr>
<th>Highest hazard level</th>
<th>Not classified*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assessment</td>
<td>Hazard unknown, because the only monomer is not classified, but there is an indication of low level of concern (2?).</td>
</tr>
</tbody>
</table>

The only monomer, vinylidene fluoride, is not classified and can not be assessed with any certainty. The SIDS initial assessment profile (2001), however, indicates low risk of concern for human health and the environment.

The surfactants PFOA, that are used in the emulsion polymerisation, are not yet classified in the CLP. However, according to a report on PFOA (ordered by the European Commission), reviewing the results from SIDS Initial Assessment Report and later studies, PFOA are persistent and toxic, and will probably be classified as reprotoxicant category 2 (van der Putte et al, 2010). Some uncertainties regarding human health and bioaccumulating properties remain, and carcinogenic properties are under evaluation (van der Putte et al, 2010). Perfluorooctane sulfonic acid, its salts, and perfluorooctane sulfonyl fluoride are listed under the Stockholm convention of persistent organic pollutants (POPs).

The global annual production is small.

POLYAMIDES (PA) (aliphatic), NYLONS

Global annual production
4 million tons of nylon (figures for 2000) according to Richards (2005).

Many different grades of polyamides exist and are polymerised by five different condensation polymerisation methods: A) reaction of a diamine with a dicarboxylic acid, B) condensation of an amino acid, C) ring opening of a lactam (Nylon-6), D) reaction of a diamine with a diacid chloride, E) reaction of a diisocyanate with a dicarboxylic acid (Ravve, 2000). Nylon 6 and nylon 6.6 are the most widely used (Richards, 2005). Some other common commercially available nylons are 6.10, 8, 11 and 12 (Harper and Petrie, 2003).

Fibre production
All nylon fibres are produced by melt spinning, and no solvents are used (Richards, 2005).

Applications
Nearly 90% of the world production of nylons is used as fibres (Chanda and Roy, 2008). The major applications are apparel (e.g. tights, lingerie and swimwear) 39 %, carpets 24 %, industrial 24 % (e.g. tyre cords, belts, airbags and ropes), and staple 12 % (used for blending with other materials) (Richards, 2005). The applications as plastic materials are largest in mechanical engineering e.g. for gears, cams, bushes, bearings and valve seats (Chanda and Roy, 2008).

5. Polyamide 6 - Nylon 6

Global annual consumption

Polymer synthesis and composition
Nylon 6 is made by ring opening polymerisation of ε-caprolactam (Chanda and Roy), typically with a batch process. A mixture of caprolactam, water (5-10% by weight of monomer) and acetic acid (0.1%) are fed into a
reactor (usually) under nitrogen atmosphere and heat (Chanda and Roy, 2008). The product contains about 10% low-molecular weight materials (mainly residual monomer) which may be removed by leaching and/or vacuum distillation (Chanda and Roy, 2008).

**Monomer concentrations**

Only one monomer (ε-caprolactam) is used.

**Monomer synthesis**

ε-caprolactam
Ex1: ← mixture of (cyclohexanol) and cyclohexanone (dehydrogenation) ← cyclohexane (oxidation) ← benzene (hydrogenation),
Ex 2: ← cyclohexanone oxime (rearrangement in sulphuric acid) ← cyclohexanone (addition reaction with hydroxylamine) ← phenol (hydrogenation) (Richards, 2005).*

*phenol is made from benzene and propylene according to the following reactions: Phenol (+ acetone (byproduct)) ← chlorine in chlorobenzene (nucleophilic substitution) ← cumene hydroperoxide (acidic decomposition) (Carraher Jr, 2007; Weber and Weber, 2010) ← benzene and propylene (reaction) (Harrington, 2010).

**Applications**

Nylon 6 is used in non-woven fabrics and tyres, and in molding process (Sharma, 2005).

**Initial assessment**

Results for nylon 6 polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard score</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>II</td>
</tr>
<tr>
<td>Assessment</td>
<td>Low hazard (2).</td>
</tr>
</tbody>
</table>

The only monomer, ε-caprolactam, is not particularly hazardous (level II), i.e. causes skin, eye and respiratory irritation, and is harmful if inhaled or swallowed. However, it is made from benzene (carcinogenic 1A and mutagenic cat. 1B; V).

The residual monomer content can be high if it has not been removed (Richards, 2005).

One advantage is that no solvents are used in the spinning of fibres.

The global annual production is large.

**6. Polyamide 6.6 – Nylon 6.6**

**Global annual consumption**

585,000 tons Nylon 6.6 (figures for 2000) (Platt, 2003).

**Polymer synthesis and composition**

Nylon 6.6 is made by polymerising adipic acid and hexamethylene diamine (Richards, 2005). The adipic acid and hexamethylene diamine is reacted in boiling water or methanol causing the nylon salt to precipitate out (Chanda and Roy, 2008; Richards, 2005). The nylon salt is dissolved in water and is polymerised under nitrogen atmosphere, elevated pressure and temperature (Richards, 2005).

**Monomer concentrations**

Equimolar quantities of adipic acid and hexamethylene diamine are used (Richards, 2005). This gives: 56 wt% adipic acid and 44 wt% hexamethylene diamine.
**Monomer synthesis**

Monomer 1: Adipic acid $\leftrightarrow$ mixture of (cyclohexanone) and cyclohexanol (oxidation with nitric acid) $\leftrightarrow$ cyclohexane (oxidation) $\leftrightarrow$ benzene (hydrogenation) (Richards, 2005).

Monomer 2: Hexamethylene diamine

- Ex 1: $\leftrightarrow$ adiponitrile (hydrogenation) $\leftrightarrow$ adipic acid amide $\leftrightarrow$ adipic acid (reaction with ammonia),
- Ex 2: $\leftrightarrow$ adiponitrile (hydrogenation) $\leftrightarrow$ 1,4-dicyanobutene (hydrogenation) $\leftrightarrow$ 1,3-butadiene (reacts with hydrogen cyanide) (Richards, 2005).
- Ex 3: $\leftrightarrow$ adiponitrile (hydrogenated) $\leftrightarrow$ acrylonitrile (hydrodimerisation) (Carraher Jr, 2007).

**Applications**

Nylon 6.6 is used both as plastic and fibres (Gowariker et al, 2003). Large amounts are used for tyre chords (Gowariker et al, 2003). Other applications include monofilament and ropes, press felts for paper making, substitute for metals in gears and bearings and fibres for dresses and undergarments (Gowariker et al, 2003).

**Initial assessment**

Results for nylon 6.6 polymer, based on monomer classifications.

| Hazard score | 63 |
| Highest hazard level | III |
| Assessment | Low-medium hazard (3.5). |

The two monomers are not particularly hazardous. Adipic acid causes serious eye irritation (II) and hexamethylene diamine i.a. causes serious skin burns and eye damage (III). However, benzene and butadiene (both carcinogenic 1A and mutagenic cat. 1B; V) are used to make the monomers.

The residual monomer content is lower than for nylon 6 and concentrations between 1-2% have according to Richards (2005) been reported.

No solvents are needed during spinning of fibres.

The global annual production is of medium-large size

**7. Polyamide 6.10 – Nylon 6.10**

**Global annual consumption**

Is used to a small extent (Richards, 2005).

**Polymer synthesis and composition**

Nylon 6.10 is made by the polycondensation between sebacic acid and hexamethylene diamine in water or methanol, forming a nylon salt (Fourné, 1999; Gnanou and Fontanille, 2008).

**Monomer concentrations**

Equimolar quantities of sebacic acid and hexamethylene diamine are used (Fourné, 1999). This gives: 63 wt% sebacic acid and 37 wt% hexamethylene diamine.

**Monomer synthesis**

Monomer 1: Sebacic acid

- Ex 1: $\leftrightarrow$ 1,3 butadiene
- Ex 2 $\leftrightarrow$ castor oil (distillation) (Carraher Jr, 2007).
Monomer 2: Hexamethylene diamine
Ex 1: adiponitrile (hydrogenation) → adipic acid amide → adipic acid (reaction with ammonia) (Richards, 2005).
Ex 2: adiponitrile (hydrogenation) → 1,4-dicyanobutene (hydrogenation)→1,3-butadiene and hydrogen cyanide (reaction) (Richards, 2005).

Applications
Nylon 6.10 is not particularly used as a fibre, but is e.g. used to make brushes and bristles (Gowariker et al, 2003). Press felts for paper making is another application, and it is used together with nylon 6.6 in self-crimping biocomponent fibres, and for the production of monofilaments, e.g. fishing nets and fishing lines (Fourné, 1999; Richards, 2005).

Initial assessment
Results for nylon 6.10 polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard score</th>
<th>47*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>III</td>
</tr>
<tr>
<td>Assessment</td>
<td>Hazard low-medium, but may be underestimated because of (63 wt%) non-classified monomer (2.5+%).</td>
</tr>
</tbody>
</table>

Only one of the two monomers, hexamethylene diamine, is classified, i.a. causes serious skin burns and eye damage (III). Sebacic acid constitutes a major part (63 wt %) of this polymer and is neither classified, nor has any SIDS Initial Assessment Report, so this part can not be assessed. Consequently, the hazard score for the polymer may be underestimated.

The least hazardous raw material options for making sebacic acid is castor oil (instead of using butadiene), for hexamethylene diamine it is adipic acid (instead of using butadiene and hydrogen cyanide).

No solvents are needed during spinning of fibres.

The global annual production is small.

8. Polyamide 11 – Nylon 11

Global annual consumption
195.000 tons (figures for 2000) of PA11, PA12 and various copolymers (Platt, 2003).

Polymer synthesis and composition
Nylon 11 is made by condensation polymerisation of 11-aminoundecanoic acid at elevated temperature and with continuous removal of water (Chanda and Roy, 2008). The polymerisation takes place in aqueous suspension (Ghosh, 2004).

Monomer concentrations
Only one monomer is used (11-aminoundecanoic acid).

Monomer synthesis
11-aminoundecanoic acid ← the resultant acid reacts with hydrogen bromide ← methyl 10-undecylenate (hydrolysis) (and heptaldehyde by-product) ← methyl ricinoleate (pyrolysis) (and glycerol by-product)← castor oil and methanol (transesterification) (OECD SIDS IAR, 2002).

Application
Nylon 11 is used as a textile fibre (Gowariker et al, 2003).
**Initial assessment**

Results for nylon 11 polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard score</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>Not classified*</td>
</tr>
<tr>
<td>Assessment</td>
<td>Hazard unknown, because the only monomer is not classified, but with indication of low level of concern (2?).</td>
</tr>
</tbody>
</table>

The only monomer, 11-aminoundecanoic acid, is not classified, and can not be assessed with certainty. According to the SIDS international assessment profile (2002), however, there is a low hazard potential both in regard to human health and the environment.

One advantage is that the raw material for making 11-aminoundecanoic acid is castor oil which comes from the castor bean which makes the polymer biobased.

No solvents are needed during spinning of fibres.

The global annual production with nylon 12 is of medium size.

---

**9. Polyamide 12 – Nylon 12**

**Global annual consumption**

195,000 tons (figures for 2000) of PA11, PA12 and various copolymers (Platt, 2003).

**Polymer synthesis and composition**

Nylon 12 is formed by ring-opening polymerisation of lauryl lactam by heating the lactam in the presence of aqueous phosphoric acid (Chanda and Roy, 2008).

**Monomer concentrations**

Only one monomer (lauryl lactam) is used.

**Monomer synthesis**

Lauryl lactam ← butadiene (trimerisation) (Gnanou and Fontanille, 2008).

**Application**

In the automotive sector as under-hood air ducts, crank case vents, and cooling lines (Avery, 1998).

**Initial assessment**

Results for polymers nylon 12 polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard score</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>Not classified</td>
</tr>
<tr>
<td>Assessment</td>
<td>Hazard unknown, because its non-classified monomer which has an indication of aquatic toxicity (?)</td>
</tr>
</tbody>
</table>

The only monomer, lauryl lactam, is not classified and cannot be assessed. According to the SIDS assessment report (2003) there is a low hazard profile for human health (however, toxicity to reproduction has not been studied). The chemical possesses properties indicating a hazard for the environment related to acute aquatic toxicity (chronic toxicity has not been studied).

No solvents are needed during spinning of fibres.

The global annual production with nylon 11 is of medium size.
POLYAMIDES (aromatic), ARAMIDES

10. Poly(m-phenyleneisophtalamide) (MPD-I) (Nomex®)

Global annual production
180.000 tons of MPD-I per year (Dupont, personal communication).

Polymer synthesis and composition
Poly(m-phenyleneisophtalamide) is made by polycondensation between isophthaloyl chloride and m-phenylenediamine, in an amide solvent, e.g. diemthylacetamide, N-methylpyrrolidone or dimethylsulfoxide (Yang, 1993). Lithium chloride, lithium hydroxide or calcium chloride or calcium hydroxide is often added to increase the solubility of the polymer (Yang, 1993).

Monomer concentrations
Equimolar quantities of 1,3-phenylenediamine and isophthaloyl chloride is used (Gabara et al, 2007). This gives: 35 wt% m-phenylenediamine and 65 wt% isophthaloyl chloride.

Monomer synthesis
Monomer 1: isophthaloyl chloride ← isophthalic acid (reaction with phosgene) (Gabara et al, 2007).

Monomer 2: m-phenylenediamine ← m-isomer (hydrogenated) ← benzene (nitration in oleum) (Gabara et al, 2007).

Fibre production
Fibres are produced by dry spinning (using dimethyl formamide and dimethylacetamide solutions), or wet spinning (consisting of solvent and non-solvent) (Gabara et al, 2007).

Applications
Due to its thermal properties and inherent flame resistance m-aramide fibres are used as protective apparel in e.g. industrial, military, fire fighting and auto racing applications, as barrier fabrics in transportation, e.g. upholstery, floor coverings, bulkheads, wall coverings and blankets, and as filter bags (Gabara et al, 2007.). M-aramide paper or pressboards are used as electrical insulation in transformers, motor, generators, and other electrical equipment, but also as core structures (honey comb structures) to minimize weight but maximise stiffness (Gabara et al, 2007).

Initial assessment
Results for MPD-I polymer, based on monomer classifications.

| Hazard score | 1187* |
| Highest hazard level | IV |
| Assessment | High hazard, but may be underestimated with regard to (65 wt%) non-classified monomer (4+?). |

On of the two monomers m-phenylenediamine is i.a. mutagenic (cat. 2; IV), very toxic to aquatic life with long lasting effects (IV) as well as very acute toxic to aquatic life (III), skin sensitising (cat. 1; IV), and toxic if inhaled (III), if swallowed (III) and in contact with skin (III). In addition m-phenylene diamine is made from benzene (carcinogenic and mutagenic cat. 1B; V).

The other monomer, isophthaloyl chloride, which makes up a substantial part (65 wt%), is neither classified nor has a SIDS assessment report, so this part can not be assessed. Consequently the hazard score for the polymer may be underestimated.
Solvents that may damage the unborn child (Repr. cat. 1B; V) are used both during polymerisation and in fibre spinning. These include N-methyl-2-pyrrolidone (during polymerisation), N,N-dimethylacetamide (during polymerisation and fibre spinning), and N,N-dimethylformamide (during fibre spinning). Substitution for less hazardous solvents should be considered.

One advantage is that the polymer has inherent flame resistance properties, so no flame retardants are required.

The global annual production is quite small.

11. Poly(p-phenyleneterephtalamide) (PPD-T) (Kevlar® and Twaron®)

Global annual production
100.000 tons of PPD-T per year (Dupont, personal communication).

Polymer synthesis and composition
Poly(p-phenyleneterephtalamide) is prepared by solution polycondensation of terephthaloyl chloride with p-phenylenediamine in a solvent composed of a mixture of hexamethylphosphoramide and N-methyl-2-pyrrolidone (2:1) at -10°C (Chanda and Roy, 2008).

Monomer concentrations
A weight proportion of 7.3 g p-phenylene diamine and 13.9 g terephthaloyl chloride is used (Gaymans, 2003). This gives 34 wt% p-phenylene diamine and 66 wt% terephthaloyl chloride.

Monomer synthesis
Monomer 1: terephthaloyl chloride ← terephthalic acid (reaction with phosgene and dimethylformamide) (Gabara et al, 2007).

Monomer 2: p-phenylenediamine ← aminoazobenzenes (hydrogenated) ← diphenyltriazine (rearrangement) ← nitrogen trioxide (reacted with aniline) ← ammonia (oxidation) (Gabara et al, 2007)

Fibre production
The polymer is spun (wet) into fibres from a solution in concentrated sulphuric acid (Chanda and Roy, 2008).

Applications
p-aramid fibers are known for their ballistic protection (Gabara et al, 2007). They are used in armor systems, e.g. vests and helmets, in protective apparel, e.g. gloves and chain-saw shaps, as reinforcing agents for belts and tyres, in composites, e.g. aerospace components, automotive parts, boats and sporting goods (e.g. hockey shafts) (Gabara et al, 2007).

Initial assessment
Results for PPD-T polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard score</th>
<th>829*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>IV</td>
</tr>
<tr>
<td>Assessment</td>
<td>High hazard, but may be underestimated with regard to (66 wt%) non-classified monomer (4+?).</td>
</tr>
</tbody>
</table>

The monomer p-phenylenediamine is i.a. classified as very toxic to aquatic life with long lasting effects (IV) as well as very acute toxic to aquatic life (III), skin sensitising (cat. 1; IV), and toxic if inhaled (III), if swallowed (III) or in contact with skin (III). The other monomer, terephthaloyl chloride, which makes up a
substantial part (66 wt%) is neither classified, nor has a SIDS Initial Assessment Report, so this part can not be assessed. Consequently, the hazard score for the polymer may be underestimated.

In the synthesis of terephthaloyl chloride the reproduction toxic (cat. 1B; V) dimethyl formamide is used as one component.

The solvents used during polymerisation are very hazardous. A mixture of the the reproductive toxic and mutagenic (cat 1B; V) hexamethylphosphoramide and the reproductive toxic (cat 1B; V) N-methyl-2-pyrrolidone are used.

The global annual production is of medium size.

**POLYESTERS**

There are both thermoplastic and thermostetting polyesters. The thermoplastic polyesters include aliphatic (linear) polyesters, e.g. polylactic acid, and aromatic polyesters, e.g. polybutylene terephthalate, polycarbonate and polyethylene terephthalate. The thermostetting polyesters are unsaturated polyesters.

**12. Polylactic acid (PLA)**

**Global annual production**

60,000 tons (figure for 2006) (Avérous, 2008). PLA has the largest share in the bioplastics market (Groot et al, 2010). The world’s largest PLA producer has an annual production capacity of 140,000 tons PLA.

**Polymer synthesis and composition**

Poly(lactic acid) mainly produced by ring-opening polymerisation (A) of D-, L- and/or L-lactide in solution or in bulk catalysed by Sn(II)-based catalysts, e.g. stannous octoate (Fradet and Tessier, 2003; Groot et al, 2010; Sivasankar, 2008). Alternative catalysts have been developed e.g. zinc lactate and a potassium based catalyst (Södergård and Stolt, 2010). The lactid is made by a condensation process of lactide acid and is purified through vacuum distillation (Platt, 2006) or melt crystallisation (Groot et al, 2010). Lactide is the dehydrated cyclic dimer of lactic acid (Groot et al, 2010).

Poly(lactic acid) may also be made by e.g. condensation polymerisation (B) of lactic acid, but this route is less common (Groot et al, 2010). This polymerisation is catalysed by e.g. Sn(II) chloride dihydrate (0.4 wt%) and p-toluenesulfonic acid monohydrate (p-TSA) (0.4wt%) (Fradet and Tessier, 2003). The polymers are dissolved in chloroform and precipitated into diethyl ether (Fradet and Tessier, 2003). The catalyst residues are needs to be removed (Avérous, 2008).

Polylactic acid is sometimes called polylactide when it is made from lactide by ring opening polymerisation, but the abbreviation PLA is used for both (Rudnik, 2008).

**Monomer concentrations**

Only one monomer lactic acid is used to make the dimer D-, L- and/or L-lactide.

**Monomer synthesis**

Polylactide is made from lactic acid, which is produced either by fermenting sugar from sugar beet or sugar cane, or by converting starch from e.g. corn or potato peel (Mwaikambo, 2004). Ex 1: Lactide ⇄ Lactic acid (condensation) ⇄ D-glucose (sugar from sugar beet or sugar cane) (bacterial fermentation)
Ex 2: Lactide ↔ Lactic acid (condensation) ↔ D-glucose (bacterial fermentation) ↔ starch from corn or potato peel (hydrolysis) (Mwaikambo, 2004; Platt, 2006).

Applications
PLA is available in a rigid or a flexible form and can be copolymerised with other materials (Platt, 2006). It is mainly used in packaging (70%) e.g. rigid packaging, flexible film packaging, and as fibres (23%) e.g. apparel and staple (figures for 2005), but also in medical applications, e.g. dissolvable sutures (East, 2005; Groot et al, 2010; Platt, 2006; Södergård and Stolt, 2010). Other applications include e.g. cutlery, bottles, speciality cards, sheets and agricultural products (Groot et al, 2010; Platt, 2006).

Initial assessment
Results for PLA polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard score</th>
<th>Highest hazard level</th>
<th>Assessment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Not classified</td>
<td>Hazard unknown, but very likely low hazard (I?).</td>
</tr>
</tbody>
</table>

The monomer lactic acid is not classified. However, according to the OECD SIDS Initial Assessment Profile (2009) for lactic acid it does not present a hazard for neither human health, nor the environment, based on its low hazard profile. Consequently, the hazard of this polymer is very likely low. For the cyclic dimer of lactic acid, lactide, there is no SIDS Initial Assessment Report is available.

PLA is bio-based. In addition it is biodegradable under industrial composting conditions with temperatures around 60°C and above (Rudnik, 2008). The high temperature is needed for the hydrolysis step, when water soluble compounds and lactic acid are formed. These can then be metabolised by micro-organisms into carbon dioxide, water and biomass. However, in the natural environment PLA-degrading organisms are limited (Rudnik, 2008).

The global annual production is of small-medium size, but growing fast.

13. Polybutylene terephthalate (PBT)

Global annual production:
477.000 tons PBT (figures from 2002) (Platt, 2003).

Polymer synthesis and composition
Poly(butylene terephthalate) is produced by reacting dimethyl terephthalate with butane 1,4-diol in an ester interchange process in two steps (Ravve, 2000). In the first step an excess of the diol is reacted with dimethyl terephthalate (1.3:1) and zinc acetate is used as catalyst (Ravve, 2000). In the second step (conducted at >60°C) zinc oxide is used as catalyst (Ravve, 2000).

Monomer concentrations
A molar amount of 1.3 moles 1,4-butanediol and 1 mole dimethyl terephthalate is used (Ravve, 2000). This gives: 38 wt% 1,4-butanediol and 62 wt% dimethyl terephthalate.

Monomer synthesis
Monomer 2: butane 1,4-diol ↔ acetylene and formaldehyde (reaction) (Mehta, 2005).

Fibre production
PBT fibres are spun by melt spinning (East, 2005).
Applications
The automotive sector accounts for 25% of the total consumption, e.g. bumpers, water pumps, breaking systems, components in doors, car windows, and rear view mirrors (Edshammar, 2002). The electrical and electronics sector also accounts for 25%, e.g. switches, relays, keys for key boards, circuit boards (Edshammar, 2002). Other applications are found in household and consumer articles, e.g. handles for irons and frying pans, structural components in vacuum cleaners, coffee machines, propellers for outboard motors (Edshammar, 2002). PBT can also be spun into fibres that mainly are used in carpets (East, 2005).

Initial assessment
Results for PBT polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard score</th>
<th>Highest hazard level</th>
<th>Assessment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Not classified</td>
<td>Hazard unknown (?), because of non-classified monomers with indication of neurotoxicity for one of the monomers (40 wt%) and low level of concern for the other (60 wt%).</td>
</tr>
</tbody>
</table>

Neither of the two monomers are classified. The SIDS initial assessment profile (2001) on dimethyl terephthalate, however, indicates that there is low level of concern for human health and the environment. The SIDS Initial Assessment Report (2000) for 1,4-butanediol indicate low level of concern for the environment, but recommend further exposure information because of observed neurotoxicity. Consequently, the hazard of this polymer cannot be assessed, but is not likely to be very high.

The catalyst zinc oxide is very toxic to aquatic life with long lasting effects (IV) as well as very acute toxic to aquatic life (III).

No solvents are needed during fibre spinning.

The global annual production is of medium size.

14. Polycarbonates (PC)

Global annual production
2.15 million tons of PC (2007) (calculated from PlasticsEurope MRG, 2008).

Polymer synthesis and composition
Polycarbonate is mostly synthesised by (A) interfacial polymerisation where bisphenol A is dissolved in a sodium hydroxide aqueous solution (Carraher Jr, 2008). Phosgene is added, usually via a chlorinated solvent, e.g. dichloromethane, and a tertiary amine, e.g. pyridine, acting as a catalyst (Carraher Jr, 2008; Peters and Arisman, 2000; Cheremisinoff, 2001).

Another method for PC synthesis (B) is by transesterification of bisphenol A with diphenyl carbonate at elevated temperature (Harper, 2000; Carraher Jr, 2008; Gnanou and Fontanille, 2008). Basic catalysts as lithium hydride, zinc oxide, or antimony oxide are used in a transesterification reaction (Ravve, 2000). Phenol is produced as a by-product (Woo et al, 2001).

Monomer concentrations
(A) Equimolar quantities of bisphenol A and phosgene are used (according to reaction charts where bisphenol A and phosgene are in sequence). This gives: 70 wt% bisphenol A and 30 wt% phosgene.

(B) The optimal ratio of diphenyl carbonate and bisphenol A is 1.05:1, since some diphenyl carbonate is lost in the reaction (Woo et al, 2001). This gives: 50 wt% bisphenol A and 50 wt% diphenyl carbonate.
Monomer synthesis

(A) Monomer 2: phosgene ← chlorine and carbon monoxide (reaction) (Carraher Jr, 2007).

(B) Monomer 2: diphenyl carbonate ← dimethyl carbonate (phenol is added, reaction) ← methanol (oxidative carbonylation) (Wittecoff et al, 2004).

Applications
PC is used in e.g. safety sheets and goggles, lenses, safety helmets, bullet proof glazing, business machine housings, instrument casings, kitchenware and microwave cookware (e.g. baby bottles), light fittings, electrical switchgear (Platt, 2003), and compact discs.

Initial assessment
Results for PC polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard scores</th>
<th>610* and 1177</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>IV</td>
</tr>
<tr>
<td>Assessment</td>
<td>High hazard for polymer with phosgene (4); Medium-high hazard for polymer with diphenyl carbonate, but maybe with some underestimation regarding the non-classified diphenyl carbonate (50 wt%) (possible environmental hazard) (3.5+?); May be underestimated for both polymers regarding bisphenol A and possible endocrine disruption properties (4+? and 3.5?).</td>
</tr>
</tbody>
</table>

One of the monomers, bisphenol A, is i.a. skin sensitising (cat. 1; IV), suspected of damaging fertility (cat. 2; III) and causes serious eye damage (III). In addition, bisphenol A has on the priority lists within the EU strategy for endocrine disruptors preliminary been assigned category 1 with evidence of human effects, and also assigned high concern due to risk of exposure. If the evaluation of bisphenol A concludes endocrine disruption, polycarbonate would be ranked as more hazardous. Phenol, which is used to produce bisphenol A, is suspected of causing genetic defects (cat. 2; IV), and is made from the carcinogenic and mutagenic (cat. 1A and 1B; V) raw material benzene.

The other monomer phosgene is i.a. fatal if inhaled (IV). The alternative to phosgene, i.e. diphenyl carbonate, is not classified. According to the SIDS Initial Assessment Report (2004) diphenyl carbonate has a low hazard profile for human health, but possesses properties that indicate a hazard for the environment. Consequently, the hazard score for polycarbonate with diphenyl carbonate may be underestimated.

The catalysts used in the polymerisation with diphenyl carbonate are hazardous. Zink oxide is very toxic to aquatic life with long lasting effects (IV) as well as very acute toxic to aquatic life (III), and antimony trioxide is suspected of causing cancer (cat. 2; III).

Phenol which is i.a. mutagenic (cat. 2; IV), and toxic if inhaled (III), if swallowed (III) and in contact with skin (III) is formed as a by-product in the production of polycarbonate with diphenyl carbonate.

Since one application for polycarbonate includes baby bottles, there has been a lot of debate and even bans in some countries, e.g. Canada (2008), and the EU member countries (from 1st March 2011) because the exposure to bisphenol A concerns a very sensitive group in their early stages of development.

The global annual production is large.
15. Polyethylene terephthalate (PET)

Global annual production:
15 million tons PET plastics (2007) excluding PET-fibres (calculated from PlasticsEurope MRG, 2008), and 18 million tons of PET fibres (2000) (East, 2005). This gives a total of 33 million tons PET plastic and fibre.

Polymer synthesis and composition
Poly(ethylene terephthalate) is most commonly (70%) formed by step-growth polycondensation reaction (A) of ethylene glycol and terephthalic acid (Scheirs and Long, 2003). In the first esterification step a prepolymer, which contains bis-hydroxyethyl terephthalate and oligomers, is formed and water is removed (Scheirs and Long, 2003). In the second polycondensation step the excess ethylene glycol is removed and polymerisation occurs with the aid of antimony trioxide (catalyst) (East, 2005; Scheirs and Long, 2003).

The prepolymer can also be formed by transesterification (B) of dimethyl terephthalate with ethylene glycol, forming methanol as a by-product (Scheirs and Long, 2003). Oxides of e.g. zinc or manganese are commonly added to catalyse the first reaction, and antimony (III) oxide is most commonly used to catalyse the second step reaction (Ravve, 2000; Stevens, 1999).

Monomer concentrations
(A) A molar amount of 1.6 moles ethylene glycol and 1 mole terephthalic acid is used (Andrady, 2003). This gives: 37 wt% ethylene glycol and 63 wt% terephthalic acid.

(B) A molar amount of 2 moles ethylene glycol (in excess) and 1 mole dimethylterephthalate is used (but the excess glycol is removed) (Ravve, 2000). This gives: 39 wt% ethylene glycol and 61 wt% dimethylterephthalate.

Monomer synthesis
Monomer 1: Ethylene glycol $\leftarrow$ ethylene oxide (hydrolysis) $\leftarrow$ ethylene (oxidation) (Carraher Jr, 2007).

(A) Monomer 2: Terephthalic acid
Ex 1: $\leftarrow$ p-xylene (oxidation) (most common),
Ex 2: $\leftarrow$ naphthalene (oxidation),
Ex 3: $\leftarrow$ terephthalonitrile (hydrolysis) (Carraher Jr, 2007; Fourné, 1999).

(B) Monomer 2: Dimethyl terephthalate $\leftarrow$ terephthalic methyl ester (esterification with methanol and zinc chloride) $\leftarrow$ p-toulualic acid methyl ester (oxidation) $\leftarrow$ p-xylene (oxidation) (Fourné, 1999).

Fibre production
PET fibres are spun by melt spinning (East, 2005).

Applications
PET is mainly used for making bottles and PET textile fibres (Gnanou and Fontanille, 2008).

PET fibres constitute the largest of the synthetic fibres (East, 2005) accounting for approximately 60 percent by weight of the total world market of synthetic fibres (calculated from East, 2005). They are used both as continuous filament yarn and staple fibre (East, 2005). Applications include textile apparel fibres, household and furnishing fabrics (e.g. carpets), industrial fibres and yarns for tyre chords, car seat belts, sail cloth, outdoor wear and sports wear (as microfibres) (East, 2005).
**Initial assessment**

Results for PET polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard scores</th>
<th>4*, 4*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>II</td>
</tr>
<tr>
<td>Assessment</td>
<td>Low hazard (2?), with uncertainties because of (~60 wt%) non-classified monomers, but which have indications of low hazards.</td>
</tr>
</tbody>
</table>

Ethylene glycol is the only monomer that is classified. It is not particularly hazardous, only classified as harmful if swallowed (II). However, the carcinogenic and mutagenic (cat. 1B; V) ethylene oxide is the precursor to ethylene glycol.

Neither the monomer terephthalic acid, nor its alternative dimethyl terephthalate are classified. However, the OECD SIDS Initial Assessment Reports (2001) for terephthalic acid and dimethyl terephthalate indicate that there is low level of concern for human health and the environment. Consequently, it is likely that the polymers will not pose a very high hazard. However, considering the very large global production these monomers ought to be assessed.

The common catalyst in the first polymerisation step, zinc oxide, is very toxic to aquatic life with long lasting effects (IV) as well as very acute toxic to aquatic life (III). The common catalyst in the second step, antimony trioxide, is suspected of causing cancer (cat. 2; III). Antimony has also been shown to migrate from PET bottles into bottled water (e.g. Reimann et al, 2010). Another migration product is acetaldehyde, which is formed at high temperature e.g. during processing (Scheirs, 2000). Acetaldehyde is the most common cause of off-flavour in mineral water stored in PET bottles (Scheirs, 2000) and is suspected of causing cancer (cat. 2; III). Due to the extensive use of PET for bottled water, the risks of migrants ought to be assessed.

One advantage is that no solvents are used during fibre spinning (Gnanou and Fontanille, 2008).

The global annual production is very large both for PET fibres and for PET plastics.

**POLYETHYLENES**

Polymers made from ethylene (LDPE, HDPE) or ethylene with copolymers e.g. LLDPE and EVA.

**Global annual production**

> 70 million tons

**16. Low-density polyethylene (LDPE)**

**Global annual production**

38.7 million tons of LDPE and LLDPE (2007) (calculated from PlasticsEurope MRG, 2008). According to data from Gnanou (2008) the LDPE share constitute 56%, which gives 21.8 million tons LDPE.

**Polymer synthesis and composition**

Low-density polyethylene is produced by free radical polymerisation of ethylene gas under high pressure (150-300 Mpa) and high temperature (150-300°C) in bulk (Gnanou and Fontanille, 2008; Andrady, 2003). The polymerisation is initiated by a peroxide (Alger 1997; Albertsson, 2007) such as benzoyl peroxide, di-tert-butyl peroxide, and dodecanoyl peroxide, or an azo compound, e.g. 2,2’-azobisisobutyronitrile (Albertsson, 2007; Aragrag et al, 2004; Gnanou and Fontanille, 2008; Ravve, 2000), or molecular oxygen (0,05-0,1%). In some practices diluents e.g. water, benzene, ethanol or methanol are used (Ravve, 2000). Chain transfer agents may be added, e.g. iso-butene and propylene (Gregory, 2009).
**Monomer concentrations**
Only one monomer (ethylene) is used.

**Monomer synthesis**
Ethylene gas
Ex 1: petroleum (thermal cracking),
Ex 2: ethanol (dehydration),
Ex 3: propylene (metathesis) (Gnanou and Fontanille, 2008).

Ethylene may also be obtained from renewable resources, e.g. sugar cane, but (green) polyethylene from renewable ethylene is not yet produced in a large scale.

**Applications**
Applications as films (59%), extrusion coating (17%), injection moulding (6%), adhesives and sealants (4%), paper, wire and cable (4%) sheets (2%) are the most important ones, but also pipes and conduit are common (Vasile and Pascu, 2005).

**Initial assessment**
Results for LDPE polymer, based on monomer classifications.

| Hazard score | 1 1 |
| Highest hazard level | II |
| Assessment | Low hazard (2). |

The only monomer, ethylene, is not particularly toxic. It may cause drowsiness and dizziness (II) and is an extremely flammable gas (I).

Dibenzoyl peroxide (skin sensitising, cat. 1; IV) can be used as initiator, but there are less hazardous alternative peroxides.

The use of benzene as diluent in some practices, should be avoided due to benzenes carcinogenic and mutagenic (cat. 1B; V) properties.

Polyethylenes are sensitive to both oxidative and photodegradation and needs antioxidants (e.g. phenols, amines and phosphates) and light stabilisers (e.g. Hindered Amine Light Stabilisers, HALS) for protection (Gugumus, 2001; Schwarzenbach et al, 2001). The HALS evaporate easily and have poor extraction resistance, causing emissions and migration of harmful amines (Xue and Toyota, 2008).

Global annual production is very large.

17. Linear-low-density polyethylene (LLDPE)

**Global annual production**
38.7 million tons of LDPE and LLDPE (2007) (calculated from PlasticsEurope MRG, 2008). According to data from Gnanou (2008) the LLDPE share constitute 44%, which gives 16.9 million tons LLDPE.

**Polymer synthesis and composition**
Linear-low-density polyethylene is made by copolymerisation of ethylene with (8-10%) of either 1-butene, 1-hexene, or 1-octene at very low pressure (< 300 psi) and temperatures below 100 °C (Harper, 2000; Carraher Jr, 2008). Ziegler catalysts are used (Gnanou and Fontanille, 2008) e.g. prepared from titaniumtetrachloride and trietylaluminium (Nicholson, 2006). The polymerisation mainly takes place in gasphase (A), but also in solution (B), or emulsion (C) (Edshammar, 2002; Lohse, 2000). In gas phase polymerisation (A) the gas mixture consists of ethylene, comonomer and hydrogen (Edshammar, 2002). Polymerisation in solvents (B) is
either made by using hydrocarbon solvents (e.g. cyclohexane), or by dissolving ethylene in melted ethylene
(Edshammar, 2002). In the emulsion process (C) ethylene is suspended in isobutan and isopentane
(Edshammar, 2002).

**Monomer concentrations**

90 wt% ethylene and 8-10 wt% comonomer (i.e. 1-butene, 1-hexene, or 1-octene) is used (Harper, 2000;
Carraher Jr, 2008).

**Monomer synthesis**

Monomer 1: Ethylene gas
Ex 1: petroleum (thermal cracking),
Ex 2: ethanol (dehydration),
Ex 3: propylene (metathesis) (Gnanou and Fontanille, 2008).

Ethylene may also be obtained from renewable resources, e.g. sugar cane, but (green) polyethylene from
renewable ethylene is not yet produced in a large scale.

Monomer 2, alt.1: 1-butene ← petroleum (cracking).


Monomer 2, alt. 3: 1-octene ← ethylene (oligomerisation) (OECD SIDS IAR, 2000).

**Applications**

Packaging, mainly film for bags and sheets, lids, buckets and containers, pipes, cable coverings, and toys
(Vasile and Pascu, 2005).

**Initial assessment**

Results for LLDPE polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard scores</th>
<th>10, 10*,10*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>II</td>
</tr>
<tr>
<td>Assessment</td>
<td>Low hazard (2) for polymers with 1-butene; maybe with underestimation regarding 1-hexene and 1-butene (10 wt% non-classified monomers)(2+?).</td>
</tr>
</tbody>
</table>

The main monomer, ethylene, is not particularly toxic. It may cause drowsiness and dizziness (II) and is an
extremely flammable gas (I). One of the comonomer options, 1-butene, is classified as extremely flammable
(I). Two of the comonomer options are not classified (1-hexene and 1-octene). The SIDS Initial Assessment
Report indicates a low hazard potential for human health for both substances, but concerning the environment
further work is recommended since computer models suggest that 1-octene may be highly toxic under chronic
exposure. Consequently, the hazard scores for LLDPE with 1-hexene or 1-butene may be underestimated.

The solvent cyclohexane, which can be used in the solvent polymerisation process, is very toxic to aquatic life
with long lasting effects (IV) as well as very acute toxic to aquatic life (III), and should be avoided.

Polyethyleneres are sensitive to both oxidative and photodegradation and needs antioxidants (e.g. phenols,
amines and phosphates) and light stabilisers (e.g. Hindered Amine Light Stabilisers, HALS) for protection
(Gugumus, 2001; Schwarzenbach et al, 2001). The HALS evaporate easily and have poor extraction
resistance, causing emissions and migration of harmful amines (Xue and Toyota, 2008).

Global annual production is very large.
18. High-density polyethylene (HDPE)

Global annual production
32.3 million tons HDPE (2007) (calculated from PlasticsEurope MRG, 2008).

Polymer synthesis and composition
High-density polyethylene is made by coordination polymerisation of ethylene under low pressure (Gnanou and Fontanille, 2008). Three different polymerisation techniques can be used. Either a liquid phase slurry process (A) with suspension in a diluent (e.g. diesel oil, heptane, toluene, mineral oil, chlorobenzene, n-pentane or n-hexane); a liquid phase solution process (B) with solution an aliphatic hydrocarbon (e.g. cyclohexane or isooctane); or a gas-phase process (C) without diluent (Gnanou and Fontanille, 2008; Ravve, 2000; Vasile and Pascu, 2005). Catalysts are used to initiate the polymerisation, most commonly Phillips catalyst system (e.g. chromium IV oxide supported on silica), but also Ziegler-Natta catalyst system are used, specifically titanium tri- and tetrahalides and trialkylaluminium compounds, (e.g. titanium tetrachloride, on a solid support, particularly magnesium chloride) (Carraher, 2008; Aragrag et al, 2004; Andrady, 2003).

Monomer concentrations
Only one monomer (ethylene) is used.

Monomer synthesis
Ethylene gas
Ex 1: ← petroleum (thermal cracking)
Ex 2: ← ethanol (dehydration)
Ex 3: ← propylene (metathesis) (Gnanou and Fontanille, 2008).

Ethylene may also be obtained from renewable resources, e.g. sugar cane, but (green) polyethylene from renewable ethylene is not yet produced in a large scale.

Applications
HDPE have very diverse areas of application. Main applications include e.g. pipe and pipe fittings for water and petroleum tanks, cable insulation, corrosion-resistant wall coverings, radiation shielding, bowls, buckets, bottles for food, containers, food wrapping materials, carrier bags, household and kitchenware, toys, prosthetic devices (implants), and yarns (Vasile 2005).

Initial assessment
Results for HDPE polymer, based on monomer classifications.

| Hazard score | 11 |
| Highest hazard level | II |
| Assessment | Low hazard (2). |

The only monomer, ethylene, is not particularly toxic. It may cause drowsiness and dizziness (II) and is an extremely flammable gas (I).

The diluent heptane, and the solvents cyclohexane and isooctane are very toxic to aquatic life with long lasting effects (IV) as well as very acute toxic to aquatic life (III), and should be substituted with the less hazardous options. The gas-phase process is run without solvents.

Polyethylenes are sensitive to both oxidative and photodegradation and needs antioxidants (e.g. phenols, amines and phosphates) and light stabilisators (e.g. Hindered Amine Light Stabilisers, HALS) for protection (Gugumus, 2001; Schwarzenbach et al, 2001). The HALS evaporate easily and have poor extraction resistance, causing emissions and migration of harmful amines (Xue and Toyota, 2008).

Global annual production is very large.
19. Ethylene vinyl acetate (EVA) and ethylene vinyl alcohol (EVOH)

**Ethylene vinyl acetate (EVA)**

**Global annual consumption**

**Polymerisation**
Ethylene is copolymerised with vinyl acetate by a free radical emulsion polymerisation (Ravve, 2000), with a redox catalyst consisting of an oxidizing agent e.g. sodium persulfate, hydrogen peroxide, tert-butyl hydroperoxide and a reducing agent e.g. a transition metal or formaldehyde sodium bisulfite (Fink, 2010).

**Monomer concentrations**
Vinyl acetate in amounts varying between 5 and 50 wt% may be used (Lokensgard, 2004). The larger the vinyl acetate share the more elastic the polymer gets (Edshammar, 2002). Generally 20 wt% vinyl acetate is used (Gnanou and Fontanille, 2008). This gives 80 wt% ethylene and 20 wt% vinyl acetate.

**Monomer synthesis**
Monomer 1: Ethylene gas
Ex 1: ← petroleum (thermal cracking),
Ex 2: ← ethanol (dehydration),
Ex 3 ← propylene (metathesis) (Gnanou and Fontanille, 2008).

Monomer 2:
Vinyl acetate ← acetic acid and ethylene (oxidative condensation) (Carraher Jr, 2007).

**Applications**
EVA are used in medical applications such as disposable syringes, squeeze pumps, droppers; as films e.g. shower curtains, disposable gloves, inflatable toys, pool liners; and as injection moulded products such as shoe soles, bumpers, disposable brushes and automobile mud flaps (Harper and Petrie, 2003).

**Ethylene vinyl alcohol (EVOH)**
EVOH is produced by a saponification reaction of EVA usually in the presence of an alkali catalyst such as sodium hydroxide or potassium hydroxide (B) (Fink, 2010). Global annual demand 65.000 tons (figures for 2003) (Pardos, 2004). EVOH is mainly used in food packeting (films and sheets), but also as a barrier layer in e.g. fuel tanks, refrigerator liners, and is used in underfloor heating (Pardos, 2004).

**Initial assessment**
Results for EVA polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard score</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>II</td>
</tr>
<tr>
<td>Assessment</td>
<td>Low hazard (2)</td>
</tr>
</tbody>
</table>

Neither of the two monomers are particularly hazardous. Ethylene may cause drowsiness and dizziness (II) and is an extremely flammable gas (I), and vinyl acetate is only highly flammable (I).

The global annual production is large.
**STYRENIC RESINS**

**Global annual production**
Of the styrene production 50% is used for polystyrene, 20% for elastomers, thermosetting resins and polymer dispersions, 15% in ABS and SAN copolymers, and 10% in EPS (Wunsch, 2000).

**20. Polystyrene (PS)**

**Global annual production**
17.2 million tons PS and EPS (2007) (calculated from PlasticsEurope MRG, 2008). According to the European Manufacturers of Expanded Polystyrene (2010) more than 4 million tons EPS were produced 2007. This gives approximately 13 million tons PS.

**Polymer synthesis and composition**
General purpose polystyrene is mainly produced via free-radical addition polymerisation of styrene (Harper, 2000) most commonly in solution (A), with ethylbenzene (20-30%) as the typical solvent (Andrady, 2003). Polymerisation is initiated by peroxides (e.g. benzoyl peroxide) or azo compounds (e.g. azoisobutyronitrile), or simply by heating, and is inhibited by e.g. p-benzoquinone (Nuyken, 2005; Wunsch, 2000; Sivasankar, 2008).

Suspension polymerisation may also be used (B) (Gnanou and Fontanille, 2008). In suspension polymerisation the monomers are suspended in water, with stabilising agents, e.g. polyvinyl alcohol, polyvinyl pyrrolidone, or kaolin, (Nuyken 2005; Wunsch, 2000), and initiators e.g. organic peroxides or azo compounds (e.g. potassium persulphate, benzoyl peroxide, 2,2’-Azobisisobutynitril) (Alger, 1997; Feldman and Barbalata, 1996; Wunsch, 2000), or a combination both (Gnanou and Fontanille, 2008). Bulk polymerisation (C) may also be used (Andrady, 2003).

**Monomer concentrations**
Only one monomer (styrene) is used.

**Monomer synthesis**
Styrene
Ex 1: \(\text{ethylbenzene (dehydrogenation)} \leftrightarrow \text{ethyl and benzene (condensation)}\),
Ex 2: \(\text{methyl phenyl carbinol (dehydration)} \leftrightarrow \text{metyl phenyl carbinol and propylene oxide (by-product)} \leftrightarrow \text{a hydroperoxide (reacted with propylene)} \leftrightarrow \text{ethylbenzene (proylation)} \leftrightarrow \text{ethyl and benzene (condensation)}\) (Carraher Jr, 2007; European Commission JRC, 2002).

**Applications**
Packaging is the largest market, e.g. bottle caps, small jars, containers, boxed goods, film for e.g. foodstuffs (Chanda and Roy, 2009).

**Initial assessment**
Results for PS polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard score</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>II</td>
</tr>
<tr>
<td>Assessment</td>
<td>Small- medium hazard (2.5), may be with some underestimation regarding suspected endocrine disrupting properties (2.5+?).</td>
</tr>
</tbody>
</table>

The monomer styrene is only classified as harmful if inhaled (II), causes serious eye irritation (II), causes skin irritation (II), and flammable liquid and vapour (I). However, within the EU strategy on endocrine disruptors styrene is on the priority list and has preliminary been assigned category 1 with evidence of human effects and
also assigned high concern due to risk of exposure. If the evaluation of styrene shows endocrine disrupting properties all styrene containing polymers would be ranked as more hazardous. During the production of styrene benzene is used as raw material, and propylene oxide is formed as a by-product in one of the two routes. Both are classified as carcinogenic and mutagenic (cat. 1B; V).

The initiators benzyl peroxide is i.a. skin sensitising (cat. 1; IV), and potassium persulphate is i.a. both skin and respiratory sensitising (cat. 1; IV).

The polystyrene backbone contains weak links and the free styrene dimers which are formed during free radical polymerisation are thermally unstable (Priddy, 2003). When the polymer is heated e.g. during fabrication there is generally an increase in the residual monomer content (Priddy, 2003), which may be available for leaching.

The global annual production is very large.

21. Expanded polystyrene (EPS)

Global annual consumption
More than 4 million tons in 2007 according to the European Manufacturers of Expanded Polystyrene (2010).

Polymer synthesis and composition
Expanded polystyrene (mainly for loose-fill material for packaging) is most commonly made by (A) swelling polystyrene beads (see above) with pentane (5-10 wt%) as a blowing agent, and with a nucleating agent, e.g. a sodium bicarbonate/citric acid system, followed by heating (Gnanou and Fontanille, 2008; Andrady, 2003; Klodt and Gougeon, 2003; Braun et al, 2005). Pentane can be replaced by carbon dioxide (Gnanou and Fontanille, 2008).

Expanded polystyrene (mainly for thermal insulation and the packaging sector) can also be made by (B) polymerising styrene in suspension of water containing a blowing agent (Klodt and Gougeon, 2003). In a first stage when polystyrene particles are formed dibenzoyl peroxide (BPO) is used as an initiator, and in the second stage tert-butyl peroxybenzoate is used (Klodt and Gougeon, 2003).

Monomer concentrations
90-95 wt% styrene (average 92.5) and 5-10 wt% pentane (average 7.5) is used (Braun et al, 2005).

Monomer synthesis
Styrene
Ex 1: ← ethylbenzene (dehydrogenation) ← ethyl and benzene (condensation),
Ex 2: ← methyl phenyl carbinol (dehydration) ← methyl phenyl carbinol and propylene oxide (by-product) ← a hydroperoxide (reacted with propylene) ← ethylbenzene (prolylation) ← ethyl and benzene (condensation (Carraher Jr, 2007; European Commission JRC, 2002).


Applications
EPS is mainly used in building and construction as thermal insulation in buildings and roads, but also as packaging material for goods (loose-fill material) and food (European Manufacturers of Expanded Polystyrene, 2010; Chanda and Roy, 2008)
**Initial assessment**

Results for EPS polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard score</th>
<th>44</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>III</td>
</tr>
<tr>
<td>Assessment</td>
<td>Small- medium hazard (2.5), maybe with some underestimation regarding suspected endocrine disrupting properties (2.5+?).</td>
</tr>
</tbody>
</table>

The monomer styrene is only classified as harmful if inhaled (II), causes serious eye irritation (II), causes skin irritation (II), and flammable liquid and vapour (I). However, within the EU strategy on endocrine disruptors styrene is on the priority list and has preliminary been assigned category 1 with evidence of human effects and also assigned high concern due to risk of exposure. If the evaluation of styrene shows endocrine disrupting properties all styrene containing polymers would be ranked as more hazardous. During the production of styrene benzene is used as raw material, and propylene oxide is formed as a by-product in one of the two routes. Both are classified as carcinogenic and mutagenic (cat. 1B; V).

The blowing agent pentane is i.a. classified as may be fatal if swallowed and enters airways (III), may cause drowsiness or dizziness (II), and toxic to aquatic life with long lasting effects (cat. 2; III).

The initiators benzyl peroxide is i.a. skin sensitising (cat. 1; IV) and potassium persulphate is i.a. both skin and respiratory sensitising (cat. 1; IV).

The polystyrene backbone contains weak links and the free styrene dimers which are formed during free radical polymerisation are thermally unstable (Priddy, 2003). When the polymer is heated e.g. during fabrication there is generally an increase in the residual monomer content (Priddy, 2003), which may then be available for leaching.

The global annual production is large.

**22. High-impact polystyrene (HIPS)**

**Global annual production**

According to Meira and Kiparissides (2007) HIPS accounts for approximately 42% of the 15.2 million tons of general purpose, HIPS and expandable beads (figures for 2004). This gives approximately 6.4 million tons (2004). The figures for styrenics are very varying.

**Polymer synthesis and composition**

High-impact polystyrene is produced by free radical polymerisation of styrene in the presence of various elastomers, most commonly polybutadiene (Harper and Petrie, 2003; Gnanou and Fontanille, 2008). First the polybutadiene rubber is dissolved in styrene containing a diluent, e.g. ethylbenzene or toluene (Wunsch, 2000). Lubricants, regulators (e.g. tertdodecyl mercaptan), or peroxide or hydroperoxide initiators may be added (Wunsch, 2000). The solution is filtered and prepolymerisation takes place (Wunsch, 2000). The polymerisation is continued, predominantly by a continuous bulk process in solution (A) (Wunsch, 2000). A bulk suspension process (B), may also be used, in which the polymer solution is dispersed in water with suspension aids, e.g. polyvinyl alcohol or polyvinyl pyrrolidone (Wunsch, 2000). The polybutadiene is made by solution polymerisation of butadiene with the aid of Ziegler-Natta catalysts (Chanda and Roy, 2008).

**Monomer concentrations**

HIPS generally contains 4-12 wt% polybutadiene rubber and 88-96 wt% styrene (Demirors, 2000). This gives an average of 8 wt% polybutadiene and 92 wt% styrene. The rubber content can then by volume be 40% (Demirors, 2000).
**Monomer synthesis**

Monomer 1: Styrene

Ex 1: Ethylbenzene (dehydrogenation) ↔ ethyl and benzene (condensation).

Ex 2: Methyl phenyl carbinol (dehydration) ↔ methyl phenyl carbinol and propylene oxide (by-product) ↔ a hydroperoxide (reacted with propylene) ↔ ethylbenzene (proylation) ↔ ethyl and benzene (condensation (Carraher Jr, 2007; European Commission (JRC), 2002).

Monomer 2 (elastomer): 1,3-butadiene

Ex 1: Butane (cracking)

Ex 2: By-product from other cracking reactions (Carraher Jr, 2007)

**Applications**

The major markets for HIPS are in packaging and disposables, followed by appliances (e.g. refrigerator liners, television and computer cabinets) and consumer electronics, building and construction, toys and recreation, but also houseware, custom sheet and furniture (Klodt and Gougeon, 2003).

**Initial assessment**

Results for HIPS polymer, based on monomer classifications.

| Hazard score | 1628 |
| Highest hazard level | V |
| Assessment | High hazard (4), maybe with some underestimation regarding styrene and suspected endocrine disrupting properties (4+?). |

The monomer styrene is only classified as harmful if inhaled (II), causes serious eye irritation (II), causes skin irritation (II), and flammable liquid and vapour (I). However, within the EU strategy on endocrine disruptors styrene is on the priority list and has preliminary been assigned category 1 with evidence of human effects and also assigned high concern due to risk of exposure. If the evaluation of styrene shows endocrine disrupting properties all styrene containing polymers would be ranked as more hazardous. During the production of styrene benzene is used as raw material, and propylene oxide is formed as a by-product in one of the two routes. Both are classified as carcinogenic and mutagenic (cat. 1B; V).

The monomer butadiene which is used to make the polybutadiene is both carcinogenic and mutagenic (cat. 1A and 1B respectively; V). The amount used greatly affects the hazard score in the ranking system.

**23. Acrylonitrile-butadiene-styrene (ABS) terpolymer**

**Global annual production**

8.6 million tons of ABS (2007) (calculated from PlasticsEurope MRG, 2008), but according to Platt (2003) only were 4.7 million tons (figures for 2002) (Platt, 2003). This gives an average of 6.6 tons.

**Polymer synthesis and composition**

Acrylonitrile-butadiene-styrene terpolymer is made by graft polymerisation of styrene and acrylonitrile with polybutadiene which is made by polymerising butadiene (Harper and Petrie, 2003). Emulsion polymerisation (A) is the most commonly used method (Niessner and Gausepohl, 2003) in which the styrene and acrylonitrile monomers are polymerised in the presence of polybutadiene seed particles (Adams et al, 1993) in water with emulsifying agents (Nuyken, 2005), e.g. ammonium oleate, or sodium palmitate (0.1-15 parts by weight of monomer) (Cincera et al, 1975).

Mass polymerisation is also used (B) in which styrene and acrylonitrile are copolymerised in the presence of a diene based rubber (Fink, 2010). A peroxide, e.g. tert-butyl peroxyneodecanoate, tert-butyl perbenzoate, may be used as initiator (Fink, 2010).
The polybutadiene rubber is made by emulsion polymerisation of butadiene with water, emulsifier and 
(Chrisochoou and Dufour, 2002). Rubber contents in conventional systems range between 5-70 wt% (Adams 
et al, 1993).

**Monomer concentrations**

40-60 % styrene, 20-30 % acrylonitrile, and 20-30 % butadiene rubber is the general ratio used (Harper and 
Petrie, 2003). The mix of styrene and acrylonitrile is usually 72 wt% and 28 wt% respectively (Sperling, 
2004) and the final rubber content is 10-30 wt% (Chrisochoou and Dufour, 2002). This example gives 20 wt% 
butadiene, 58 wt% styrene and 22 wt% acrylonitrile.

**Monomer synthesis**

Monomer 1: Styrene

Ex 1: \(\text{ethylbenzene (dehydrogenation)} \leftrightarrow \text{ethyl and benzene (condensation)},\)

Ex 2: \(\text{methyl phenyl carbinol (dehydration) } \leftrightarrow \text{methyl phenyl carbinol and propylene }\)

Ex 3: \(\text{a hydroperoxide (reacted with propylene) } \leftrightarrow \text{ethylbenzene (proylation) } \leftrightarrow \text{ethyl and benzene (condensation})\) (Carraher Jr, 2007; European Commission JRC, 2002).

Monomer 2: acrylonitrile \(\leftrightarrow \text{propylene (oxidation in the presence of ammonia)}\) (Gnanou and Fontanille, 
2008).

Monomer 3: 1,3-butadiene

Ex 1: \(\leftrightarrow \text{butane (cracking)}\)

Ex 2: \(\leftrightarrow \text{by-product from other cracking reactions (Carraher Jr, 2007)}\).

Polybutadiene rubber is made by polymerising 1,3-butadiene (Gnanou and Fontanille, 2008).

**Applications**

The automotive sector is the main market, e.g. instrument panels and consoles, door handles, door trim, and 
loudspeaker grilles (Platt, 2003). Housings for consumer products is another main use, e.g. for cameras, TVs, 
television sets and audio equipment, vacuum cleaners, food mixers, transformers. Other applications are pipes, 
medical equipment, tubes and caps, sports equipment, luggage, furniture, switches and safety helmets (Platt, 
2003).

**Initial assessment**

Results for ABS polymer, based on monomer classifications.

| Hazard score | 6552 |
| Assessment | High-very high hazard (3.5), maybe with some underestimation regarding styrene and suspected endocrine disrupting properties (3.5+?). |

The monomer acrylonitrile, one out of three monomers, is hazardous and i.a. classified as carcinogenic (cat. 
1B; V), skin sensitising (cat. 1; IV), toxic if inhaled (III), if swallowed or in contact with skin (III).

The monomer styrene is only classified as harmful if inhaled (II), causes serious eye irritation (II), causes skin 
irritation (II), and flammable liquid and vapour (I). However, within the EU strategy on endocrine disruptors 
styrene is on the priority list and has preliminary been assigned category 1 with evidence of human effects and 
also assigned high concern due to risk of exposure. If the evaluation of styrene shows endocrine disrupting 
properties all styrene containing polymers would be ranked as more hazardous. During the production of 
styrene benzene is used as raw material, and propylene oxide is formed as a by-product in one of the two 
routes. Both are classified as carcinogenic and mutagenic (cat. 1B; V).
The monomer butadiene, which is used to make the polybutadiene, is both carcinogenic and mutagenic (cat. 1A and 1B respectively; V). The more butadiene that is used, the higher the hazard score the ABS polymer gets.

The global annual production is large-very large.

### 24. Styrene-acrylonitrile (SAN) copolymer

#### Global annual production
No data on annual consumption of SAN has been found. But according to International Trader Publications (ITP) (2009) 100.128 tons of SAN was traded during three months (January to March) 2009, representing 80-90% of the world trade (ITP, 2009). If the same amount is traded the rest of the year this gives 0.5 million tons SAN per year. There is however a great uncertainty in this figure.

#### Polymer synthesis and composition
Styrene-acrylonitrile copolymer is made by polymerisation of styrene and acrylonitrile monomers most commonly using a bulk process (Chrisochoou and Dufour, 2002). Styrene and acrylonitrile are fed into one or several reactors, with or without solvents, e.g. ethylbenzene or toluene (Chrisochoou and Dufour, 2002). The solvent and the unconverted monomers are removed by heating and distillation (Chrisochoou and Dufour, 2002).

#### Monomer concentrations
SAN copolymers with 15-30 wt % acrylonitrile are available, but 24 wt% acrylonitrile is ideal (Demirors, 2000) which gives 76 wt% styrene.

#### Monomer synthesis
Monomer 1: Styrene
Ex 1: \[ \text{ethylbenzene (dehydrogenation) \rightarrow ethyl and benzene (condensation)}, \]
Ex 2: \[ \text{methyl phenyl carbinol (dehydration) \rightarrow methyl phenyl carbinol and propylene oxide (by-product) \rightarrow a hydroperoxide (reacted with propylene) \rightarrow ethylbenzene (proylation) \rightarrow ethyl and benzene (condensation) (Carraher Jr, 2007; European Commission JRC, 2002).} \]

Monomer 2: Acrylonitrile \[ \rightarrow \text{propylene (oxidation in the presence of ammonia) (Gnanou and Fontanille, 2008, p549).} \]

#### Applications
SAN is mainly used in household articles (Niessner and Gausepohl, 2003). Other applications are e.g. transparent parts for kitchen appliances (e.g. coffee machines), packaging for cosmetics, toothbrushes, lamp covers, and housings for large industrial batteries (Niessner and Gausepohl, 2003).

#### Initial assessment
Results for SAN polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard score</th>
<th>2788</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>V</td>
</tr>
<tr>
<td>Assessment</td>
<td>High hazard (4), maybe with some underestimation regarding styrene and suspected endocrine disrupting properties (4+?).</td>
</tr>
</tbody>
</table>

The monomer styrene is only classified as harmful if inhaled (II), causes serious eye irritation (II), causes skin irritation (II), and flammable liquid and vapour (I). However, within the EU strategy on endocrine disruptors styrene is on the priority list and has preliminary been assigned category 1 with evidence of human effects and also assigned high concern due to risk of exposure. If the evaluation of styrene shows endocrine disrupting properties all styrene containing polymers would be ranked as more hazardous. During the production of
styrene benzene is used as raw material, and propylene oxide is formed as a by-product in one of the two routes. Both are classified as carcinogenic and mutagenic (cat. 1B; V).

The monomer acrylonitrile is hazardous, is hazardous, and i.a. classified as carcinogenic (cat. 1B; V), skin sensitising (cat. 1; IV), toxic if inhaled (III), if swallowed or in contact with skin (III).

The figure of global annual production uncertain, but may be quite small.

**OTHER THERMOPLASTICS**

25. Polyoxymethylene (POM) and copolymers

**Global annual production**
604,000 tons POM (figures for 2002) (Platt, 2003).

**Polymer synthesis and composition**
Two types of poly(oxymethylene) exist: (A) homopolymer and (B) copolymer (Harper, 2000). The homopolymer (A) is formed by anionic polymerisation of formaldehyde (Harper, 2000). Gaseous formaldehyde is usually polymerised in an inactive solvent such as saturated aliphatic or cyclo-aliphatic hydrocarbon e.g. hexane (Ebewele, 2000; Salamone, 1996). Amines (e.g. pyridine) and the soluble salts of alkalimetals are used as initiators (Harper, 2000; Braun et al, 2005). Acetic anhydride is added for thermal stability (Harper, 2000). Methylene diacetate is formed as a byproduct (Salamone, 1996).

The copolymer (B) is prepared by cationic polymerisation of trioxane (a cyclic trimer of formaldehyde) with a second monomer, particularly ethylene oxide (B1) or dioxolane (B2) (Gnanou and Fontanille, 2008; Carraher Jr, 2008). The polymerisation can be initiated by e.g. boron trifluoride (Salamone, 1996).

**Monomer concentrations**
(A) Only one monomer (formaldehyde) is used for the homopolymer.
(B) The copolymer is made by reacting trioxane with 0.1 to 15 mole% of ethylene oxide or 1,3-dioxolane (Sandler and Karo, 1992). This gives a median of 7.5 mol% of either ethylene oxide or 1,3-dioxolane. This gives: (B1) 96 wt% trioxane and 4 wt% ethylene oxide, or (B2) 94 wt% trioxane and 6 wt% 1,3-dioxolane.

**Monomer synthesis**
(A) Monomer: formaldehyde ← methanol (hot-air oxidation) (Carraher Jr, 2007).
(B1 & B2) Monomer 1: trioxymethylene ← formaldehyde (Campo, 2007).
(B2) Monomer 2, alt 2: dioxolane
Ex 1: ← glycol and formaldehyde (reaction),
Ex 2: ← ethylene oxide and H₂SO₄ (heating) (Weissemel and Arpe, 2003).

**Applications**
Homopolymers are suited in applications where good abrasion and a low friction coefficient are required, e.g. gears, bearings, conveyer belt links and seat belts (Platt, 2003). Copolymers are suited in applications where a low friction coefficient is needed, e.g. electric kettles and water jugs, chemical pumps, components with snap fits, bathroom scales, telephone keypads and housings for domestic appliances (Platt, 2003).
Initial assessment

Results for POM and copolymers, based on monomer classifications.

| Hazard scores | 103, 871 and 1500 |
| Highest hazard level | V, or III |

Assessment

- Medium hazard (3) for one copolymer with trioxymethylene;
- High hazard (4) for both homopolymer and comonomer with ethylene oxide.

Formaldehyde, the only monomer used for the homopolymer, is i.a. classified as skin sensitising (cat. 1; IV), suspected of causing cancer (III), and toxic if inhaled (III), in contact with skin (III) and if swallowed (III).

For the copolymers the less toxic trioxymethylene is used as the main monomer instead of formaldehyde, but is made from formaldehyde. Trioxymethylene is suspected of damaging the unborn child (III). The use of ethylene oxide as co-monomer should be avoided since it is both carcinogenic and mutagenic (cat. 1; V), and can be substituted with dioxolane which is only a highly flammable liquid and vapour (I). However, one of the two routes for making dioxolane uses ethylene oxide as raw material, so the glycol / formaldehyde route is preferable.

The initiator, boron trifluoride, which can be used for the copolymers, is fatal if inhaled (IV).

Formaldehyde is one of the most common indoor air pollutants and is slowly released from formaldehyde resins used in e.g. construction materials (Hemat, 2006). Thermal degradation of POM releases formaldehyde (at 230°C) (Lokensgard, 2004).

The global annual production is of medium-large size.

26. Polyphenylene ether (PPE), also called Polyphenylene oxide (PPO)

Global annual production

353,000 tons PPE (figures for 2002) (Platt, 2003).

Polymer synthesis and composition

Polyphenylene ethers are most commonly produced by oxidative coupling of 2,6-dimethylphenol (Fink, 2008; Gnanou and Fontanille, 2008). The polymerisation takes place in an organic solvent such as benzene, toluene, xylene or o-dichlorobenzene in the presence of oxygen and a metal-amine complex catalyst (Fink, 2008). Copper is the most common metal for the catalysts, but manganese and cobalt may also be used (Fink, 2008). Examples of metal-amine complexes include copper (I) chloride and a pyridine solution, or cuprous bromide and di-n-butyl amine in toluene (Fink, 2008; Hay, 2001). The catalyst is removed from the reaction mixture and a promoter of inorganic alkali metal bromide, or an alkaline earth metal bromide is added (Fink, 2008).

Other phenols that can be used as monomers for PPE are 2,3,6-trimethylphenol, 2,4,6-trimethylphenol, p-phenylphenol, 2,6-diphenylphenol, 4-bromo-4’,4’’-dihydroxytriphenylmethane, or 2-allyl-6-methylphenol (Gnanou and Fontanille, 2008; Fink, 2008).

Monomer concentrations

Only one monomer (2,6-dimethylphenol) is used.

Monomer synthesis

2,6-dimethylphenol $\leftarrow$ phenol* and methanol (reaction with metaloxide catalyst) (Fink, 2008).

*phenol is made from benzene and propylene according to the following reactions:
Phenol (+ acetone (byproduct)) ⇐ chlorine in chlorobenzene (nucleophilic substitution) ⇐ cumene hydroperoxide (acidic decomposition) ⇐ benzene and propylene (reaction) (Carraher Jr, 2007; Harrington, 2010; Weber and Weber, 2010).

Applications
PPE is not used in its pure form (Fink, 2008). It is mainly used mixed with styrene and copolymers of butadiene and styrene, but can also be mixed with polyamide and polybutuleneterephthalate (Edshammar, 2002). The automotive industry uses 40% of the PPE-mixtures for e.g. interior fittings, dashboards, casings for rear-view mirrors, and electrical applications (Edshammar, 2002).

Initial assessment
Results for PPE polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard score</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>III</td>
</tr>
<tr>
<td>Assessment</td>
<td>Medium-high hazard (3.5).</td>
</tr>
</tbody>
</table>

The most commonly used only monomer, 2,6-dimethylphenol, is toxic to aquatic life with long lasting effects (III), toxic if inhaled (III) and in contact with skin (III), and causes severe burns and eye damage (III). The alternative monomers are not classified and cannot be assessed.

The use of benzene (carcinogenic and mutagenic, cat. 1B; V) as a solvent should be substituted with the less hazardous options, e.g. xylene. In addition benzene is used as raw material to produce the phenol from which 2,6-dimethylphenol is made.

Of the catalysts copper chloride is very toxic to aquatic life with long lasting effects (IV) as well as very acute toxic to aquatic life (III), and cobalt may cause long lasting harmful effects to aquatic life (IV) and is skin and respiratory sensitising (cat. 1; IV).

The global annual production is of medium size.

27. Polyphenylene sulphide (PPS)

Global annual production
50,000 tons PPS (figures for 2002) (Platt, 2003).

Polymer synthesis and composition
Polyphenylene sulfide is most commonly produced by reacting 1,4-dichlorobenzene with sodium sulphide in an aprotic solvent e.g. N-methylpyrrolidone under a nitrogen atmosphere (Fink, 2008). Sodium acetate is commonly used as a catalyst (Fink, 2008).

Monomer concentrations
The only data of monomer concentration that has been found is from the Office of federal register (2005) where polyphenylene sulphide resins may be used in food contact material if equimolar parts of 1,4-dichlorobenzene and sodium sulphide is used, and if they meet other prescribed specifications. This example gives: 65 wt% 1,4-dichlorobenzene and 35 wt% sodium sulphide.

Monomer synthesis
Monomer 1: 1,4-dichlorobenzene ⇐ benzene (chlorination with gaseous chlorine) (Smittinger, 2000).
Monomer 2: sodium sulphide (aqueous solution) ⇐ sodium hydroxide and sodium hydrosulfide (reaction) (Shonaike, 1997).
Applications
PPS are used in electronic components e.g. bobbins, coil formers, connectors, relay components, terminal blocks, moulded bulb sockets for electrical power station control panels, brush holders, motor housings, switch components and thermostat parts (British Plastics Federation, 2010). It is also used in the automotive sector e.g. in exhaust gas return valves, carburettor parts, ignition plates and flow control valves for heating systems, due to its resistance to corrosive engine exhaust gases, ethylene glycol and petrol (British Plastics Federation, 2010). Other applications include dental and laboratory equipment, cooking appliances, hair dryer grills and components, and sterilisable medical equipment (British Plastics Federation, 2010).

Initial assessment
Results for PPS polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard score</th>
<th>897</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>IV</td>
</tr>
<tr>
<td>Assessment</td>
<td>High hazard (4).</td>
</tr>
</tbody>
</table>

Both of the two monomers are hazardous. 1,4-dichlorobenzene is i.a. very toxic to aquatic life with long lasting effects (IV) as well as very acute toxic to aquatic life (III), and suspected of causing cancer (III). In addition it is made from benzene (carcinogenic and mutagenic, cat. 1B; V). Sodium sulphide, is i.a. very toxic to aquatic life (III) (acute toxicity), toxic in contact with skin (III) and causes sever skin burns and eye damage (III).

The solvent N-methylpyrrolidone may damage the unborn child (cat. 1B; V) and ought to be substituted.

The global annual production is of small-medium size.

28. Polypropylene (PP)

Global annual production
45.2 million tons PP (2007) (calculated from PlasticsEurope MRG, 2008).

Polymer synthesis and composition
Polypropylene is made by anionic coordination polymerisation of propylene (Ravve 2000), by slurry, bulk, or gas phase process (Soares et al, 2007). Ziegler-Natta catalysts are mainly used consisting of titanium halogenides and alkylaluminium compounds, e.g. titanium trichloride/magnesium chloride or titanium tetrachloride/triethylaluminium, and a third component e.g. aromatic esters, alkoxy silanes and hindered amines (for instance 1,2,4-trimethylpiperazine or 2,3,4,5-tetraethylpiperidine), but also metallocene catalysts are used (Gnanou and Fontanille, 2008; Ravve 2000; Kaminsky, 2005). For polymerisation in slurry (A) diluents such as naphtha, hexane or heptane are used (Ravve, 2000; Andrady, 2003). After polymerisation the slurry is centrifuged to remove the solvent and other material that is soluble in the diluent (Brydson, 1999). The polymer is treated with an agent, typically methanol, which decomposes the catalyst and dissolves the residue (Brydson, 1999).

Monomer concentrations
Only one monomer (propylene) is used.

Monomer synthesis
Propylene gas ← petroleum (cracking) (Gnanou and Fontanille, 2008).

Applications
Few materials are used in as many applications as PP (Chanda and Roy, 2008).
• Fibres and filaments (largest market area) e.g. carpet backing face yarns, indoor/outdoor construction, automotive interior mats, trunk linings, synthetic turf and disposable diaper,
• Packaging film (second largest market), e.g. packaging for foods,
• Automotive and truck battery cases,
• Medical applications, e.g. disposable syringes, hospital trays, labware,
• Washing machines, dish washers, pump housings, vacuum cleaners (Chanda and Roy, 2008).

Initial assessment
Results for PP polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard score</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>I</td>
</tr>
<tr>
<td>Assessment</td>
<td>Very low hazard (1).</td>
</tr>
</tbody>
</table>

The monomer propylene is not toxic, only classified as an extremely flammable gas (I).

In slurry polymerisation naphta which is carcinogenic and mutagenic (cat 1B; V) is used, and should be substituted with the less hazardous options.

Since PP is very sensitive to oxidative degradation and UV-radiation it needs to be stabilised with large amounts of antioxidants (e.g. phenols, amines and phosphates) and light stabilisers (e.g. Hindered Amine Light Stabilisers, HALS) for protection (Gugumus, 2001; Schwarzenbach et al, 2001; Ravve, 2000). The HALS evaporate easily and have poor extraction resistance, causing emissions and migration of harmful amines (Xue and Toyota, 2008).

The global annual production is very large.

29. Polyvinyl acetate (PVAc) and polyvinyl alcohol (PVOH)

Polyvinyl acetate (PVAc)
Global annual production
2.5 million tons PVAc and VA containing copolymers per year (Gnanou and Fontanille, 2008).

Polymer synthesis and composition
Poly(vinyl acetate) is primarily made by free radical emulsion polymerisation of vinyl acetate (Nuyken et al, 2005). The polymerisation takes place in water with an emulsifier and/or a protective colloid, (e.g. poly(vinyl alcohol), hydroxyethyl cellulose, styrene allyl alcohol copolymers or gummi arabicum) and a water soluble initiator (e.g. potassium peroxodisulphate, or hydrogen peroxide) (Nuyken et al, 2005).

Monomer concentrations
Only one monomer (vinyl acetate) is used.

Monomer synthesis
Vinyl acetate ← acetic acid and ethylene (oxidative condensation) (Carraher Jr, 2007).

Applications
PVAc is mainly used for producing poly(vinyl alcohol) and polyacetals (Barbalata and Feldman, 1996). PVAc have excellent adhesion properties and are used as adhesives (e.g. wood adhesives), coatings (e.g. sealable coatings, grease proofing of paper), as latex paints, and as binders for pigmented paper and non-woven fabrics (Barbalata and Feldman, 1996).

Polyvinyl alcohol (PVOH)
Polyvinyl alcohol (PVOH) is a water soluble polymer made by hydrolysis of polyvinyl acetate in the presence of an alkaline catalyst. It is used for producing poly(vinyl acetals), in adhesive formulations, for coating textile fibres or papers, and is used as a viscosifying agent in solution polymerisations (Gnanou and Fontanille, 2008). The figures for global annual consumption are very varying, with 1.5 million tons according to Gnanou and Fontanille, 2008), and with an estimated 550.000 tons (figures from 2004) according to Pardos (2004). Applications include water soluble films e.g. for the packaging sector, water treatment chemicals, dyes, disinfectants, industrial cleaning chemicals, and laundry detergents (Massey, 2003). The polymer dissolves in water giving a solution of PVOH with a small amount of e.g. glycerol which is used as plasticiser (0-20%). These substances can degrade within 30 days in the presence of microorganisms (de Bragança and Fowler, 2007).

**Initial assessment**

Results for PVAc and PVOH polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard score</th>
<th>Highest hazard level</th>
<th>Assessment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I</td>
<td>Very low hazard (1).</td>
</tr>
</tbody>
</table>

The monomer, vinyl acetate, is only classified as a highly flammable liquid (I).

The adhesive properties of PVAc are enhanced if plasticisers (10-15%) is added to the PVAc latex. PVAc can be plasticized either by plasticisers e.g. dibutyl phthalate, tritolyl phosphate or by internal plasticisation by copolymerisation with copolymers (up to 20%) e.g. butyl acrylate, 2-ethylhexyl acrylate, diethyl fumarate, vinyl propionate or vinyl caprate (Feldman and Barbalata, 1996). The use of external plasticisers could enhance the hazardousness of the polymer.

The fact that PVOH can dissolve in water and degrades easily makes it favourable from an environmental degradation perspective, for instance for use in packaging applications.

The global annual production is large.

**30. Polyvinyl chloride (PVC)**

**Global annual production**

36.6 million tons of PVC (2007) (calculated from PlasticsEurope MRG, 2008).

**Polymer synthesis and composition**

Poly(vinyl chloride) is most commonly (>80%) made by free radical suspension polymerisation (Nuyken et al, 2005) of vinyl chloride, often in batch reactors or stirred autoclaves (Ravve, 2000).

Suspension polymerisation (A) is carried out with liquid vinyl chloride monomer dispersed as droplets in demineralised water containing suspending agents (most commonly polyvinyl alcohol, or hydroxypropyl methylcellulose) under pressure (Gnanou and Fontanille, 2008; Wypych, 2008). A monomer soluble initiator is also added, usually azo compounds or a peroxide (Andrady, 2000), e.g. azobis(isobutyronitrile), or dilauroyl peroxide (Nuyken et al, 2005).

Emulsion polymerisation (B) is not so common (<12%), but is used in plastisols and organisols (Pritchard, 2002; Harper, 2000). In emulsion polymerisation a water soluble initiator is used, e.g. potassium persulfate, ammonium persulfate, hydrogen peroxide, and emulsifiers such as sodium dodecylbenzenesulfonate (Feldman and Barbalata, 1996; Nuyken et al, 2005).
Heat stabilising additives

PVC is inherently thermally unstable and heat stabilisers are required to allow processing without degrading and discolouring the polymer (Campo, 2007; Patrick, 2005). Large amounts of heat stabilisers and lubricants are needed, approximately 4 wt% of which primary stabilisers account for half the amount (Jennings and Starnes, 2005). These are incorporated into the polymer (Crompton, 2007). More heat stabilisers are needed in rigid PVC due to higher processing temperatures (Rosato, 2010).

The primary heat stabilisers are mainly lead stabilisers but their use is decreasing due to environmental concerns (Jennings and Starnes, 2005). These are followed by mixed metal stabilisers and organotin stabilisers (Jennings and Starnes, 2005). Lead stabilisers consists of primary lead salts, typically tribasic lead sulphate, dibasic lead phthalate, dibasic lead phosphate, which are combined with lead stearates e.g. dibasic lead stearate, neutral lead stearate and lead soaps with some lubricating action (Bacalogulu and Fisch, 2001; Patrick, 2005). These are to be replaced in the EU by 2015 (Rosato, 2010). Common mixed metal stabilisers are barium/zink or zink/calcium stabilisers (Wilkes, 2005) while the cadmium containing stabilisers are being replaced worldwide, e.g. banned in EU from 2007 (Rosato, 2010). The most important organotin stabilisers are: mono- and dibutyl, methyl or octyltin isooctyl mercaptocetates, mono- and dimethylin 2-mercaptoethyl carboxylate sulfides, and mono- and dibutyltin sulfides (Zweifel et al, 2009), e.g. dibutyltin diacetate, and dibutyltin dilaurate (Jennings and Starnes, 2005). The primary heat stabilizers contain lubricating substances such as metallic soaps of lead, barium, calcium and zinc. Lubricants must be added since PVC gets sticky when the temperature increases (Jennings and Starnes, 2005). The secondary heat stabilisers are mainly epoxidised oils and esters (Jennings and Starnes, 2005).

Plasticising additives

Plasticisers are additives and are not needed to make the PVC polymer, but since a considerable amount may be added to make flexible (soft) PVC they are addressed here. The amounts of plasticisers added to PVC vary between 15 and 60 percentages by weight, but most commonly 35-40 weight percent is used (Navarro et al, 2010). Plasticisers are used in many thermoplastics to increase processability, or to extend the range of properties by making it repeatedly flexible, or to enhance flexibility (Murphy, 2001). Approximately 80% of the plasticiser consumption is used in PVC compounds (Murphy, 2001). Plasticisers are not only needed in flexible PVC, but also in rigid PVC to enable processing (Murphy, 2001). The plasticisers are capable of migrating to the surface since they are not bound chemically to the polymer and are only held by relatively weak intermolecular forces (Patrick, 2005).

The most commonly used plasticisers are the phthalate esters (accounting for approximately 80% of the plasticisers used) (Wypych, 2004). Of these the most common in descending order are di-(2-ethylhexyl) phthalate (DEHP), diisodecyl phthalate (DIDP), and diisononyl phthalate (DINP) (Wypych, 2004), but also dibutyl phthalate (DBP), benzylbutyl phthalate (BBP) and di-n-octylphthalate (DNOP) are among the six most common ones (Swedish Chemicals Agency, 2007). Alternatives to phthalates are aliphatic esters (generally diesters of adipic acid, e.g. di-2-ethylhexyl adipate (DEHA) also called diocyl adipate (DOA)), epoxy esters (most commonly epoxidized soybean oil), phosphate triesters, trimellitates (e.g. trioctyl trimellitate and tris-2-ethylhexyl trimellitate) and citrates (e.g. acetyl tributyl, and acetyl trihexyl citrate) (Harper and Petrie, 2003; Marcilla, 2008; Patrick, 2005).

Monomer concentrations

Only one monomer is used for rigid PVC. For plasticised PVC between 10 and 100 pph plasticiser is added (Edshammar, 2002), i.e. 5-50 wt%.

Monomer synthesis

Vinyl chloride

Ex 1: ← 1,2-dichloroethane (pyrolysis) ← ethylene (chlorination).
Ex 2: ← ethylene (oxychlorination) (Gnanou and Fontanille, 2008).
Applications
PVC is one of the most versatile plastics with rigid grades as well as plasticized (soft) flexible grades, and its usage range from building construction to toys and footwear (Chanda and Roy, 2008). Rigid PVC is e.g. used for pipes and fittings, which is the largest application (Chanda and Roy, 2008). For plasticised PVC the largest applications are cable insulation, film and sheet (Chanda and Roy, 2008). Other major applications are floor coverings, leather cloth, tubes and profiles, injection moldings, laminates and paste processes (Chanda and Roy, 2008).

Initial assessment
Results for PVC (rigid and plasticized) polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard score</th>
<th>10001, 10551 and 5001*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>V</td>
</tr>
<tr>
<td>Assessment</td>
<td>Very high hazard (5) for rigid PVC and for the BBP plasticised PVC; and likely high-very high hazard for the (50wt% non-classified) DIDP plasticised PVC (4.5?).</td>
</tr>
</tbody>
</table>

The only monomer, vinyl chloride, is carcinogenic (cat. 1A; V).

Several of the plasticisers that are used in plasticised PVC (in amounts up tp 50%) are very hazardous. Examples include the most common phthalate plasticiser DEHP and the two other common ones BBP and DBP. These are i.a. toxic for reproduction (cat. 1B; V) both with regard to fertility and the unborn child. DBP and BBP are also very toxic to aquatic life (acute toxicity) (III), and BBP is in addition very toxic to aquatic life with long lasting effects (IV). There are many less hazardous alternatives. The plasticiser DIDP is not classified. In the EU final risk assessment report (European Commission (JRC), 2003) no classifications were suggested for DIDP.

Among the heat stabilisers the most hazardous ones are cadmium and lead stabilisers. The cadmium stabilisers are i.a. carcinogenic (cat. 1B, V), suspected of causing genetic defects (cat. 2; IV), fatal if inhaled (IV), causes damage to organs through repeated exposure (IV), suspected of damaging fertility and the unborn child (cat. 2; III), and like the lead stabilisers are also very toxic to aquatic life with long lasting effects (IV) as well as very acute toxic to aquatic life (III). The lead stabilisers are more toxic for reproduction i.a. may damage the unborn child and suspected of damaging fertility (cat. 1A; V). Fortunately there is an EU ban on cadmium stabilisers (from 2007) and ongoing replacement world wide, and the lead stabilisers are to be replaced in the EU by 2015.

PVC requires most additives of all plastics types (accounting for 73% of the world production of additives by volume), followed by polyolefins (PE and PP), and styrenics (Murphy, 2001).

The global annual production is very large.

**THERMOPLASTIC ELASTOMERS**

31. Thermoplastic polyurethanes (TPU) (linear polyurethanes)

**Global annual production**
320.000 tons (figures for 2004) (Drobny, 2007).
**Polymer synthesis and composition**

Thermoplastic polyurethanes belong to the family of thermoplastic elastomers and are linear segmented copolymers, composed of an alternation of rigid and soft segments (Meckel et al, 2004; Gnanou and Fontanille, 2008).

**Rigid segments**

The rigid segments are formed by addition of a chain extender, e.g. ethylene glycol, 1,4-butanediol, 1,6-hexanediol and hydroquinine bis(2-hydroxyl) ether, to a diisocyanate, most commonly diphenylmethanediisocyanate (MDI), but also hexamethylene diisocyanate (HDI) and 3´3-Dimethyl-4-4´-biphenyl diisocyanate (TODI) are used (Drobny, 2007).

**Soft segments**

The soft segments consist of oligomers of either a polyester (which is most common), or a polyether (Drobny, 2007). Examples of polyesters include poly(ethylene butylene-1,4 adipate) glycol, poly(ethylene adipate) glycol, and poly(butylene-1,4 adipate) glycol (Drobny, 2007). Other polyester examples are poly(hexamethylene-2,2 dimethylpropylene adipate) glycol, poly(diethylene glycol adipate) glycol, polycaprolactone glycol, and poly(hexandiol-1,6 carbonate) diol (Drobny, 2007). The latter are not included in Table S1. The polyester oligomers are most commonly made from adipic acid and excess of a diol, e.g. ethylene glycol, 1,4-butanediol, 1,6 hexanediol, neopentyl glycol, or mixtures of these (Meckel, 2004).

Examples of polyethers include poly(oxytetramethylene) glycol and polypropylene glycol (Drobny, 2007). These polyethers are made by polymerising tetrahydrofuran and propylene oxide, respectively (Meckel, 2004).

TPU polymerisation can be carried out with the one-shot method (A) mixing all the ingredients together, or the prepolymer method (B), in which the isocyante is reacted with the polyol creating a prepolymer which is then reacted with the chain extender (Drobny, 2007). Polymerisation in solution (e.g. toluene, xylene, chlorobenzene and 1,2-dichlorobenzene) is preferred for creating a high molecular weight polymer with a linear structure (Braun et al, 2005).

**Monomer concentrations**

The ratio of isocyanate groups to the sum of isocyante reactive groups should be close to one (Meckel et al, 2004). If the ratio is higher than 1.1 cross-linking and other reactions occur (Drobny, 2007). By varying the molecular weight of the segments, their ratio and chemical type a wide variety of combinations of properties can be obtained. For instance by increasing the diisocyanate and diol content the harder the TPU gets (Meckel et al, 2004). The molar ratios for polyol: chain extender: diisoyanate typically range from 1:0.5:1.5 for soft grades up to 1:20:21 for hard elastomers (Meckel, 2004).

**Example 1: soft (hard segment content 31%):**

1 mole poly(ethylene butylene adipate) glycol (M=2000), 1.77 moles butanediol, and 2.8 moles MDI (Meckel et al, 2004). This gives 70 wt% poly(ethylene butylene adipate) glycol* made from (adipic acid, ethylene glycol and butanediol), 24 wt% MDI and 6 wt% butanediol.

**Example 2: more rigid (hard segment content 65%):**

1 mole poly(ethylene butylene adipate) glycol (Mn=2000), 10 moles butanediol, and 11 moles MDI (Meckel et al, 2004). This gives 35 wt% poly(ethylene butylene adipate) glycol* made from (adipic acid, ethylene glycol and butanediol), 49 wt% MDI and 16 wt% butanediol.

*A grade of 10 has been used for all the monomers for poly(ethylene butylene adipate) glycol, only representing adipic acid, ethylene glycol, since no data on monomer concentration was found.
Monomer synthesis

Rigid sequence (diisocyanate)
diphenylmethanediisocyanate (MDI) (and HCl by-product) → carbonyl chloride (decomposition) → a diamine (phosgenation with phosgene) → aniline and formaldehyde (reaction with hydrochloric acid) (Witcoff et al, 2004).

Rigid sequence (chain extender) & polyester soft sequence diol
Ethylene glycol ← ethylene oxide (hydrolysis) ← ethylene (oxidation) (Carraher Jr, 2007).
1,4-butanediol ← 1,4-butynediol (hydrogenation) ← acetylene and formaldehyde (reaction) (Witcoff et al, 2004).

Soft sequence
The polyesters are most commonly made from adipic acid and excess of a diol, e.g. ethylene glycol, 1,4-butanediol, 1,6 hexanediol, neopentyl glycol or mixtures of these (Meckel, 2004). The polyethers are made by polymerising tetrahydrofuran and propylene oxide, respectively (Meckel, 2004).

Soft sequence - Polysters
Adipic acid ← mixture of (cyclohexanone) and cyclohexanol (oxidation with nitric acid) ← cyclohexane (oxidation) ← benzene (hydrogenation) (Richards, 2005).

And diols, see above.

Soft sequence - Polyeters
Polypropylene glycol (also called polypropylene oxide) ← propylene oxide (also called propylene glycol) (ring opening polyaddition) (Sen, 2007).
Ex 1: Propylene oxide ← propylene and tert-butyl hydroperoxide (obtained from oxidation of isobutane) (oxidation).
Ex 2: Propylene oxide (and byproduct: phenylmethylcarbinol (whose dehydration gives styrene)) ← propylene and ethylbenzene hydroperoxide (epoxidation) ← ethylbenzene (reaction with air) ← benzene and ethylene (reaction) (Witcoff et al, 2004).

Polytetramethylene glycol ← tetrahydrofuran (ring opening polyaddition) (Sen, 2007).

Applications
There is a great variety of applications for TPUs:
• automotive applications (e.g. gaskets, seals, bushings, bellows, steering gear parts, shock absorbers, bumpers, instrument panels and their skins, gear shift knobs),
• hose and tubings (e.g. irrigation hose, garden hose, firehose, fuel line hose, medical tubing),
• wire and cable (e.g. seismographic cable, audio wire, camera cable, computer cable),
• films and sheets (e.g. films to be laminated to PU foams and textiles, breathable films in the textile industry),
• adhesives, sealants and coatings (e.g. coating fabrics for inflatable boats, life rafts, life jackets, oil barriers, car seats, office chairs, shoe laquers, luggage),
• mechanical, consumer and sporting goods (handles of machines, tools, shoe soles and heels, foot ball, parts of ski bindings),
• medical applications (e.g. catheters and tubings) (Drobny, 2007).
• Elastic fibres (e.g. Spandex and Lycra) (Chanda and Roy, 2008).

The main applications for TPU as rubbers are seals, bushes, convoluted bellows and bearings, and as the elastic fibre known as Spandex (Chanda and Roy, 2008).
Fibre synthesis
Elastomeric polyurethane fibres are mainly made by dry or wet spinning (Petrović, 2005). In dry spinning (accounting for 80% of spandex fibre production) the elastomer is dissolved in a solution containing dimethylformamide (DMF) or dimethylacetamide (DMA) and the fibres are extruded in a chamber heated with hot air (Petrović, 2005; Gnanou and Fontanille, 2008). In wet spinning the solution e.g. of dimethylformamide (DMF) or dimethylacetamide (DMA) is extruded into a coagulating bath (Petrović, 2005).

Initial assessment
Results for TPU polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard scores</th>
<th>556* and 1094*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>IV</td>
</tr>
<tr>
<td>Assessment</td>
<td>Medium-high hazard (3.5+?) for TPU cured with HDI; High hazard (4+?) for TPU cured with MDI, but maybe with some underestimation regarding the non-classified butanediol for both polymers.</td>
</tr>
</tbody>
</table>

Most of the monomers for the polyester polyols that are used for TPU are not particularly hazardous, however if the polyether polyols polypropylene glycol or polyethylene glycol are used (which is less common) their monomers are classified as carcinogenic and mutagenic (cat. 1B; V).

The main isocyanate used (MDI) is i.a. classified as skin and respiratory sensitising (cat. 1; IV) and suspected of causing cancer (cat. 2; III) and the alternative isocyanate HDI is also skin and respiratory sensitising (cat. 1; IV).

The chain extender 1,4-butanediol is not classified. The SIDS Initial Assessment Report (2000) for 1,4-butanediol indicate low level of concern for the environment, but recommend further exposure information because of observed neurotoxicity.

The solvent 1,2-dichlorobenzene is i.a. very toxic to aquatic life with long lasting effects (IV) and acute toxic to aquatic life (III) and should be substituted with eh less hazardous alternatives. The solvents used for fibre spinning dimethylformamide and N’N-dimethylacetamide are toxic for reproduction (cat. 1B; V).

To produce soft grades of TPU plasticisers in amounts up to 30 wt% are added (Drobny, 2007).

The global annual production is of medium size.
Thermosetting polymers

Thermosetting polymers are crosslinked and can, therefore, neither soften while heated, nor be remoulded.

**AMINO PLASTICS (resins)**

**32. Melamine-formaldehyde resin (MF)**

**Global annual production**

250,000 tons (Gnanou and Fontanille, 2008).

**Polymer synthesis and composition**

Melamine-formaldehyde resin are produced by monomeric addition of formaldehyde and melamine (2,4,6-triamino-1,3,3,5-triazine) under slightly alkaline conditions, forming mixtures of hexamethylol melamine (Harper, 2000; Ravve, 2000) which condense under heating (Nicholson, 2006). Methanol is often used to etherify the resin (Ravve, 2000). Acidification is then needed for networks to be formed, for instance by using an acid catalyst, e.g. p-toluene sulfonic acid (Ibeh, 1998; Ravve 2000).

**Monomer concentrations**

6 moles formaldehyde and 1 mole melamine is used (Harper, 2000). This gives: 59 wt% formaldehyde and 41 wt% melamine.

**Monomer synthesis**

Monomer 1: formaldehyde $\leftarrow$ methanol (hot-air oxidation) (Carraher Jr, 2007).

Monomer 2: melamine

Ex 1: Cyanodiamide (heating) $\leftarrow$ cyanamide (heating) (Carraher Jr, 2007).

Ex 2: $\leftarrow$ Urea (Fink, 2005).

**Applications**

MF resins are used as adhesives for wood, as resins for laminates, varnish, mouldings (e.g. dinnerware), foams, and is also used to improve properties of paper and cellulosic textiles (Fink, 2005).

**Initial assessment**

Results for MF polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard score</th>
<th>882*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>IV</td>
</tr>
<tr>
<td>Assessment</td>
<td>Medium – high hazard, with some uncertainties because of (≈40wt%) non-classified monomer but which have an indication of low level of concern (3.5?).</td>
</tr>
</tbody>
</table>

One of the two monomers, formaldehyde, is i.a. skin sensitising (cat. 1; IV), suspected of causing cancer (III), and toxic if swallowed (III), in contact with skin (III) and if inhaled (III).

The other monomer melamine is not classified, so this part cannot be assessed with certainty. However, according to the SIDS Initial Assessment Report (1998) there is a low level of concern for human health and the environment. Consequently the hazard score for the polymer may be fairly correct.

Formaldehyde is one of the most common indoor air pollutants and is slowly released from formaldehyde resins used in e.g. construction materials (Hemat, 2006). The emissions of formaldehyde form the MF resin can be decreased by increasing the melamine content (Fink, 2005).
The global annual production is of medium size.

33. Urea-formaldehyde resin (UF)

Global annual production
ca 1 million ton (Gnanou and Fontanille, 2008).

Polymer synthesis and composition
Urea-formaldehyde resin is produced by monomeric addition of formaldehyde and urea forming dimethylolurea (Harper, 2000), which condense under heating (Nicholson, 2006) in alkaline or slightly acidic conditions, e.g. with ammonia (Fink, 2005). Urea formaldehyde resins for surface coatings are commonly reacted with alcohols, usually n-butanol, to increase their solubility in organic solvents (Ravve, 2000). Curing of the resin is achieved by lowering the pH by adding acids, e.g. phosphoric acid or maleic acid, or acidic salts, e.g. ammonium salt (2-3wt%) or urea phosphate (Fink, 2005)

Monomer concentrations
2 moles formaldehyde and 1 mole urea is used (Harper, 2000, p2.2). This gives 50 wt% formaldehyde and 50 wt% urea.

Monomer synthesis
Monomer 1: formaldehyde $\leftarrow$ methanol (hot-air oxidation) (Carraher Jr, 2007).
Monomer 2: urea $\leftarrow$ ammonium carbamate (decomposition) $\leftarrow$ ammonia and carbon dioxide (condensation) (Carraher Jr, 2007).

Applications
UF resins are mainly used in the adhesive industry as glues, e.g. in pressed wood products (Fink, 2005). UF resins can also e.g. be used as binders for glass fibre, in high pressure laminates, in soil amendment (enhancing porosity), and in liquid fertilizers as a nitrogen source in agricultural applications (Fink, 2005).

Initial assessment
Results for UF polymer, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard score</th>
<th>750*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>IV</td>
</tr>
<tr>
<td>Assessment</td>
<td>Medium-high hazard, with some uncertainties because of (50wt%) non-classified monomer, but which have an indication of low level of concern (3.5?).</td>
</tr>
</tbody>
</table>

One of the two monomers, formaldehyde, is hazardous. It is i.a. skin sensitising (cat. 1; IV), suspected of causing cancer (cat. 2: III), and toxic if swallowed (III), in contact with skin (III) and if inhaled (III).

The other monomer urea is not classified. However, the OECD SIDS Initial Assessment (2002) gave no indication for concern for human health and the environment. Consequently the hazard score for the polymer may be fairly correct.

The curing agent maleic acid is i.a. classified as skin senzitizing (cat. 1; IV) and could be substituted with the less hazardous options. Formaldehyde is released during curing, and from cured resins, especially those exposed to acidic environments (Fink, 2005). Formaldehyde is one of the most common indoor air pollutants and is slowly released from formaldehyde resins used in e.g. construction materials (Hemat, 2006).

The global annual production is large.
34. EPOXY RESINS

Global annual production
800,000 tons epoxy resins (Gnanou and Fontaniille, 2008).

Resin synthesis
Epoxy resins are produced by a two-step polymerisation sequence (Hallensleben, 2005). First a step-growth polymerisation reaction gives the prepolymer, and then curing takes place with curing agents (Hallensleben, 2005). The most important epoxy resin (>80% of the market) is a diglycidyl ether of bisphenol A (DGEBPA), which is based on bisphenol A and epichlorohydrin as raw materials (Gnanou and Fontaniille, 2008). The diglycidether is formed by dissolving bisphenol A in an aqueous solution of sodium hydroxide and adding epichlorohydrine (Edshammar, 2002). The curing agents that are used are described below.

In other epoxy resins (not investigated in this study) the bisphenol A is substituted by: chlorinated or brominated bisphenol A (Alt. B), bisphenol F (Alt. C), epoxy cresols or epoxy phenol novolacs (Alt. D.), or cycloaliphatic carboxylic acids (Alt D) (Harper and Petrie, 2003; Gnanou and Fontaniille, 2008; Edshammar, 2002).

Diluents are sometimes added to reduce viscosity, increase storing time, and reduce heat release during curing (Hoa, 2009). They often become an integral part of the cured resin, examples include diglycidyl ethers of neopentylglycol or butanediol, and glycidyl ethers e.g. cresyl glycidyl ether, and glycidaldehyde (Lewis and Sullivan Jr, 2001).

Curing agent synthesis (Crosslinking agents, Hardeners)
Epoxy resins are cured through step polymerisation with crosslinking agents (hardeners) or catalysts (Harper and Petrie, 2003; Gnanou and Fontaniille, 2008). The most widely used hardeners are aliphatic amines (curing at room temperature) (e.g. hexamethylene diamine, diethylene triamine, triethylene tetramine) and aromatic amines, (e.g m-phenylenediamine (MPDA), methylene dianiline (MDA), diamino diphenyl sulfone (DDS or DADS), p-phenylenediamine), but also acid anhydrides (e.g. phthalic anhydride, hexahydropthtalic anhydride, nadic anhydride) and catalytic curing agents (which cure at elevated temperature) are used (e.g. piperidine, boron trifluoride ethylamine complex, benzyl dimethylamine (BDMA)) (Harper and Petrie, 2003, p164-165; Gnanou and Fontaniille, 2003; Ravve, 2000). The catalytic curing agents (i.e. tertiary amines and accelerators) act as catalysts and are therefore added in small non-stochiometric (catalytic) quantities (Hoa, 2009; Nicholson, 2006). Typical hardeners for liquid resins are polyamines, and for solid resins dicyandiamide with imidazoles as accelerators are common (Edshammar, 2002). Some epoxy resins may also be cured by UV-light (Edshammar, 2002).

Monomer concentrations
By varying the ratio of the epichlorohydrin to bisphenol A resins of different molecular weights can be made (Harper and Petrie, 2003). DGEBPA epoxy resins have molecular weights between 450 and 4000 (Braun et al, 2005). The molecular weight decreases with increasing amounts of epichlorohydrine, and the more liquid is the resin (Braun et al, 2005; Edshammar, 2002). In the simplest case 2 moles of epichlorohydrine react with 1 mole of bisphenol A to produce a liquid epoxy resin with a molecular weight of 450 (Braun et al, 2005; Edshammar, 2002). To produce a solid epoxy resin (with a molecular weight of 3750) 1.11 moles of epichlorohydrine is reacted with 1 mole of bisphenol A (Edshammar, 2002). In simple epoxy systems the resin and hardeners are mixed in equal proportions, 1:1 in concentration (Strong, 2008).

Resin to curing agent share
The optimal proportion between resin and curing agent depends partly on the number of active sites on the resin and curing agent, and partly on their molecular weight (Strong, 2008). So the weight percentages used will vary greatly between different resins and curing agents. To obtain the maximum amount of crosslinks
equal amounts of active sites on the resin and on the curing agent are used (at approximately stochiometric quantity 1:1) (Strong, 2008).

**Example 1: Epoxy resin, liquid, low molecular weight with most toxic curing agent (MDA)**

DGEBPA (mw 450) example equivalent weight = \( \frac{M_{DEGPA}}{2 \ \text{epoxy groups}} = \frac{450 \ \text{(g/mole)}}{2} = 225 \ \text{g/mole} \); and 4,4'-methylene dianiline (MDA) amine hydrogen equivalent weight = 49.5 g/eq (Hoa, 2009). Calculation: 49.5/225 = 22 parts MDA (for 100 parts epoxy) \( \rightarrow \) 22 g MDA and 100 g DGEBPA resin (Hoa, 2009). This gives 18 wt% MDA, and 45 wt% bisphenol A and 37 wt% epichlorihydrine.

**Example 2: Epoxy resin, liquid, low molecular weight with least toxic curing agent (DDS)**

DGEBPA (mw 450) example equivalent weight = \( \frac{M_{DEGPA}}{2 \ \text{epoxy groups}} = \frac{450 \ \text{(g/mole)}}{2} = 225 \ \text{g/mole} \); and 4,4'-diamino diphenyl sulfone (DDS) amine hydrogen equivalent weight = 62 g/eq (Hoa, 2009). Calculation: 62/225 = 28 parts DDS (for 100 parts epoxy) \( \rightarrow \) 28 g MDA and 100 g DGEBPA resin (Hoa, 2009). This gives 22 wt% DDS and 43 wt% bisphenol A and 35 wt% epichlorihydrine.

**Example 3: Epoxy resin high molecular weight with non-classified curing agent (dicyandiamide)**

A typical curing agent for solid epoxy resins are dicyandiamide which is used in about 3.4 pph per 100 parts of solid epoxy resins (Edshammar, 2002; Murphy, 2001). DGEBPA (mv 3750) cured with 3.5 pph dicyandiamide. This gives 3.4 wt% dicyandiamide, 66.6 wt% bisphenol A, and 30 wt% epichlorohydrine.

**Resin synthesis - DGEBPA**

Monomer 1 (resin): Epichlorohydrin \( \rightarrow \) 2,3-dichloro-1-propanol (dehydrochlorination) \( \rightarrow \) allyl chloride (chlorohydrination) \( \rightarrow \) propylene (chlorination) (Fink, 2005; Carraher Jr, 2007).

Monomer 2 (resin): Bisphenol A \( \rightarrow \) phenol and acetone (acidic condensation) \( \rightarrow \) chlorine in chlorobenzene (nucleophilic substitution) \( \rightarrow \) cumene hydroperoxide (acidic decomposition) \( \rightarrow \) benzene and propylene (reaction) (Carraher Jr, 2007; Harrington, 2010; Weber and Weber, 2010).

**Applications**

Epoxy resins are mainly used in coatings for heavy corrosion protection and chemical resistance, in applications in paints, white ware, and automotive and naval sectors (Fink, 2005). Other applications include foams, adhesives (5%) and molded articles (e.g. laminated sheets for circuit boards, reinforced pipes) (Fink, 2005).

**Initial assessment**

Results for epoxy resins, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard scores</th>
<th>4226, 4551 and 7139</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>( \text{V} )</td>
</tr>
<tr>
<td>Assessment</td>
<td>High-very high hazard (4.5).</td>
</tr>
</tbody>
</table>

Epichlorohydrin, which is the monomer present in all of the different epoxy resins, is very hazardous. It is i.a. carcinogenic (cat. 1B; V), and skin sensitising (cat. 1; IV).

The most common monomer used with epichlorohydrine is bisphenol A, which also hazardous. Bisphenol A is i.a. skin sensitising (cat. 1; IV), suspected of damaging fertility (cat. 2; III) and causes serious eye damage (III). In addition, bisphenol A has on the priority lists within the EU strategy for endocrine disruptors preliminary been assigned category 1 with evidence of human effects, and also assigned high concern due to risk of exposure. If the evaluation of bisphenol A concludes endocrine disruption, polycarbonate would be ranked as more hazardous. Phenol, which is suspected of causing genetic defects (cat. 2; IV), is used to produce bisphenol A, and is in its turn produced from the carcinogenic and mutagenic (cat. 1A and 1B; V) raw material benzene.

The curing agent MDA is i.a. carcinogenic (cat. 1B; V) and skin sensitising (cat. 1; IV) and should be substituted with less hazardous options. Many of these options are, however, at least skin and respiratory
sensitising (cat. 1; IV). Both the curing agents p- and m- phenylenediamine are in addition also i.a very toxic to aquatic life with long lasting effects (IV) as well as very acute toxic to aquatic life (III). The curing agent dicyandiamide is not classified, however the SIDS Initial Assessment Report (2003) indicate a low concern for human health and the environment. Consequently the hazard score for the polymer example with this curing agent may be fairly correct.

The global annual production is large.

35. PHENOL FORMALDEHYDE RESINS (PF)

Global annual production
More than 5 million tons (Pilato, 2010).

Polymer synthesis and composition
Phenol formaldehyde resins are made by condensation reactions between an aldehyde and a phenol, most commonly formaldehyde and phenol (Fink, 2005). Two different reactions are mainly used (Ravve, 2000). In the Novolacs (two-stage) reaction (A) phenol in excess reacts with formaldehyde in the presence of acid catalysts e.g. sulphuric acid, hydrochloric acid, p-toluenesulfonic acid or benzenesulfonic acid (Fink, 2005; Nicholson, 2006; Harper, 2000) The prepolymer are cured by a hardener, most commonly hexamethylenetetramine (5-15 wt%) which decompose to formaldehyde and ammonia upon heating (Ravve, 2000; Pascault, 2002). The ammonia acts as catalyst during curing (Harper, 2000).

In the resole (single-stage) reaction (B) formaldehyde is in excess instead of phenol, and the reaction takes place in the presence of alkaline catalysts, e.g. sodium hydroxide (most common) or ammonia (Fink, 2005; Nicholson, 2006). The resol resins can be cured by heat, and require no curing agents (Fink, 2005).

Monomer concentrations
A variety of phenolic resins exist which can be obtained by changing the phenol:aldehyde ratio, reaction temperature and catalyst (Fink, 2005). In resol resins 0.5-4.5 moles of formaldehyde is used per mole phenol (Fink, 2005).

Example (A)
1.25 moles phenol, 1 mole formaldehyde and 10wt% hexamethylenetetramine is used (Nicholson, 2006; Pascault, 2002). This gives 72 wt% phenol, 18 wt% formaldehyde and 10 wt% hexamethylenetetramine.

Example (B)
1 mole phenol and 2 moles formaldehyde is used (Nicholson, 2006). This gives 61 wt% phenol and 39 wt% formaldehyde.

Monomer synthesis
Monomer 1: formaldehyde \( \xrightarrow{\text{methanol (hot-air oxidation)}} \) Carraher Jr, 2007).
Monomer 2: phenol (+ acetone (byproduct)) \( \xrightarrow{\text{chlorine in chlorobenzene (nucleophilic substitution)}} \) cumene hydroperoxide (acidic decomposition) (Carraher Jr, 2007; Weber and Weber, 2010) \( \xrightarrow{\text{benzene and propylene (reaction)}} \) Harrington, 2010).

(A) Curing agent: hexamethylenetetramine \( \xrightarrow{\text{formaldehyde and ammonia (reaction)}} \) Bruckner and Harmata, 2010).

Applications
PF resins are used in consolidated wood products (e.g. plywood, fibreboard), fibreglass insulation, laminates, abrasive coatings, and foams (Fink, 2005). Novolak PF resins are used as reinforcement in rubber preparations
in e.g. belts, tubes and tires (Fink, 2005). Resol resins are used as binders for fibre glass (Fink, 2005). Other applications include ashtrays, bottle caps, domestic plugs and switches, electrical iron parts, lamp holders, saucepan handles and welding tongs (British Plastic Federation, 2010).

**Initial assessment**

Results for PF resins, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard scores</th>
<th>1450 and 1500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>IV</td>
</tr>
<tr>
<td>Assessment</td>
<td>High hazard (4).</td>
</tr>
</tbody>
</table>

The two monomers are hazardous. Phenol is i.a. suspected of causing genetic defects (cat. 2; IV), and is made from the carcinogenic and mutagenic (cat. 1A and 1B; V) raw material benzene. Formaldehyde is i.a. skin sensitising (cat. 1; IV), suspected of causing cancer (III), and toxic if swallowed (III), in contact with skin (III) and if inhaled (III). The curing agent for the novolac reaction, hexamethylenetetramine is also skin sensitising (cat. 1; IV).

A typical resol resin contains a high percentage of residual monomers, i.e. phenol (typically between 0.1%-20%) and formaldehyde (typically between 0.1% and 15%) which are both highly toxic and volatile and may be released to air during curing (Fink, 2005). Formaldehyde is one of the most common indoor air pollutants and is slowly released from formaldehyde resins used in e.g. construction materials (Hemat, 2006).

The global annual production is large.

### 36. POLYURETHANES (PUR) (three-dimensional)

Polyurethanes are a very versatile group of polymers. There are both thermoplastic and thermosetting polyurethanes. They can be divided into elastic polyurethanes (e.g. flexible foams, elastomers, coatings, adhesives and fibres), and rigid polyurethanes (e.g. rigid PUR foams, structural foams, wood substitutes and solid PUR) (Ionescu, 2005). Around 72% of the global PUR use is foams (flexible, semiflexible and rigid) (Ionescu, 2005).

**Global annual production**

9 million tons cross-linked polyurethanes (Gnanou and Fontanille, 2008).

**Polymer synthesis and composition**

Polyurethanes are produced by reacting an oligomeric polyol (i.e. a low molecular weight polymer with terminal hydroxyl groups) with a diisocyanate (and sometimes a polyisocyanate), with the aid of catalysts (Andrady, 2003; Ionescu, 2005).

**Polyether polyols**

The most used polyols are polyether polyols (e.g. polypropylene glycol, polyethylene glycol, polytetramethylene glycol), block copolymers of ethylene oxide (10-15%) with propylene oxide, and polyols based on polystyrene or styrene-acrylonitrile copolymer (Andrady, 2003). The most important polyether polyol are polyether triols which are used in flexible foam, and the majority of these are copolymers of propylene oxide and ethylene oxide (Ionescu, 2005). The global annual production of polypropylene oxides exceeds 1 million tons and their main use is as precursors for polyurethanes (Gnanou and Fontanille, 2008).

The polyether polyols are obtained by the polymerisation of propylene oxide, and /or ethylene oxide, or tetrahydrofuran (Ionescu, 2005). The polymerisation is initiated by starters (chain initiators) which also are polyols, e.g. glycerol (for triols), 1,2-propylene glycol, and ethylene glycol (Ionescu, 2005). Common
catalysts include potassium hydroxide and catalysts based on aluminium and zinc (Ionescu, 2005). The polyols may be blended with other polyols, such as sorbitol.

**Polyester polyols**

Also polyester polyols (accounting for 18% of all PUR polyols) are used. Examples include poly(ethylene adipate) made from adipic acid and ethylene glycol; poly(ethylene succinate) made from succinic acid and ethylene glycol, polycaprolactone diol made from ε-caprolactone; or polybutylene adipate made from adipic acid and butanediol (Gnanou and Fontanille, 2008; Petrović, 2005; Ionescu, 2005).

**Diisocyanate**

The most used isocyanate is a mixture of 2,4 and 2,6 isomer (ratio 80:20) of toluene di-isocyanate (TDI), followed by diphenylmethane di-isocyanate (MDI), and to a lesser extent e.g. hexamethylene di-isocyanate (HMDI) is used (Andrady, 2003; Ionescu, 2005).

**Catalysts**

The usual catalysts used are amines (e.g. triethylene diamine, trialkyl amines, peralkylated aliphatic amines and N-ethylmorpholine, diazobiscyclooctane (DABCO)) added in an amount of ca 1%, or organotin compounds e.g. tin octoate dibutyltin dilaurate, dibutyltin dioctoate, and tributyltin acetate, added in amounts of ca 0.3% (Petrović, 2005; Ravve, 2000).

**Blowing agents**

For PUR foams auxiliary blowing agents (ABA) are used to increase foaming and to obtain lower density foams (Andrady, 2003). In flexible slabsstock and moulded foam methylene chloride or CO2, and water is used (Andrady, 2003). In rigid insulation foam hydrofluorocarbons (e.g HFC-134a), or liquid CO2 is used, and in integral skin PUR products, CO2, water or hydrocarbons (e.g. n-pentane or cyclopentane) (Andrady, 2003).

Foams are today mostly made by a one step process in which all components are mixed simultaneously (Petrović, 2005). PUR foams are made with the following components: polyol, isocyanate, blowing agent, water, and catalysts (amine and metal) and surfactants (Petrović, 2005).

The hardness of the PUR is determined by the molecular weight of the polyol (Ionescu, 2005). A low molecular weight polyol gives a hard PUR, and high molecular weight PUR gives an elastic, flexible PUR (Ionescu, 2005).

**Polyol and monomer concentrations**

The amount of isocyanate that is needed is calculated from the hydroxyl content of the polyol (Thomson, 2005) and the NCO-content of the isocyanate.

**Example 1: Flexible PUR foam**

A typical formulation of flexible foam is 100 pph polypropylene glycol triol (M 3000) (made from propylene oxide and terminated with ethylene oxide (e.g. 10 wt%)), 45 pph toluene diisocyanate (TDI 80/20), and 10 pph fluorocarbon blowing agent (Petrović, 2005). This gives approximately 29 wt% TDI, 58 wt% polypropylene oxide, 7 wt% ethylene oxide, and 6 wt% fluorocarbon ex HCF-134a.

The glycerol share in the polypropylene glycol triol accounts for between 1.5 to 1.9 wt% of the polypropylene glycol (calculated from Ionescu, 2005; personal communication Chemicals industry), which only constitute approximately 1% of the foam. It has, therefore, been omitted in the calculations and hazard ranking.

In addition water (3.5 pph), amine catalysts (e.g. diazobiscyclooctane (DABCO) 0.45 pph, and N-ethylmorpholine 0.6 pph), metal catalyst (e.g. tin octoate; 0.15 pph), and a surfactant (e.g. of silicone; 1-2 pph) are added (Petrović, 2005). These have also been omitted in the ranking.
Example 2: Rigid PUR foam (for isolation)

An example of a formulation for rigid PUR foam (for isolation) has been obtained from the Chemicals industry (personal communication). In this formulation the following monomers and blowing agents were present: a polyetherol based on propylene oxide and sorbitol, crude MDI, C-pentane and water. The formulation was recalculated into weight % shares, giving approximately 31 wt% propylene oxide, 13 wt% sorbitol, 52 wt% crude MDI, and 4 wt% C-pentane. Water has been omitted in this calculation.

Polyether polyol synthesis

Polyol, alt 1: Polypropylene glycol (also called polypropylene oxide) \( \leftrightarrow \) propylene oxide (also called propylene glycol) (ring opening polyaddition) (Sen, 2007).
Ex 1: Propylene oxide \( \leftrightarrow \) propylene and tert-butyl hydroperoxide (obtained from oxidation of isobutane) (oxidation) (Wittcoff et al, 2004).
Ex 2: Propylene oxide (and byproduct: phenylmethylcarbinol (whose dehydration gives styrene)) \( \leftrightarrow \) propylene and ethylbenzene hydroperoxide (epoxidation) \( \leftrightarrow \) ethylbenzene (reaction with air) \( \leftrightarrow \) benzene and ethylene (reaction) (Wittcoff et al, 2004).

Polyol, alt 2: Poly(ethylene glycol) (also called polyethylene oxide) \( \leftrightarrow \) ethylene oxide (ring opening polymerisation) \( \leftrightarrow \) ethylene (oxidation) (Sen, 2007; Carraher Jr, 2007; Gnanou and Fontanille, 2008).

Polyol, alt 3: Polytetramethylene glycol \( \leftrightarrow \) tetrahydrofuran (ring opening polyaddition) \( \leftrightarrow \) (Sen, 2007).

Polyester polyol synthesis

The polyesters are most commonly made from adipic acid and excess of a diol, e.g. ethylene glycol, 1,4-butandiol, or mixtures of these (Meckel, 2004). See polyester polyols above.

Diisocyanate synthesis

Alt. 1: toluene di-isocyanate (TDI) \( \leftrightarrow \) dinitrotoluene \( \leftrightarrow \) toluene (nitration and hydrogenation) (Fink, 2005).

Alt. 2: diphenylmethane di-isocyanate (MDI) \( \leftrightarrow \) isomers (phosgenation) \( \leftrightarrow \) aniline and formaldehyde (condensation) (Fink, 2005).

Applications

The major part of polyurethane application is flexible foams (44%) and rigid foams (28%), and the remaining 28% are coatings, adhesives, sealants and elastomers (figures from 2000-2002) (Ionescu, 2005). Flexible foams are often used in furniture, the automotive industry and for packaging, while rigid foams are mainly used for heat insulation in construction, refrigeration and partly in the automotive industry (Petrović, 2005). The main applications are for PUR: furniture/mattresses (30%), automotive (15%), construction (13%), technical insulation (10%), shoe soles (3%) and others (29%) (Ionescu, 2005).

Initial assessment

Results for PUR polymers, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard scores</th>
<th>13844* and 7384</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>V</td>
</tr>
<tr>
<td>Assessment</td>
<td>High hazard level (5). The unclassified sorbitol in the flexible foam example is very likely of very low concern.</td>
</tr>
</tbody>
</table>

Both isocyanates and the monomers for making the major polyether polyols are hazardous. The choice of polyol has a great influence on the hazard score of the PUR. Polyurethane made from polyester polyols are made from much less hazardous chemicals (see Table S1). The most toxic monomers that are used are propylene oxide (for polypropylene glycol) and ethylene oxide (for polyethylene glycol). Polypropylene glycols dominate in the foam technology (Petrović, 2005). Sorbitol, which is used as a comonomer in the flexible foam example, is not classified. However, according to the SIDS initial assessment profile (2009) its intrinsic properties indicate a low hazard. Consequently the hazard score for this polymer example may be fairly correct.
The exposure hazard of isocyanates depends on the volatility and molecular weight of the isocyanate (Lewis and Sullivan Jr, 2001). The common isocyanates, TDI, MDI and the less common HDI, are at least skin and respiratory sensitising (cat. 1, V). Toluenediisocyanate (TDI), which is the most commonly used, is in addition fatal if inhaled (IV), and suspected of causing cancer (cat. 2; III). It has a low molecular weight and is very volatile (Lewis and Sullivan Jr, 2001). MDI is less volatile and has a higher molecular weight, and is classified similar to TDI, but is not fatal if inhaled, instead it may cause damage to organs through repeated exposure (III).

The blowing agent HCF 134a (1,1,2,2-Tetrafluoroethane) neither classified nor has a SIDS Initial Assessment Report. Of the other blowing agents pentane is i.a. toxic to aquatic life with long lasting effects (cat 2; III) and fatal if swallowed and enters airways (III), and dichloromethane is suspected of causing cancer (cat. 2 ; III). Carbon dioxide is the least toxic option. Chlorofluorocarbons (CFCs) were historically frequently used as blowing agents but were banned for industrial use due to their negative effect on the ozone layer ((Andrady, 2003; Petrović, 2005). They were first replaced by e.g. hydrochlorofluorocarbons (HCFCs) still with ozone depleting properties, although to a lesser extent (Ashida, 2007). These were then replaced by hydrofluorocarbons, (HFCs), e.g HCF-134a and HCF-245fa, but due to high global warming potential they too will be restricted in the future (Ashida, 2007).

The catalyst tributyltin acetate is i.a. very toxic to aquatic life with long lasting effects (IV) as well as very acute toxic to aquatic life (III) and should be substituted with the less hazardous options.

Emissions of diisocyanates mainly occur during isocyanate synthesis and during curing (Fink, 2005).

The global annual production is very large.

37. UNSATURATED POLYESTER RESINS (UP)

Global annual production
>2 million tons for preimpregnated UP fabrics (prepolymer) (Gnanou and Fontanille, 2008).

Polymer synthesis and composition
Unsaturated polyester (UP) resins are made by radical polymerisation of low molar mass UP dissolved in a cross-linking agent, most commonly styrene, but also methyl methacrylate is common (Gnanou and Fontanille, 2008; Strong, 2008; Braun et al, 2005). Peroxides are used as initiators for the curing reaction (1.5-2%) (Strong, 2008), e.g. benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, or di-t-butyl peroxide (for curing at elevated temperatures), and methyl ethyl ketone peroxide, or cyclohexanone peroxide (for curing in room temperature) (Nicholson, 2006; Gnanou and Fontanille, 2008).

PrePolymer synthesis and composition - Low molar mass UP
The low molar mass UP (prepolymer) its turn is made in a step polymerisation process of a glycol, an unsaturated dicarboxylic acid/anhydride, and a saturated dicarboxylic acid/anhydride (Nicholson, 2006). A typical composition is 1,2-propylene glycol with phthalic anhydride and maleic anhydride (Nicholson, 2006), but many possible monomers can be used:

- Monomer 1 (glycol) – e.g. 1,2-propylene glycol, ethylene glycol, diethylene glycol, neopentyl glycol or bisphenol A
- Monomer 2 (unsaturated dicarboxylic acid/anhydride) – e.g. phthalic anhydride, o-phthtalic acid, isophthalic acid, or dicyclopentadien
- Monomer 3: (saturated dicarboxylic acid/anhydride) – e.g. maleic anhydride, maleic acid, or fumaric acid (Nicholson, 2006; Fink, 2005; Strong, 2008)
Monomer concentrations
A typical ratio for a general purpose UP resin is 1.1 mol 1,2-propylene glycol, 1 mol phthalic anhydride and 1 mol maleic anhydride (Fink, 2005). In a conventional UP resin up 50 % of styrene can be used (Fink, 2005), but usually 30 wt% of styrene is used (Kotsilkova, 2007). Methyl methacrylate can be used instead of styrene (Strong, 2005).

Example 1:
This gives 18 wt% 1,2-propylene glycol, 31 wt% phthalic anhydride, 21 wt % maleic anhydride and 30 wt% styrene.
Example 2
No data on share of methyl methacrylate has been found, but the same figure as for styrene, i.e. 30 wt%, has been used.

Monomer synthesis
Monomer 1, example: 1,2-propylene glycol ← propylene oxide and water (reaction) ← propylene (PO/PG sector group, 2011).
Monomer 2: example: phthalic anhydride ← o-xylene (oxidation) (Sheldon, 1983).
Monomer 3: example maleic anhydride
Ex1: ← butane (oxidation)
Ex 2:← benzene (oxidation) (OECD SIDS IAP, 2004).

Crosslinking agent, most common: Styrene
Ex 1: ← ethylbenzene (dehydrogenation) ← ethyl and benzene (condensation),
Ex 2: ← methyl phenyl carbinol (dehydration) ← methyl phenyl carbinol and propylene oxide (by-product) ← a hydroperoxide (reacted with propylene) ← ethylbenzene (proylation) ← ethyl and benzene (condensation) (Carraher Jr, 2007; European Commission JRC, 2002).

Crosslinking agent, second most common: Methyl methacrylate
Ex 1: ← propylene and methanol (oxidative carbonylation) (Carraher Jr, 2007).
Ex 2: ← methacrylamide sulphate (reaction with methanol and water)← cyanohydin (reaction with sulphur acid)← acetone and hydrogen cyanide (Edshammar, 2002).
Several other methods are used (Edshammar, 2002).

Application
UP are the most commonly used thermosetting resins for composites e.g. for boats, corrugated sheets and golf carts (Strong, 2008) More than 80% of UP resins are commonly compounded with fibers (mainly glass) (Odian, 2004). UP are used in construction (tub and building facades, speciality flooring, chemical storage tanks), in transportation (truck cabs, auto body repair), in marine applications (boat hulls) and in industry (business machines, handtool-moulded parts (Odian, 2004).

Initial assessment
Results for UP resins, based on monomer classifications.

<table>
<thead>
<tr>
<th>Hazard scores</th>
<th>1117*, and 1414*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest hazard level</td>
<td>IV</td>
</tr>
</tbody>
</table>

Assessment: High hazard, and the non-classified monomer propylene glycol (18wt%) has an indication of low hazard (4?).

Of the possible monomers for making the prepolymer the most hazardous ones are phthalic and maleic anhydride (i.a. skin and respiratory sensitising (cat. 1, IV)), bisphenol A (i.a. skin sensitising (cat. 1; IV) and suspected of damaging fertility (III)), and maleic acid (i.a.skin sensitising, (cat. 1; IV)). The monomer propylene glycol is not classified, but the SIDS Initial Assessment Report (2001) indicates that there is a low level of concern for human health and the environment. With regard to this, the hazard scores for the polymers may be fairly correct. However, propylene glycol is made by reacting the carcinogenic and mutagenic (cat. 1A and 1B; V) propylene oxide with water.
The most common crosslinking agent styrene is only classified as harmful if inhaled (II), causes serious eye irritation (II), causes skin irritation (II), and flammable liquid and vapour (I). However, within the EU strategy on endocrine disruptors styrene is on the priority list and has preliminary been assigned category 1 with evidence of human effects and also assigned high concern due to risk of exposure. If the evaluation of styrene shows endocrine disrupting properties all styrene containing polymers would be ranked as more hazardous.

During the production of styrene benzene is used as raw material and propylene oxide is formed as a by-product in one of the two routes. Both are classified as carcinogenic and mutagenic (cat. 1B; V). Benzene is also used as raw material in one of the routes for maleic anhydride.

The other common crosslinking agent methyl metacrylate is i.a. skin sensitising (cat. 1; IV).

The global annual production is large.

**POLYELECTROLYTES**

A polyelectrolyte is a polymer with an ionisable group (Gowariker et al, 2003) that binds water. It is also called a hydrogel (Kabiri et al, 2009). One example is polyacrylic acid crosslink, char and decompose while heated and does therefore not behave as a thermoplastic, but as a polyelectrolyte (Gowariker et al, 2003).

38. Polyacrylic acid (PAA), superabsorbent polymer

**Global annual production**

Approximately 300,000 tons of poly(acrylic acid) and poly(methacrylic acid) per year, with acrylic acid being the most important (Gnanou and Fontanille, 2008). Close to 2 million tons superabsorbent polymers are produced per year (Emerging Technologies, 2010). Polyacrylic acid is the primary superabsorbent polymer (Elias, 2002).

**Polymerisation**

Polyacrylic acid (superabsorbent polymer) can be made by aqueous solution polymerisation of acrylic acid which is partially neutralized by sodium hydroxide (Kabiri et al, 2009). Initiators, e.g. a mixture of ammonium peroxydisulfate and tetramethylenediamine are used (Elias, 2002). A small amount of cross-linkers e.g. polyethylene glycol dimethacrylate (PEGDMA) or N,N'-methylenebisacrylamide are used (Kabiri et al, 2009; Elias, 2002).

**Monomer concentrations**

Only one monomer is used.

Example: Acrylic acid (15.0 g), PEGDMA (0.04 g), sodium hydroxide solution (6.25 g NaOH in 20 mL H₂O) (Kabiri et al, 2009). This gives less than 0.3 wt% crosslinker and is therefore omitted in the ranking.

**Monomer synthesis**

Acrylic acid
Ex 1: ← acrolein (oxidation) ← propylene (oxidation) (Fink, 2007).
Ex 2: ← ethylene cyanhydrin and sulphuric acid (reaction) (Gowariker et al, 2003).

**Applications**

Polyacrylic acid is used as a superabsorbent polymer (SAP) in e.g. hygienic products such as baby napkins and other napkins; agricultural applications as soil additives to retain moisture in the soil; water blocking tapes to keep away moisture from e.g. underwater cables; oil/water separation removing water from fuel tanks and filters; liquid spill absorption, meat and fish package linings to keep packaging dry; pesticide gels, solidifier for human toilet waste etc (Elias, 2002).
**Initial assessment**
Results for PAA polymers, based on monomer classifications.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Hazard score</td>
<td>230</td>
</tr>
<tr>
<td>Highest hazard level</td>
<td>III</td>
</tr>
<tr>
<td>Assessment</td>
<td>Medium hazard (3).</td>
</tr>
</tbody>
</table>

The monomer acrylic aid is very toxic to aquatic life (acute 1; III) and is skin corrosive (cat. 1A; III). The initiator part ammonium persulphate is i.a. skin and respiratory sensitising (cat. 1; IV).

The polymer is to a large extent used as absorbing material in napkins, which is used in contact with skin.

The global annual production is of medium size.
## Table D. Summary of results

<table>
<thead>
<tr>
<th>Results</th>
<th>Hazard classification (hazard level)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Most hazardous polymers</strong></td>
<td>PUR (the most common type), PAN, PVC, epoxy, ABS, SAN, and HIPS. Mainly carcinogenic and mutagenic (cat. 1A and 1B) (V).</td>
</tr>
<tr>
<td><strong>Least hazardous polymers</strong></td>
<td>PP, PVAc, EVAc, LLDPE, HDPE and LDPE. May cause drowsiness or dizziness and/or extremely flammable (II).</td>
</tr>
<tr>
<td><strong>Most health hazardous monomers</strong></td>
<td>acrylamide, ethylene oxide, propylene oxide, 1,3-butadiene, 4,4-methyleneedianiline, epichlorohydrin, BBP (plasticizer!), and vinyl chloride. Mainly carcinogenic and mutagenic (cat. 1A and 1B) (V).</td>
</tr>
<tr>
<td><strong>Most environmental hazardous monomers</strong></td>
<td>m-phenylenediamine (for MPD-I), p-phenylenediamine (for PPD-I), 1,4-dichlorobenzene (for PPS), and BBP (plasticizer!). Very toxic to the aquatic environment with long lasting effects (IV).</td>
</tr>
<tr>
<td><strong>Substances under evaluation for endocrine disrupting properties</strong></td>
<td>styrene (for EPS, ABS, SAN, HIPS and UP example); bisphenol A (for polycarbonate, the main epoxy resin DGEBPA); and epichlorohydrin (for the main epoxy resin DGEBPA) Could be ranked as more hazardous if the evaluation concludes endocrine disrupting properties.</td>
</tr>
<tr>
<td><strong>Most health hazardous solvents</strong></td>
<td>benzene (for PPE, some LDPE and PMMA); hexamethylphosphoramide (for PPD-T); N-methylpyrrolidone (for MPD-I, PPD-T, and PPS); N,N-dimethylacetamide (for MPD-I), N,N-dimethyldiformamide (for PAN); and naptha (for PP). Mainly carcinogenic, mutagenic and toxic for reproduction (cat. 1A and 1B) (V).</td>
</tr>
<tr>
<td><strong>Most environmental hazardous solvents</strong></td>
<td>methanol (for some LDPE, Nylon 6.6); cyclohexane (LLDPE, HDPE); heptane (for HDPE, PP); isooctane (for HDPE); and 1,2-dichlorobenzene (for PPE, TPU) Very toxic to the aquatic environment with long lasting effects (IV).</td>
</tr>
<tr>
<td><strong>Most hazardous initiators</strong></td>
<td>potassium persulphate, benzoyl peroxide and ammonium persulfate Respiratory and/or skin sensitizing (cat. 1) (IV).</td>
</tr>
<tr>
<td><strong>Most hazardous catalysts</strong></td>
<td>tibutyltin (for PUR); zinc oxide (for PBT, PC and PET); and copper chloride (for PPE). Antimony trioxide (for PC and PET) Very toxic to the aquatic environment with long lasting effects (IV).</td>
</tr>
<tr>
<td><strong>Most hazardous raw material for monomer synthesis</strong></td>
<td>benzene and butadiene used to make 13 of the monomers used in 16 of the polymers. Mainly carcinogenic and mutagenic (cat.1A and 1B) (V).</td>
</tr>
<tr>
<td><strong>Non-classified monomers (Ncm)</strong></td>
<td>21 of 61</td>
</tr>
<tr>
<td>5 monomers not classified and lack SIDS initial assessment reports:</td>
<td>PTFE (100 wt% Ncm); PPD-T, MPD-I, and Nylon 6.10 (&gt; 60 wt% Ncm).</td>
</tr>
<tr>
<td>SIDS reports indicate elevated concern or has data gap.</td>
<td>Nylon 12 (100 wt% Ncm); PBT (38 wt% Ncm); TPU (&gt;6 wt% Ncm); LLDPE (10 wt% hexane or octane Ncm); PC with diphenyl carbonate (50 wt% Ncm). For 10 non-classified monomers.</td>
</tr>
<tr>
<td>SIDS reports indicate low level of concern.</td>
<td></td>
</tr>
<tr>
<td><strong>Level V-classifications in number of polymers</strong></td>
<td>16 of 55</td>
</tr>
<tr>
<td><strong>Level IV-classifications in number of polymers</strong></td>
<td>31 of 55</td>
</tr>
<tr>
<td><strong>Most common classifications among the monomers in the polymers</strong></td>
<td>Allergic skin reaction (IV); respiratory, skin, or eye irritation (II); toxic if inhaled, if swallowed or in contact with skin (III); and may cause cancer (V).</td>
</tr>
<tr>
<td><strong>Polymers with largest global annual production (million tons)</strong></td>
<td>PP (45), LDPE &amp; LLDPE (39), PVC (37), PET (plastics &amp; fibres) (33), HDPE (32), PS (13).</td>
</tr>
<tr>
<td><strong>Most hazardous polymers with high global annual production (million tons)</strong></td>
<td>PVC (37); PUR (9); ABS (7); HIPS (6.4); PAN (3); epoxy resins (1).</td>
</tr>
</tbody>
</table>
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