'We are the makers - IOT' Learning Scenario:
The Chemistry of PLA

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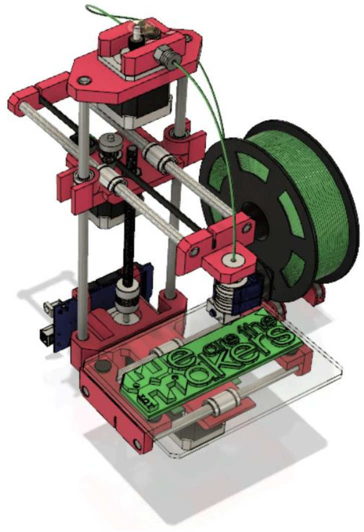
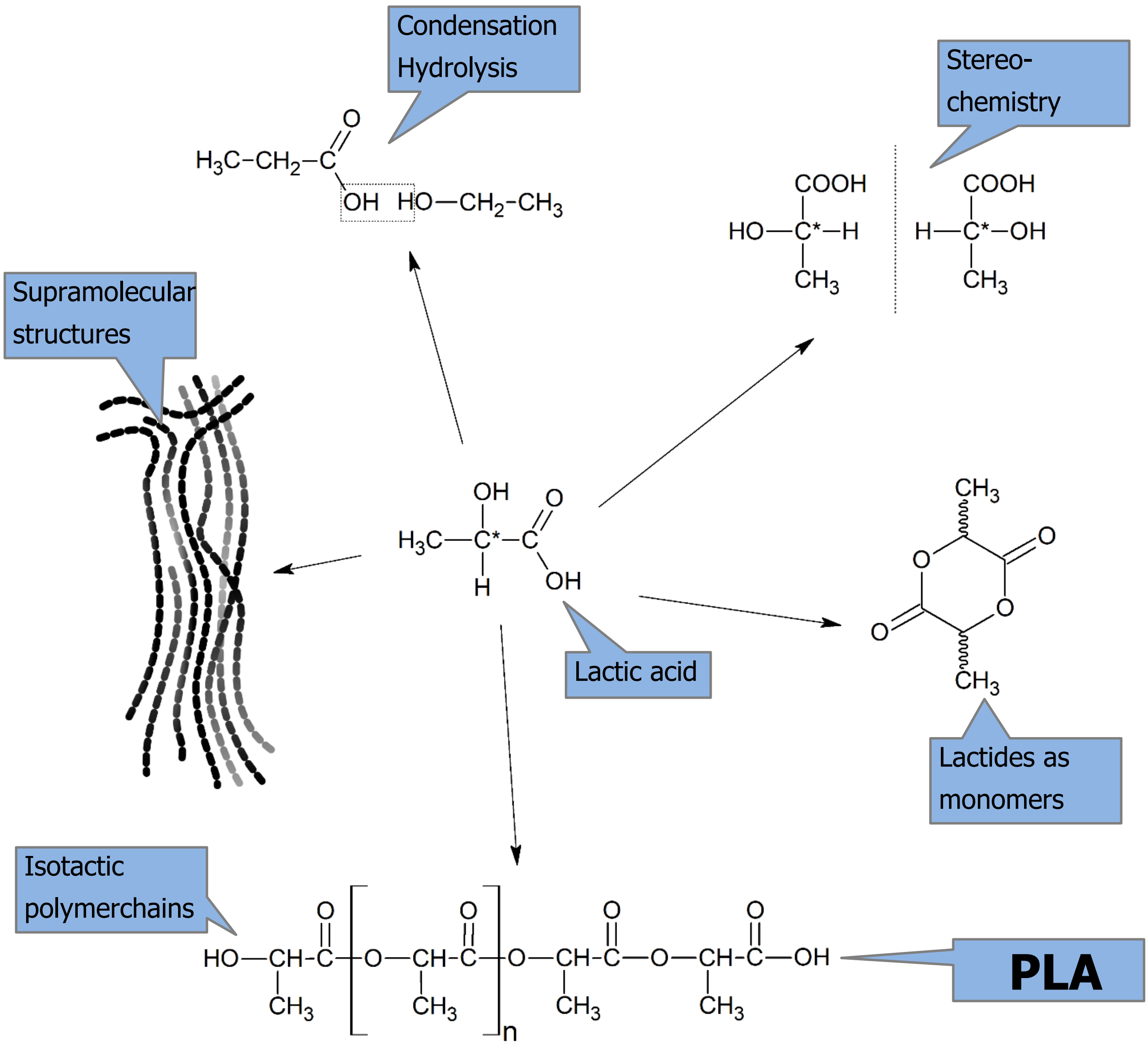
1. Title of the Scenario	**Learn the chemistry of PLA, a common 3D-printing-material**
2. Target group	16 - 18 years
3. Duration	At minimum 5 weeks of 2*45min-lessons per week: in sum about 6-8 hours.
4. Learning needs which are covered through the exercise	▪ Monomer/Polymer: lactic acid as a renewable educt for PLA ▪ Principles of condensation reactions: acid catalyzed esterification ▪ Principles of hydrolysis reaction: hydroxide catalyzed depolymerization ▪ How to build a polyester chain of PLA using tin(II)-chloride-catalysis ▪ Principles of lactic-acid stereochemistry: D- and L in fisher-projections ▪ Thermoplastic properties of PLA and the influence of stereochemistry ▪ PLA properties which are useful in 3D-printing ▪ Recycling: raw-material cycle of PLA
5. Expected learning outcomes	▪ Basic understanding of thermoplastic polymers, structure-properties-model ▪ Formation of polymers via chemically connecting monomers ▪ Influence of stereochemistry on physical properties (e.g. melting point): ▪ amorph versus semicrystalline molecule structures ▪ biocompatible and renewable plastic chemistry: engineering challenges
6. Methodologies	In this scenario students will learn PLA as a 3D-printing material which is renewable and recyclable. Learning goals are how these properties can be achieved from a chemical point of view.
7. Place/ Environment	▪ a molecular model set (for lessons on stereochemistry) ▪ A projector for teaching tutorials and presenting students works; ▪ worksheets on stereochemistry, esterification, polymer-forming, ▪ each student has to keep a laboratory journal

8. Tools/ Materials/ Resources	About 3-4 3D-printers in a laboratory environment: students need to print the materials for their chemical experiments by themselves  the following reagents: ▪ Isopropanol ▪ tin-(II)-chloride ▪ Universal indicator ▪ 0,01M NaOH-solution ▪ acetic acid (100%) or better acetic anhydride ▪ ethanol (can be methylated) ▪ concentrated sulfuric acid (in case of anhydride: semiconc.) ▪ lactic acid (D-lactic acid or L-lactic acid, enantiopure) ▪ Kalium hydroxide pellets ▪ Aluminium hydroxide ▪ Natural (uncolored) PLA-filament for the 3D-printer The following laboratory equipment: ▪ Magnetic stirrers ▪ Three-neck round bottom flasks ▪ Erlenmeyer flasks ▪ Grahams condensers ▪ Beakers ▪ Bunsen burners or heating guns ▪ Infrared thermometers ▪ Pipettes ▪ Tripods About 3-4 computers with the following software preinstalled: ▪ Autodesk Fusion 360 (or any other 3D-modeling-Software, e.g. Wings3D) ▪ CURA slicing software, ▪ An internet connection

Overview about the chemical topics covered throughout this lesson:
from lactid acid to PLA



9. Step by step description of the activity/ content

Lesson 1 & 2 (90min): Intro to the chemistry of 3D-Printing

A 3D-printer with PLA-filament is introduced.

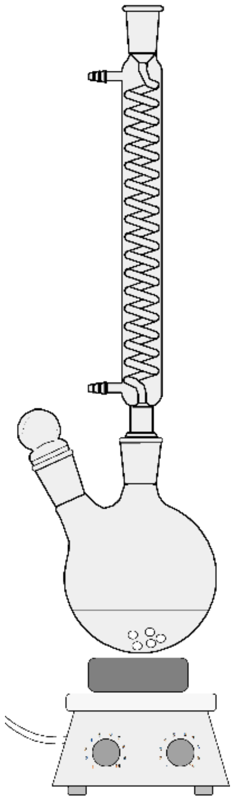
Central topic is the so-called filament. It consists of PLA, which stands as an abbreviation for "polylactic acid". It cannot be found in nature, but it can be synthetized from a natural compound: lactic acid.

After usage (at the end of its lifecycle) it can be recycled in two ways: Hydrolysis to lactic acid again or composting because of its biodegrability.

Much effort is done in research of optimizing the physical properties of PLA. Students brainstorm, what kind of properties are desirable, what properties have to be avoided or at least optimized.

Information for the teacher: "natural", uncolored PLA was used with the following properties: Typical Molar mass of PLA ca. 217kg/mol (217.000g/mol; degree of polymerisation n≈3000 *(NatureWorks LLC, NW2002D)*

How to synthetize PLA, STEP 1: Esterification of Ethanol and Acetic Anhydride.



Students take a smell on the educts ethanol and acetic anhydride (with caution; **wafting technique**). After that, the two educts are filled in equal amounts into a standard reaction apparatus. Some boiling stones are added and at the very end two drops of sulfuric acid are poured into the flask. The grahams cooler is started and then the mixture can be heated with caution (heating mantle, **NO Bunsen burner**! Ethyl acetate vapor is explosive).

The reaction usually begins suddenly! (looks impressive)
After 3-4 minutes the equilibrium concentrations of product/educts are reached and the reaction flask can be cooled and shown to the students. A very characteristical smell of nail polish remover can be noticed: Ethyl acetate.

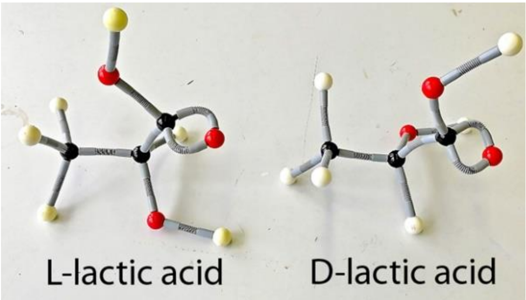
Students do standard reports of the experiment and the reaction mechanisms are discussed and practised. Esterification as a so-called "condensations reaction", since a watermolecule is separated during the reactions to form one of the two products. Practice can be motivated with the following aroma compounds (if available in laboratory):

Methyl Butyrate: pineapple aroma
Isopentyl Butyrate: apple aroma
Ethyl propylate: pear aroma

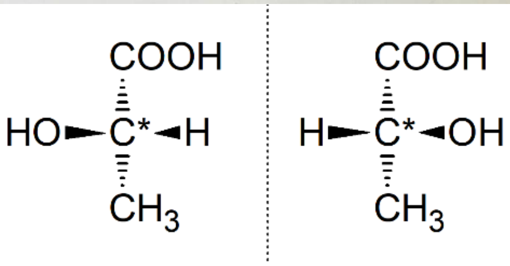
Lesson 3&4 (90 min): Lactic acid, the raw material of PLA

Lactic acid is introduced as a chemical compound and as a molecule. Teacher gives a short overview about the characteristics as a natural compound.

Reaction mechanism of protolysis: acid reaction of lactic acid and water.
Also, the pK_A-values of propionic acid and lactic acid can be compared: pK_A(propionic acid) = 4,75, pK_A(lactic acid) = 3,9. This difference is caused by the inductive effect of the hydroxide-group in alpha-position: Lactic acid is an alpha-hydroxy-carboxylic acid. Meaning of alpha-hydroxy and alpha-amino carboxylic acids in natural chemistry are discussed.



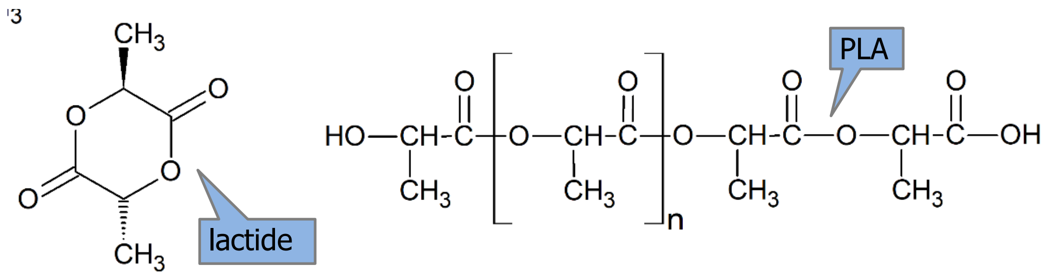
Introducing stereochemistry:
students will build the lactic acid molecule using a molecular model set. They have to compare their models. Probably some students will recognize that there exist two different molecules which can be distinguished from each other.



Students are encouraged to describe the aspects in which those two molecules differ: on carbon-2 (alpha-carbon) the ligands can differ in their geometric arrangement. Fisher projections of lactic acid are introduced. Stereochemistry has to be practiced in detail! Students have to build models until they have fully understood the topic.

Lesson 5&6 (90 min) Esterification of lactic acid: two possibilities

Students shall do a practice on esterification again, this time with lactic acid as the educt. Some of the students will recognize that there are many possibilities to do the reaction: Since lactic acid has exactly those two necessary functional groups for esterbuilding combined in one single molecule, the reaction products are not clearly defined.



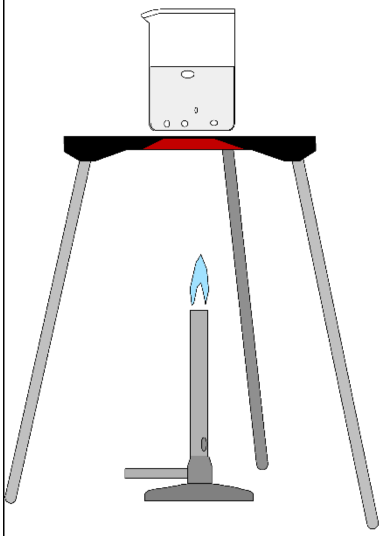
Students in this class level should be able to make some predictions of the compound properties. The lactide should dissolve in water because it can build H-bonding to water molecules. In fact, lactides dissolve in water.

The second molecule is a linear chain. It also has the ability to form H-bonds, but since it is a nearly endless molecule, it should be a solid compound.

Introducing Polymer-chemistry:
this nearly 'endless chain' is build of thousands of single lactic acid molecules, which are called 'monomers' in this context.

Polymer formation through polycondensation
Many chemically bonded monomers form a polymer, which generates new properties – although similarities of the monomer can also be found.
Building can be achieved through a repetitive condensation reaction, the so-called 'polycondensation'.

How to synthetize PLA, STEP 2: Polycondensation of lactic acid



L-Lactic acid is filled together with a catalytic amount of dry tin-(II)-chloride and some boiling stones into a beaker. Then it can be heated with a Bunsen burner inside a fume cupboard because of the lactic acid vapors.
After a few minutes the lactic acid changes color to brown, this indicates the reaction has finished.

The reaction mixture is allowed to cool down. While cooling the liquid substance solidifies:
PLLA has formed.

Attention: Since L-Lactic acid was used as the educt, the poly-L-lactic-acid should have formed, which is called as an isotactic polymer.
But: Tinchloride as a catalyst probably destroys the stereochemistry, so a racemic and therefore randomized mixture of D- and L-lactic acids were building the polymerchain. This- P-DL-LA is a atactic polymer.

Students have to discuss, why a beaker was used. (reaction water can evaporate more easily, shifting the equilibrium to the product side) How can this disadvantage be avoided? What about "lactic anhydride"? The technical process of 'ring opening polymerisation' of Lactides is introduced.

Lesson 7&8 (90 min) Physical properties of commercial PLA

Commercial available PLA has well documented physicochemical properties:

- A glass transition temperature of about 65°C
- A melting range between 160°C-200°C (depending on filament-color and PLA-crystallinity)
- It is stable in its form up to a temperature of about 70-80°C. This temperature is called heat deflection temperature (HDT).
- A Density of 1,25 g/cm^3

These properties can be experimentally analysed by the students to answer the following questions:

a) What kind of properties must a 3D-printing material have?
(must be solid and durable at low temperatures, liquid at moderate high temperatures)

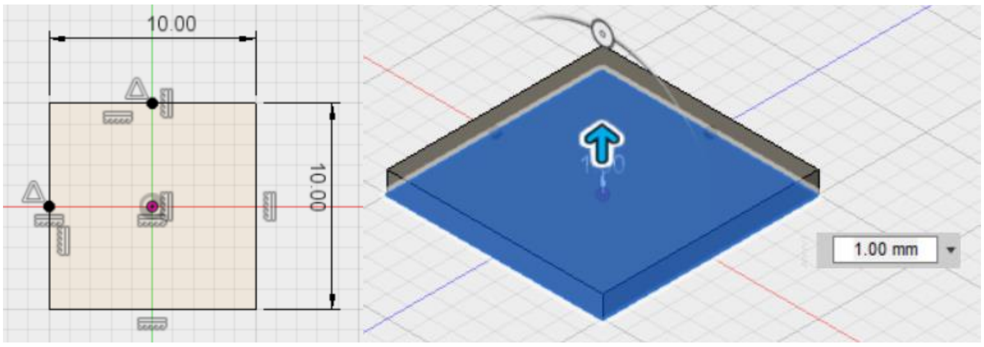
b) What is the optimal temperature range for 3D-printing?
(about 200°C, safely above the melting temperature, which can vary. Depending on Filament)

c) Why could it be a good idea to heat the bed while printing?
(to avoid warping: small thermal expansion coefficient, since thermal contraction causes warping)

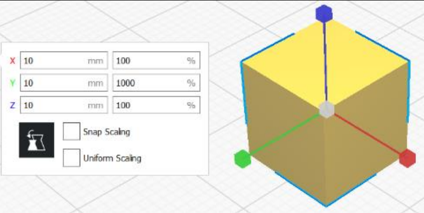
d) What is the optimal temperature for the heat bed? (keywords "first layer adhesion")
(the heat bed temperature must be below the heat deflection temperature)

<u>Experiments on physical properties:</u>

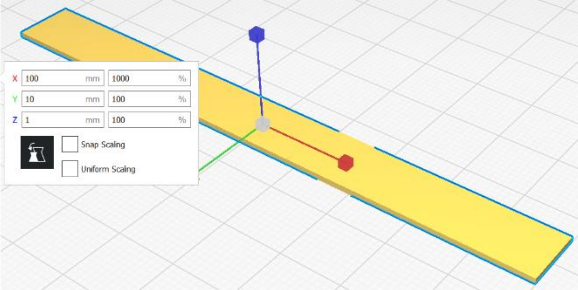
Students should prepare some easy printing parts for measuring the thermoplastic and physical properties of PLA. Screenshot of Fusion 360:



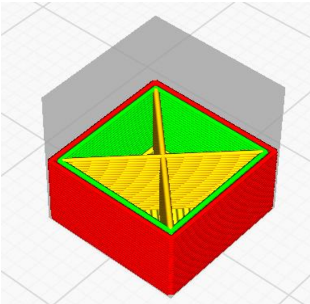
This very simple geometric chip can easily be modified inside the slicing software to fit the particular needs for the experiment:



a) Standard 1cm^3-cubus for measuring the density.
Printing time with 100% infill: 9min on an Anycubic I3 Mega.



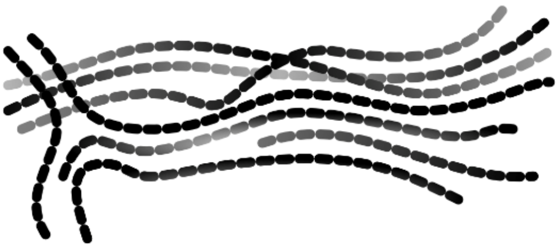
b) same volume, different shape: measuring the heat deflection temperature HDT: Put into water with different temperatures and monitor the flexibility.
Printing time: 100% infill, 9min on an Anycubic I3 Mega.



c) This hollow cubus can be used for measuring the melting temperature range: the cubus is put on a laboratory tripod with ceran glass and is heated with a Bunsen burner from below or a heat gun from above. Temperature can be taken with an infrared thermometer.

Printing time: 1cm x 1cm x 1cm, infill 10%, cross-fill, 4 minutes.

Chemical explanation on molecule level:
These so called thermoplastic properties are caused by the behaviour of the polymer molecules:



linear polyester chains are beginning to move with increasing temperature, but are still solid over a wide range. This is caused by intermolecular interactions (here: Van der Waals-interactions). These properties depend strongly on monomer properties and chain-length; both affect the interaction between the single polymer chains.

After cooling the thermoplast will retain its stability again: switching between flexible and solid properties depending on the temperature is a reversible process.

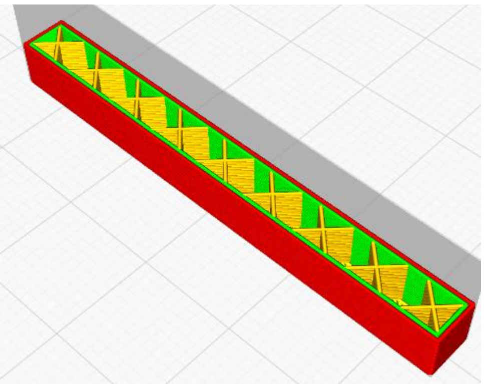
Advanced polymer topic:
the influence of stereochemistry on polymer properties. Differentiate between:

- atactic polymer chains through polymerisation of racemates, resulting compound property is very soft because of amorph chain distributions

- Isotactic polymer chains through polymerisation of enantiopure educts, resulting in strong and stable compounds because of semicrystal effects

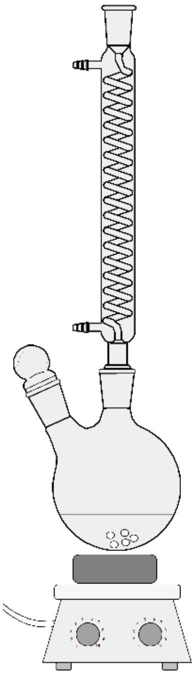
- Block-Copolymeres, consisting of PLLA / PDLA-chains, resulting in very strong chain-to-chain interactions.

Lesson 9&10 (90 min) Recycling: Hydrolysis and composting of PLA



Model: X: 5mm x Y: 50mm x Z: 10mm, Print interrupted after 50%, so actual Z-height is 5mm. 20% cross-infill. Printing time 4min on an Anycubic I3 Mega.

This object has a large surface and can easily be dissolved and composted.



Experiment 1: complete hydrolysis of PLA in a mixture of KOH / isopropanol

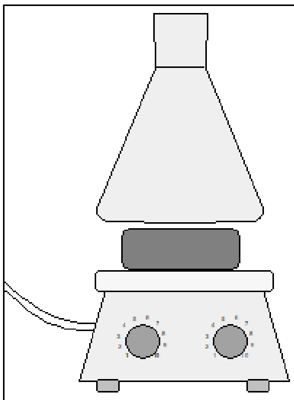
2,5g KOH is dissolved in 50ml isopropanol while stirring and heating to ca. 60 -70°C (boiling point of isopropanole 82°C). A catalytic amount of Aluminiumhydroxide can be added, it accelerates the reaction.

While heating and stirring, one or more PLA-sticks are added. After ca. 10 minutes, the PLA has completely decomposed. During the depolymerisation process, kalium lactate is built, which is an flavour enhancer (E326).

caution (heating mantle, **NO Bunsen burner**! Isopropanol vapor is explosive).

If possible, verification of lactate can be done using this procedure: http://www.bdsoft.de/demo/index.htm?/demo/chemie/analytik/arzneibuchmethoden/identitaetspruefungen/lactat.htm

Co-funded by the Erasmus+ Programme of the European Union

	Experiment 2: changing of pH-value of pure water during hydrolysis of PLA 100ml deionised water are filled in an Erlenmeyer flask. Universal indicator is added. If color of the pure water is not green (pH 7), some drops of 0,01M NaOH-solution is added until color changes to green. Then a PLA-stick is added and the mixture is heated to 100°C. After ca. 5min the color of the universal indicator is changing from green to orange, indicating lactic acid as a product of depolymerisation of PLA.
10. Feedback	At the end, students should have a well-grounded knowledge of the commonly used thermoplastic compound PLA and its impact on 3D-printing. They have experienced by themselves chances and limitations of current technology. And: during the lesson, important aspects of the curriculum in chemistry have been taught: Introductory biochemistry, stereochemistry, polymer synthesis, physical properties of polymers, polymer recycling, impact on the environment.
11. Assessment & Evaluation	Students keep their labor journal, which can be reviewed by the teacher. Students can also present the results of their experiments. In addition, a standard in-class-test has to be conducted at the end of the lessons.