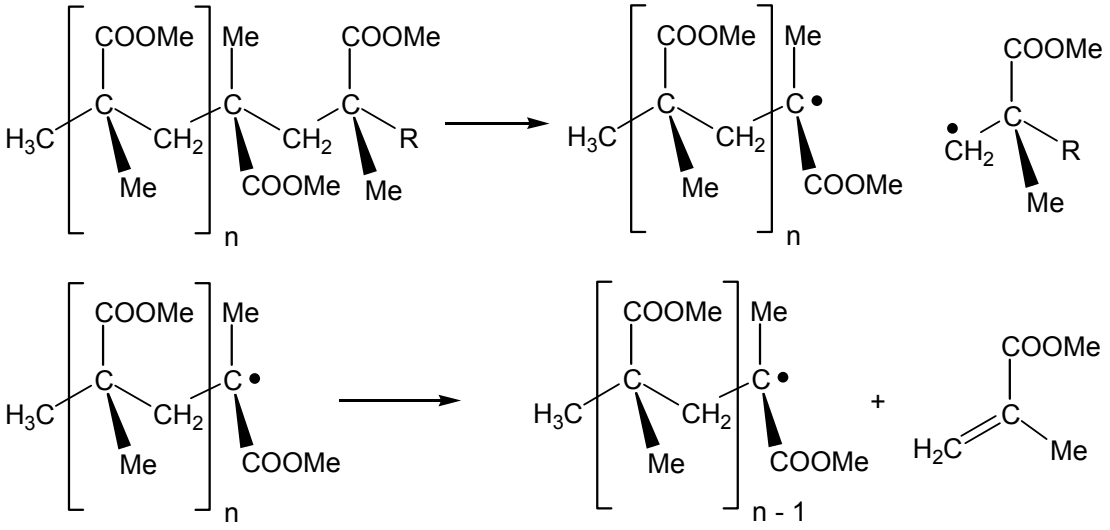
Problem 38: Recycling of polymethylmethacrylate

Introduction

The regeneration of monomers from plastic waste followed by their repolymerization is an ideal recycling method, especially when the plastic waste is dirty, variously coloured or contains filling materials. Unfortunately, only a few polyolefins depolymerize into their monomers when heated. One example is polymethylmethacrylate (PMMA, Plexiglas), a plastic that starts to depolymerize into its monomers at 150°C. At temperatures between 300°C to 350°C, the reaction is quantitative, the polymer chains are decomposed consecutively and the formation of the fragments is not statistical:



In the case of polymethylmethacrylate, the reformation of monomers proceeds in a high yield, as during the pyrolytic degradation tertiary radicals are formed from the quaternary carbon atoms. These are more stable and chemically less reactive than the corresponding secondary and primary radicals. Hence, degradation is the preferential reaction compared to other radical reactions such as recombination.

Subsequent polymerization of the purified monomer gives a product that cannot be distinguished from the starting material.

Equipment

Bunsen burner
2 small test tubes (diameter ca. 3 cm)
rubber stopper that fits to the test tube with a hole bored through
a right-angled bent glass tube (inner diameter ca. 0.5 cm) that is passed through the hole of the stopper
test tube (diameter ca. 2.0 cm)
rubber stopper that fits to the test tube with a hole bored through
a straight glass tube (reflux condenser, inner diameter ca. 0.5 cm) that is passed through the hole of the stopper
ice water bath (for cooling)
distillation apparatus with thermometer and 50 mL distillation flask
sand bath on heating plate or heating mantle (50 mL)
stand

Chemicals

30 g Polymethylmethacrylate (pulvarized) or
30 g Polymethylmethacrylate-waste (for example covers of rear lamps that have been pulvarized)
0.6 g dibenzoylperoxide ($C_{14}H_{10}O_4$)

Safety measurements: Hazard Symbols and Safety Codes

The experiment should be carried out in a fume hood. Avoid inhaling methyl methacrylate produced in the experiment and do not allow it to come into contact with the skin.

methyl methacrylate	irritant Xi, highly flammable F
	R 11, 37/39, 43; S 24, 37, 46
dibenzoylperoxide	irritant Xi, explosive E
	R 2, 36, 43; S 3, 7, 14, 24, 26, 36/37/39

Procedure

Fill a weighed test tube with small pieces of polymethylmethacrylate-waste to about one third and weigh the filled tube. Set up the apparatus shown in figure 1. The apparatus should be clamped to a stand.

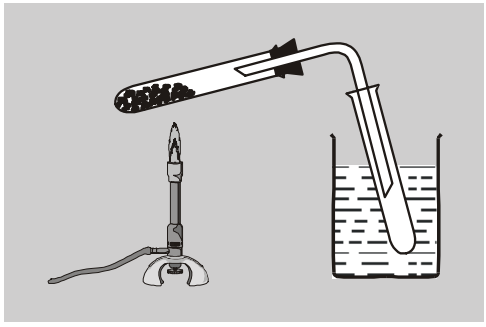


Figure 1: Experiment set-up for the pyrolysis of polymethylmethacrylate.

Heat the test tube containing the plastic waste carefully with a Bunsen burner (move the Bunsen burner continually to ensure uniform heating of the plastic and to prevent the liquid foaming). If bubbles are formed in some parts of the melt, heat more strongly but do not overheat. Overheating causes effervescence of the melt and the resulting vapour can no longer be condensed. In the cooled test tube a fruity smelling liquid is formed which can have a variety of colours, depending on the nature of the dyes carried over with it.

Transfer the liquid to a distillation flask, add boiling chips and support the flask on a sand bath arranged in a way that the level of the sand is about the same height as the condensate. Distill under atmospheric pressure and collect the methyl methacrylate. The product is a colourless liquid. Determine the boiling point of methyl methacrylate.

Place 8 g of the purified methyl methacrylate into a large, carefully dried test tube, add 0.6 g of dibenzoylperoxide and mix the two components using a glass rod. Place a rubber stop containing a straight piece of glass tubing, that will act as a condenser, in the neck of the test tube and clamp it to a stand. Heat the mixture cautiously with a small Bunsen flame till an exothermic reaction takes place. Within minutes, a hard and bubbly plastic is formed.

Disposal:

Test tubes that were used for the depolymerization can be reused in the same experiment, as any plastic residual in them will not interfere with any subsequent reaction.

Sources of error
In some cases, the repolymerization does not readily take place. If there is no observable reaction, the mixture should be heated in a water bath for about 10 minutes.

38.1 Determine the experimental yield of the isolated methyl methacrylate in g.

38.2 Determine the theoretical yield of methyl methacrylate in g.

38.3 Calculate the yield as a percentage of the theoretical yield.

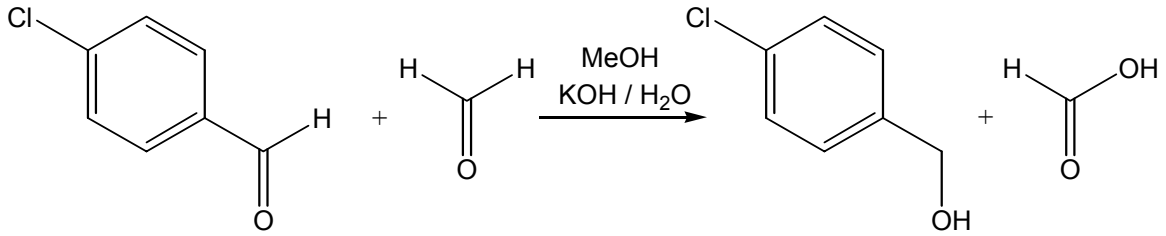
38.4 Determine the refractive index of the isolated pure methyl methacrylate.

38.5 What is the boiling temperature of methyl methacrylate under standard pressure?

38.6 Write down the polymerization reaction using the decomposition of dibenzoyl-peroxide as the initial step.

Problem 39: Synthesis of *para*-chlorobenzyl alcohol – an example of the Cannizzaro Reaction

Introduction
The Italian scientist Stanislao Cannizzaro (1826-1910) was a professor at the Technical Institute of Alessandria (1851) and subsequently held professorships at Genoa (1855), Palermo (1861), and Rome (1871). In Rome, he also became a member of the senate and of the council of public instruction. He is known for his discovery of cyanamide, for obtaining alcohols from aldehydes – an organic reaction named after him – and for distinguishing between molecular and atomic weights.
The Cannizzaro reaction is a base-catalyzed disproportionation reaction of aromatic or aliphatic aldehydes with no α-hydrogens to the corresponding acid and alcohol. In this disproportionation reaction, one molecule of aldehyde oxidizes another to the acid and is itself reduced to the primary alcohol. Aldehydes with an α-hydrogen do not react in this manner, since for these aldehydes the aldol condensation is much faster.



In cases where two different aldehydes are used, the reaction is called a crossed Cannizarro reaction. In the present reaction of *para*-chlorobenzaldehyde with formaldehyde, the latter reduces the sooner to the corresponding alcohol, here *p*-chlorobenzylalcohol, and is itself oxidized to formic acid.

List of Equipment

three-necked flask (250 mL)	reflux condenser
dropping funnel	internal thermometer
magnetic stirrer with heating plate	magnetic stirrer bar

water bath on heating plate
heating mantle (250 mL) or sand bath on heating plate
vacuum filter (Ø 5 cm) or Hirsch funnel
Bunsen burner
test tubes
beaker (500 mL and 250 mL)
glass rod
vacuum filtration apparatus
chromatography tank
capillary tubes

List of Chemicals

para-chlorobenzaldehyde
potassium hydroxide
distilled water
formalin (aqueous formaldehyde solution, 37%)
light petroleum ether (boiling range 40-70°C)
TLC plates (silica gel 60 F254)
methanol
ethanol
ethyl acetate

Safety measurements: Hazard Symbols and Safety Codes

para-chlorobenzaldehyde	harmful Xn, dangerous for the environment N, R 22, 36/38; S 22, 26, 37/39
methanol	highly flammable F, toxic T R 11, 23/25; S 7, 16, 37/39
potassium hydroxide	corrosive C R 22, 35; S 26, 36/37/39, 45
ethanol	highly flammable F R 11; S 7, 16
ethyl acetate	highly flammable F, irritant Xi R 11, 36, 66,67; S 16, 26, 33
formalin (37%)	toxic T R 23/24/25, 34, 39, 40, 43; S 26, 36/37/45, 51
light petroleum ether	highly flammable F, harmful Xn, dangerous for the environment N, R 11, 20, 38, 48, 51/53, 62, 65, 67; S 26, 36/37/45, 51
para-chlorobenzylalcohol	harmful Xn, dangerous for the environment N, R 22, 36/38, 51, 53; S 23, 26, 61

Procedure

Place 28.1 g of *para*-chlorobenzaldehyde into a 250 mL three-necked, round bottomed flask containing a magnetic stirrer bar and fitted with a reflux condenser, an internal thermometer, and a dropping funnel that contains a solution of 33.7 g of potassium hydroxide in 25 mL of water. Add 60 mL of methanol and 21 g of formalin. Support the flask in a water bath arranged in a way that the level of the water in the bath is at about the same height as the reaction mixture. Stir and heat the solution. When the internal temperature rises to 65°C, remove the heating source and add the solution of potassium hydroxide dropwise. Ensure that the temperature remains between 65°C and 75°C. If necessary, cool the flask with a cold water bath. When the reagent has been added, heat the reaction mixture for 40 minutes at 70°C followed by further 20 minutes under reflux. If necessary, use a heating mantle or a sand bath instead of the water bath.

Allow the reaction mixture to cool down to ambient temperature, transfer the reaction mixture to an appropriate beaker and add 100 mL of water to induce crystallization. Collect the crude product via vacuum filtration. Wash the crude product with several small aliquots of cold distilled water. Reserve a small sample of the crude product for use in the TLC and for the determination of the melting point.

Recrystallize the crude product from an appropriate solvent, collect the purified crystals by vacuum filtration, dry the product and determine its melting point.
In order to determine the appropriate solvent for the recrystallation, place small samples of the crude product in test tubes and recrystallize them from the following solvents:

1. water
2. water : ethanol (5 : 1)
3. ethyl acetate : petroleum ether (1 : 5)

The procedure of the recrystallization from ethyl acetate / petroleum ether is different from standard recrystallization techniques. Dissolve the sample in ethyl acetate at room temperature and slowly add fives times the volume of petroleum ether.
The purity of the crude product and of the recrystallized product are determined by thin-layer chromatography (silica gel 60 F254) using petroleum ether, ethyl acetate or a mixture of these two solvents as the eluting solvent. As a reference, run the starting material on the same plate.

Sources of Error
The starting material *para*-chlorobenzaldehyde is a solid that is most conveniently transferred in the liquid state by heating the whole storage bottle in a warm water bath. The melting point of *para*-chlorobenzaldehyde is 47.5°C .
If no crystals of the crude product form or an aqueous emulsion or an oily substance are formed, scratch the base and side of the beaker with a glass rod to initiate crystallization.

39.1 Which is the most appropriate solvent or solvent mixture for the recrystallization?

39.2 Describe the appearances and the colours of the crystals.

39.3 Determine the melting points of both the dried crude and recrystallized products.

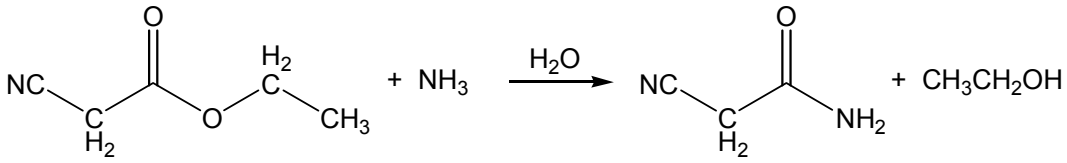
39.4 Which is the most appropriate solvent or solvent mixture for the thin-layer chromatography (silica gel 60 F254) to obtain R_f-values between 0.3 and 0.7?

39.5 Determine the respective R_f-values.

39.6 Describe the reaction mechanism.

Problem 40: Ammonolysis of an activated carbonic acid ester: synthesis of cyano acetamide

Introduction
Unsubstituted amides are readily prepared by the ammonolysis of carboxylic acid derivatives, e.g. esters, as they are more reactive than the corresponding free acid. Thus, the reaction using carboxylic acid derivatives can be carried out under milder conditions. Esters are amongst the most reactive , particularly when the carbonyl group is further activated by electron-attracting groups. The latter are termed activated carboxylic acid esters. Cyanoacetic ethyl ester is an example of an activated carboxylic acid ester that readily reacts with ammonia easily to give the corresponding amide.



List of Equipment

magnetic stirrer with heating plate	magnetic stirrer bar
Erlenmeyer flask (250 mL)	beaker (250 mL)
2 pipettes (10 mL) with pipette control	thermometer
vacuum filter (Ø 5 cm) or Hirsch funnel	dropping funnel
vacuum filtration apparatus	crystallizing dish or beaker
graduated measuring cylinder	balance (precision 0.01 g)
spatula,	stand

List of Chemicals

cyanoacetic ethyl ester	aqueous ammonia (25 %)
ethanol	distilled water
ice	

Safety measurements: Hazard Symbols and Safety Codes

aqueous ammonia (25 %)	corrosive C, dangerous for the environment N R 34, 50; S 26, 36/37/39, 45, 61
ethanol	highly flammable F R 11; S 7,16

Procedure

Place 32.0 mL (0.3 mol) of cyanoacetic ethyl ester into a 200 mL Erlenmeyer flask equipped with a magnetic stirrer bar and an internal thermometer. Support a dropping funnel, containing 37.4 mL (0.5 mol) of aqueous ammonia above the neck of the flask. Add the ammonia solution dropwise, being careful to ensure that the temperature remains between 30 and 35 °C. If necessary, cool the flask with cold water or an ice water bath. When the addition is complete, the reaction mixture is stirred for 30 minutes at room temperature.

Cool the reaction mixture to 0°C to induce crystallization. Collect the colourless crystals on a Hirsch funnel by vacuum filtration. Transfer the remaining crystals from the flask by adding small amounts of cold alcohol. Wash the crude product with several small aliquots of chilled ethanol. Reserve a small sample of the crude product for the determination of its melting point.

Transfer the crude product into a 250 mL beaker and recrystallize it from 70 mL of hot ethanol. Upon complete dissolution of the crude product the reaction mixture should be allowed to cool to room temperature and finally cooled in an ice bath. Collect the product by vacuum filtration and weigh the dried product.

40.1 Determine the experimental yield of the cyano acetamide product in g.

40.2 Calculate the theoretical yield of the pure amide in g.

40.3 Calculate the yield as a percentage of the theoretical yield.

40.4 Determine the melting point of the crude product and of the recrystallized product.

Avoiding culture shock or **The German way of life**

People of different countries have different ways of doing things. So, to avoid culture shock, it's important to be prepared before you visit another country. Here are some notes students made after their year in Germany. This list is supposed to help you while you stay in Germany.

- Germans close room doors and pull shades.
- They worry about their health. (There's something wrong with them if they don't.)
- They get up early – and go to bed early.
- They have small refrigerators. (You shouldn't raid them.)
- There is more fresh food, less processed stuff.
- Meals are social events (so hold back with your fork until everybody is there.)
- If guests want more food, they take it. (Don't wait to be asked or you'll wait for ever.)
- Germans absolutely love mineral water.
- They would never visit other people's home without an invitation.
- They bring flowers when they visit friends. (Uneven number, no red or white roses unless in love.)
- They shake hands any time they meet people.
- They don't stand in line. (You have to push your way to the front of stores and onto trains.)
- Few people use credit cards for shopping.
- There are often restroom attendants. (They expect money.)
- Weekends are totally dead.
- German families go for long walks on Sundays.
- Germans don't waste time on polite phrases – they say what they mean.