EXPERIMENT 5

Copolymerization of styrene with maleic anhydride
(polymerization in solution)

The aim of this experiment is to get knowledge on method of polymerization in solution, method of analysis of the resulting copolymer and to get technical skills to prepare polymer.

To carry out copolymerization of styrene with maleic anhydride you have to sequentially perform the operations listed below. **The documentation of exercise also includes a resulting data sheet and worksheet (checklist) which will be marked with all the tasks, together with exact time when you started and finished any particular operation.**

1) Prepare a solution of styrene, maleic anhydride and benzoyl peroxide in acetone (quantities and concentration will be given by instructor).
2) Using a peristaltic pump transfer the monomer solution to glass reactor equipped with a removable lid, stirrer, reflux condenser and a heating mantle.
3) Turn on the stirrer and heating. Heat to a temperature of 60°C.
4) Polymerization should be carried out under reflux for 1.5 hours. During the polymerization vigorous stirring must be ensured .
   NOTE: during the implementation of step 4, go forward with points 11-12 and then continue with the points 5-10.
5) After 1.5 hours, turn the heating off and set heating mantle aside. If the reaction mixture is very viscous, add some acetone (note the added volume of acetone)
6) After cooling the reaction mixture stop the stirrer and enter the glass tip of the hose from the peristaltic pump.
7) Begin slow pumping the reaction mixture into a beaker equipped with a stirrer, containing 500 mL of methanol (methanol is a precipitant for resulting copolymer). Pump at a slow pace to allow dropwise addition of the reaction mixture.
8) After the dropwise addition (precipitation of the copolymer), continue stirring the precipitated copolymer in methanol for another 10 minutes.
9) Filtrate precipitated copolymer under vacuum, rinsing the residue on the filter with methanol. If necessary, divide the mixture into 2-3 fractions.
10) Filtered product (copolymer) put on the previously weighed filter paper sheet, sign the names of persons performing the exercise, weigh and leave to dry. After drying, weigh again. Calculate the polymerization yield in % (with respect to the sum of the monomer weights). Plot Sankey diagram (on graph paper) for 1 kg of product, remembering the drying process.

Make a material balance of the process according to the Table:

No.	Substance	In [g] [1]	Out [g][2]
1	Maleic anhydride		
2	Styrene		
3	Initiator		
4	Solvent		
5	Precipitant(MeOH)		
6	Copolymer		
7	Filtrate		
		Σ=	Σ=

11) ***This part of experiment (analysis of copolymer) is to be done simultaneously with point 4.***
Make two weighed portions of dried copolymer using analytical balance (about 0.5 g with an accuracy of 1 mg), place in conical flasks, add 20.00 ml of 0.5 M NaOH and heat on a water bath to dissolve the polymer. Allow to cool. Titrate with 0.5 M solution of hydrochloric acid using phenolphthalein as indicator. Calculate the content of maleic anhydride (% by weight, and mole) in copolymer basing on the volume of NaOH and HCl used in titrations, assuming that all of maleic anhydride in the polymer was hydrolyzed to maleic acid residues when heated with NaOH.

$$n_{MA} = 0{,}5*(n_{NaOH} - n_{HCl})$$

where:
n_{MA} - number of moles of maleic anhydride in the titrated sample,
n_{NaOH} – number of moles of NaOH contained in twenty milliliters added to the sample,
n_{HCl} - number of moles of HCl consumed in the titration of excess NaOH,

$$m_{MA} = n_{MA}*M_{MA} = 0{,}5*(n_{NaOH} - n_{HCl})*M_{MA}$$

where:
m_{BM} - mass of maleic anhydride in a sample,
M_{BM} – molar mass of maleic anhydride,

$$\%_{mass\ MA} = m_{MA}/m_{wp} * 100\ \%$$

where:
m_{wp} – mass of weighed portion taken to analysis.

[1] The materials entering the process.
[2] The materials leaving the process.

Results Sheet **date:.....**

EXERCISE 5

COPOLYMERIZATION OF STYRENE WITH MALEIC ANHYDRIDE
(polymerization in solution)

THE MATERIAL BALANCE:

Lp.	Substance	In [g]	Out [g]
1	Maleic anhydride		
2	Styrene		
3	Initiator		
4	Solvent		
5	Precipitant (MeOH)		
6	Copolymer		
7	Filtrate		
		Σ=	Σ=

The titer determination of NaOH concentration:
volume taken for titration:

volume of 0.500 M HCl used: 1. .....mL 2. .....mL
calculation of the titer:

mass of copolymer samples1. ..... 2. .....

volume of HCl consumed in titrating the excess NaOH in solutions of weighed copolymer samples:
1. .....mL 2. .....mL

Calculate the content of maleic anhydride (% by weight, and mole) in copolymer:

PROPOSED STRUCTURE OF THE COPOLYMER:

Signature of instructor

The report of the exercise should include:

1. **Purpose of the exercise**

2. **Description of the experiment, including:**

a. general scheme of the apparatus (according to the rules posted on the website)

b. concise description of performed operations,

c. raw data (results sheet / data protocol signed by the instructor),

3. Results development:

a. chemical equations*,*

b. calculations,

c. Sankey diagram (according to the rules posted on the website)

d. Gantt chart (according to the rules listed below)

4. **Discussion of the results*.***

a. error sources,

b. yield,

c. proposed structure of the copolymer.

5. **Conclusions. In particular:**

a. advantages and disadvantages of this method of polymerization*,*

b. economic side of the process (propose methods which enable to recover unused reagents),

c. toxicological aspects (see material safety data sheets),

d. influence of the way of industrial process on environment, suggestions for improvement,

e. comment on whether the aims of the experiment have been achieved.

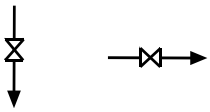
TABLE OF OPERATIONS FOR THE EXPERIMENT **Nr. 5**

(Copolymerization of styrene with maleic anhydride)

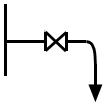
student A:……student B: ……student C:……

lp.	Step to be performed	**student**		**Time**	
				Start	**Stopt**
1	Reading the Material Safety Data Sheet (MSDS)	**all**			
2	Prepare a solution of monomers and initiator in acetone.	**A, C**			
3	Check the seals.	**B**			
4	Open the cooling water valve.	**B**			
5	Turn on the stirrer.	**B**			
6	Transfer the monomer and initiator solution into a reactor.	**B**			
7	Rinse the peristaltic pump hose with acetone.	**A**			
8	Turn on the heating mantle.	**A**			
9	Starting (initialization) of the process **(1-2 hours. At this time, please perform steps 19-23)**	**all**			
10	Turn the heating mantle off and set it aside	**all**			
11	Assemble the apparatus for precipitation	**B**			
12	Prepare the precipitant solution, turn the stirrer on.	**B**			
13	Collect the first fraction of polymer.	**all**			
14	Assemble a filtration kit.	**A**			
15	Filtrate the first fraction of copolymer.	**B**			
16	Collect the second fraction of polymer.	**B**			
17	Wash the reactor.	**A**			
18	Dry of the polymer in drier.	**all**			
19	*Preparations for the titration.*	**C**			
20	*Set the titre of NaOH on 0.500 M hydrochloric acid.*	**C**			
21	*Weigh two fractions of the copolymer, 0.500 g each.*	**A,B**			
22	*Hydrolyze the samples in hot NaOH solution.*	**A,B**			
23	*Titre of the hydrolyzed samples .*	**C**			
24	Turn the thermostat off.	**B**			
25	Turn off the cooling water.				
26	Clean the glass.	**all**			
27	Calculate of the MA content in the copolymer	**all**			
28	Check the amount of glass and equipment.	**all**			
29	Fill the data protocol to be signed by instructor.	**all**			
30	Check and clean analytical balances.	**all**			

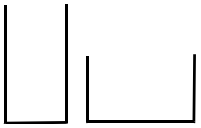
SYMBOLS USED FOR THE IMPLEMENTATION OF APPARATUS SCHEME



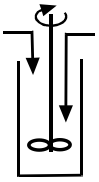
valves



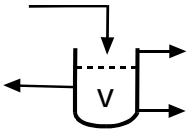
tap



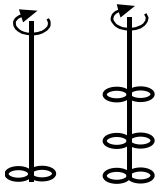
open container (horizontal and vertical)



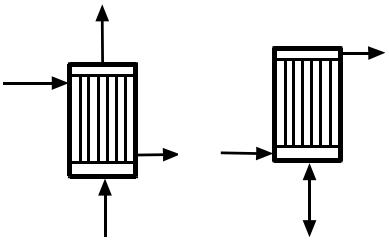
Precipitation apparatus



Filtration kit

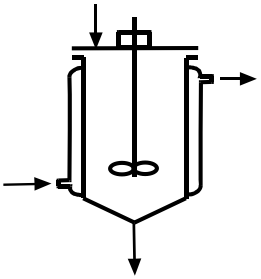


stirrers

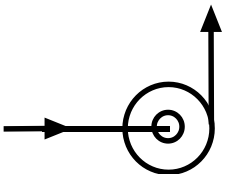


heat exchanger

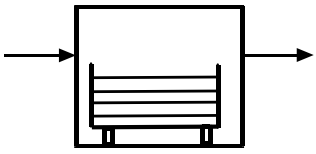
reflux condenser



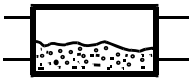
reactor with heating mantle and stirrer



pump



dryer chamber



dryer

How to prepare the Gantt's chart

The Gantt's Chart is a two-dimensional diagram applied for a visual description of the project.

From correctly-made chart we can quickly read the structure of the project, the tasks (activities) and the time of their performance (start and end time, and the order of tasks performed). Gantt Chart can be made by hand (on graph paper) or by the use of computer. It is always necessary to unambiguously determine the time intervals. To prepare Ganntt's Chart you have to use the checklist sheet on which you noticed the start time and end time of each activity.

activity name	start	end
A	8:30	8:45
B	8:35	8:45
…	….	….
…	….	….
N	12:25	12:50
O	12:50	13:00

On the axis of ordinates, please put the name of the activity and on the axis of abscissae put time scale (eg hours with division into minutes, quarters, etc.):