

**Basic Laboratory Course
For
Polymer Science M. Sc. Program**

**POLYMER SYNTHESIS
AND
CHARACTERIZATION**

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1. Experiments

1.1. Free Radical Chain Growth Polymerization

1.1.1. Bulk Polymerization of MMA with AIBN (Trommsdorff-Norrish Effect)

SAFETY PRECAUTIONS

Dangerous chemicals are used in this experiment. AIBN is oxidant (O), harmful (Xn), irritant (Xi); the monomer is harmful (Xn); DCM, methanol are harmful (Xn), toxic (T), flammable (F). The polymerization is highly exothermic and has to be conducted in the fume hood wearing personal safety equipment at all time.

REAGENTS AND MATERIALS

Name
Azobisisobutyronitrile (AIBN)
Methyl methacrylate (MMA)

PROCEDURE

6.09×10^{-4} mol AIBN and 9.99×10^{-2} mol of freshly distilled methyl-methacrylate (MMA) are added into a 25 mL round bottom flask, and shaken carefully to dissolve the initiator. Oxygen is removed by bubbling inert gas (nitrogen, argon) via a syringe through the solution. Using a 2 mL pipette, the solution is divided into five portions (3 with 2 g and 2 with 1 g) and filled into five 10 mL vials. Oxygen has to be removed again and the vials are closed with covers (do not forget to add the magnetic stir bars). The polymerization reaction is carried out in an oil bath at 70 °C (exact temperature control is important!!!). After 10, 20, 30 minutes one of the 2 g test tubes is removed from the oil bath and cooled down in an ice/salt bath. One of the 1 g test tubes is removed when gas is generated (bubbles). Write down the time (ca. 40-50 min) and take out the last sample 2 min later.

Work up: Dilute each of the samples with 2-5 ml dichloromethane. By dropping each of these solutions into 50 ml of stirred methanol, the polymers are precipitated. The precipitates are filtered with suction, washed with methanol and dried overnight at 60 °C in a vacuum oven. The next day the polymers are weighed.

FUNDAMENTAL EQUATIONS

$$V_{poly} = -\frac{d[M]}{dt} = k_{pr} \sqrt{\left(\frac{2k_{df}[I]}{k_t}\right)} [M] = k_{poly} [M_t] \sqrt{[I_t]} \quad (\text{Equ. 1})$$

$$[I] = [I_0] e^{-k_d t} \quad (\text{Equ. 2})$$

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EVALUATION

Q1. Why should oxygen be excluded?

Q2. Make a plot of the time dependence of the conversion (**P**).

The conversion is calculated from:

$$P(t) = \frac{[M]_0 - [M]_t}{[M]_0} \quad \rho_{\text{PMMa}}^{20^\circ\text{C}} = 0.944 \text{ g/ml} \quad \rho_{\text{PMMa}}^{70^\circ\text{C}} = 0.90 \text{ g/ml}$$

$[M]_0$: amount of monomer at $t = 0$

$[M]_t$: amount of monomer at time t

How would the graph look like without a Trommsdorff-Norrish effect?

Q3. The slope of the conversion vs. time plot represents the relationship ($V_{\text{Poly}}/[M]_0$). Determine the rate constant of polymerization (k_{Poly}).

From k_{Poly} and $f = 0.5$; $k_d = 2.75 \cdot 10^{-6} \text{ [1/s]}$; $k_t = 3.7 \cdot 10^{-5} \text{ [l/mol*s]}$, calculate k_{pr} and compare it with the value from the literature.

Q4. Calculate the amount of initiator, which is not dissociated at the end of the reaction and comment this.

Q5. Why is gas produced in the last two samples?

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Principles of polymerization 3rd Ed., *J. Polym. Sci. A Polym. Chem.* **1991**, 30, 7, 1508

Stanley R. Sandler, Wolf Karo, Eli M. Pearce, **Polymer Synthesis and Characterization: A Laboratory Manual**, Academic Press **1998**

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1.1.2. Suspension Polymerization of Styrene with DBPO

REAGENTS AND MATERIALS

Name
Poly(vinyl alcohol) (PVA)
Dibenzoyl peroxide (DBPO)
Styrene ($\rho = 0.909 \text{ g/mL}$)

PROCEDURE

In a 100 mL three neck flask equipped with a magnetic stir bar and a coil condenser with gas inlet, a solution of 50 mg PVA in water (30 mL) is prepared. In the beginning, the oxygen is removed by bubbling inert gas through the mixture for about 1 min using a syringe and afterwards the third neck is closed with a glass stopper. Heat the mixture to 60-70°C in an oil bath while stirring until the PVA is completely dissolved. In the meanwhile, dissolve 3.10×10^{-4} mol DBPO in 4.80×10^{-2} mol of freshly distilled styrene in a separate flask (room temperature) and pour the solution into the 100 mL flask while stirring. The stirring velocity is adjusted that the monomer mixture can form small droplets of about 0.1- 0.5 cm diameter and kept constant throughout the polymerization process. Do not stir too fast! The gas inlet on the coil condenser is connected to nitrogen and the temperature is increased to 85 °C.

Under nitrogen atmosphere take a 2 mL sample with a glass tube/syringe at reaction time $T = 0$ (end of Styrene addition), 30, 60, 90, 120, 150, 180, 240, 300 and 360 minutes. Pour each sample into 20 mL dichloromethane in a separator funnel. The organic layer is extracted with water and DCM is evaporated at the rotation evaporator to a volume of approximately 1 mL. Afterwards the polymer is precipitated in 80 mL methanol. The precipitate is filtered with suction, and dried at 50 °C overnight. After 6 h the polymerization mixture is cooled down to room temperature with stirring. Then stop stirring. After a few minutes water phase is decanted, the polystyrene pearls are filtrated, washed with methanol and water, and dried at 50 °C. Weigh the samples and calculate the total yield.

Store the samples for molecular weight determination and spectroscopy measurement.

EVALUATION

- Q1 Make a plot of the time dependence of the conversion (**P**). (see 1.1.1 Q2)
- Q2 Calculate the rate of polymerization (r_p) and comment on it. (see 1.1.1 Q3)
- Q3 What happens with the droplets if the stirring speed is adjusted too fast?

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1.1.3. Emulsion Polymerization of Styrene

REAGENTS AND MATERIALS

Name
Styrene
Ammonium peroxodisulfate solution (0.68 wt%) in H ₂ O
Sodium dodecyl sulfate (SDS) in 10 mL H ₂ O
H ₂ O
Sodium chloride (NaCl)
Toluene
Propanol

PROCEDURE

In a 100 mL round bottom flask equipped with a magnetic stir bar, a solution of sodium dodecyl sulfate (1.23×10^{-3} mol) in water (24 mL) is prepared. After dissolving the initiator ammonium peroxodisulfate (9.24×10^{-3} mol) in the SDS/water solution, 6.82×10^{-2} mol freshly distilled styrene is added to the solution under vigorous stirring. After extensive degassing (bubbling nitrogen with a syringe), the flask is equipped with a coil condenser and the reaction mixture is heated to 50 °C. After 2 h reaction time, the heating is removed and the mixture is cooled to ambient temperature. The micellar suspension has a milky appearance. Take and store a 1 mL sample for particle size characterization by Dynamic Light scattering (DLS). From residual reaction mixture, remove the magnetic stir bar and add saturated NaCl solution under vigorous stirring using a glass rod. The polystyrene immediately starts to precipitate and the remaining solution is decanted (solvent waste!).

The polymer is dissolved in toluene, precipitated into propanol, filtered with suction, washed with methanol, water and dried at 50 °C *in vacuo* overnight.

EVALUTION

- Q1 Why do you need to add SDS?
- Q2 How do you control the latex particle size?
- Q3 How is a surfactant characterized? What physio-chemical characteristics are required?
- Q4 What is the particle stabilization mechanism? Which other types of surfactant do you know and how do those stabilize the emulsion droplets?
- Q5 Draw a cartoon description of the three stages of emulsion polymerization including all the particles and indicating their relative sizes.
- Q6 How does DLS work?

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1.1.4. Polymer Analogues Reaction: Synthesis and Characterization of Sodium Carboxymethylcellulose

REAGENTS AND MATERIALS

Name	Amount
Cellulose powder	5 g
Sodium hydroxide solution (5 wt%) in H ₂ O	20 mL
i-Propanol	100 mL
Sodium monochloro acetate (NaMCAc)	7 g
1M HCl	
Ethanol (70 wt%)	

PROCEDURE

To a 250 mL flask equipped with a magnetic stir bar cellulose powder (5 g), NaOH_{aq.} (20 mL, 5 wt%) and isopropanol (100 mL) is added. The cellulose is alkalinized at ambient temperature for 1 h. In the following, sodium monochloro acetate (NaMCAc, 7g) is added, the temperature raised to 55 °C and the reaction continued for 3 h.

The slurry is converted to the acid form by adding acidified (HCl) isopropanol. Excess acid is removed by washing with a 70 wt% ethanol water solution (until pH is neutral) over a Büchner funnel equipped with a suction flask and the material is dried in the vacuum oven. Weighed samples of the free acid are dissolved in distilled water, containing an excess of standard sodium hydroxide, and the excess base is back-titrated with standard hydrochloric acid (over a burette), using phenolphthalein as pH indicator.

EVALUATION

- Q1 Which possible side reactions could you imagine?
- Q2 Calculate the degree of substitution in amount of carboxyl groups per polymer chain.
- Q3 Why do you use NaMCAc and not the free acid?
- Q4 Why do you use phenolphthalein as indicator? Name three other pH indicators with their properties (e.g. transition point).

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R.W. Eyles, E. D. Klug, F. Diephuis, *Anal. Chem.* **1947**, 19, 24-27

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1.1.5. Free Radical Copolymerization of MMA and Styrene

REAGENTS AND MATERIALS

Name
Styrene
MMA
AIBN
Petrol ether

MONOMER PREPARATION PROCEDURE (*for Experiments: 1.1.5, 1.2.2, 1.3.1*)

Prepare a monomer mixture of 7.68×10^{-2} mol styrene with 7.67×10^{-2} mol MMA in a well dried, nitrogen flushed 50 mL Schlenk flask. The flask is closed carefully and stored in the refrigerator until further use.

PROCEDURE

Mix 5 mL of the prepared monomer mixture and 9.74×10^{-5} mol AIBN in a well dried and nitrogen flushed 50 mL Schlenk flask (equipped with a magnetic stir bar). After addition exchange the septum with a greased glass stopper under a slight nitrogen stream and fix it with a metal clamp. The polymerization is performed at 60 °C in an oil bath.

After 4 h the flask is cooled to 0 °C using an ice bath and the mixture is diluted with 25 mL of toluene. Precipitate the copolymer by dropping the solution into 250 mL petrol ether. The polymer is isolated by filtration with suction (Büchner funnel, suction flask), washing with n-hexane and drying at 70 °C *in vacuo*.

Copolymerization parameters: $r_{\text{Styrene}} = 0.52$, $r_{\text{MMA}} = 0.46$

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1.1.6. Precipitation Polymerization of Acrylonitrile with Redox Initiator in Water

REAGENTS AND MATERIALS

Name
Acrylonitrile
Sodium disulfite solution (5 wt%) in H ₂ O
Potassium peroxodisulfate solution (5 wt%) in H ₂ O
Fe(II) sulfate heptahydrate solution in H ₂ O
H ₂ SO ₄ (conc.)

PREPARATORY WORK

The sodium metabisulfite solution and the potassium peroxodisulfate solution are prepared according to the table. For the Fe(II) solution, 10 mg of Fe(II) SO₄ x 7 H₂O are dissolved in 100 mL distilled water and 2 mL of conc. sulfuric acid are added using a pipette.

PROCEDURES

a) *Polymerization dependency on the oxidizing/reducing agent ratio*

Four 50 mL Schlenk flasks are evacuated carefully and flushed with nitrogen. Afterwards the flasks are equipped with the reagents in the following table, whereas the potassium peroxydisulfate solution is simultaneously added last to all four reaction flasks:

Sample	H ₂ O (mL)	Acrylonitrile (mL)	Na ₂ S ₂ O ₅ (mL)/(mmol)	FeSO ₄ (mL)/(mmol)	K ₂ S ₂ O ₈ (mL)/(mmol)
1	18	1.5	0.05 / 1.3x10 ⁻²	0.25 / 9x10 ⁻⁵	0.25 / 4.6x10 ⁻²
2	17	1.5	0.25 / 6.6x10 ⁻²	0.25 / 9x10 ⁻⁵	0.25 / 4.6x10 ⁻²
3	17	1.5	0.5 / 1.32x10 ⁻¹	0.25 / 9x10 ⁻⁵	0.25 / 4.6x10 ⁻²
4	16	1.5	1.0 / 2.63 x10 ⁻¹	0.25 / 9x10 ⁻⁵	0.25 / 4.6x10 ⁻²

After complete addition of all reagents, the reaction flasks are swirled shortly and allowed to stand at 20 °C under nitrogen atmosphere. Note down the time until the first turbidity for each sample.

In the meanwhile prepare four suction flasks with Büchner funnels. After 20 min reaction time all four samples are filtered simultaneously, washed with H₂O and methanol and dried at 50 °C *in vacuo* overnight.

b) *Influence of the initiator concentration (on reaction rate) with constant oxidizing/reducing agent ratio*

Prepare four round bottom flasks as described in section a) and fill with the reagents described in the following table. The samples are allowed to stand for 20 min at 20 °C and worked up as described in section a).

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Sample	H ₂ O (mL)	Acrylonitrile (mL)	Na ₂ S ₂ O ₅ (mL)/(mmol)	FeSO ₄ (mL)/(mmol)	K ₂ S ₂ O ₈ (mL)/(mmol)
1	18	1.5	0.05 / 1.3x10 ⁻²	0.05 / 1.8x10 ⁻⁵	0.05 / 9.0x10 ⁻³
2	17	1.5	0.25 / 6.6x10 ⁻²	0.25 / 9.0x10 ⁻⁵	0.25 / 4.6x10 ⁻²
3	17	1.5	0.5 / 1.32x10 ⁻¹	0.5 / 1.8x10 ⁻⁴	0.5 / 9.3x10 ⁻²
4	16	1.5	1.0 / 2.63 x10 ⁻¹	1.0 / 3.6x10 ⁻⁴	1.0 / 1.85x10 ⁻¹

EVALUATION

- Q1 Why is it necessary to add concentrated sulfuric acid to the Fe(II) sulfate solution?
- Q2 For section a), plot the conversion (reaction rate) vs. oxidizing/reducing agent ratio and explain.
- Q3 For section b), plot the reaction rate (in % conversion/min) vs. $\sqrt{c_i}$ (in mol K₂S₂O₈) and explain.

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1.1.7. Photo polymerization of PEG-400-diacrylate

REAGENTS AND MATERIALS

Name
PEG-400-diacrylate
IRGACURE® 2959 (photo initiator), MW = 224.25 g/mol

PROCEDURE

In a 50 mL round bottom flask, 9.57×10^{-3} mol of PEG-400-diacrylate and 8.92×10^{-4} mol photo initiator are stirred (glass bar) to form a homogeneous mixture (might take up to 1 h to dissolve). The resulting solution is evacuated at high vacuum to remove gas bubbles generated by stirring.

Using a spatula or a glass bar, the mixture is applied onto a glass slide (from microscope). The layer has to be as thin as possible. In a distance of approximately 20 cm, irradiate the film using an UV lamp ($\lambda = 250$ nm) overnight (until a hard coating is received). There are two possible irradiation procedures:

- a) Irradiate the whole film (example for coating by polymerization)
- b) Use a mask (e.g. coin) near the surface to shield a part of the film. After hardening of the film the non-irradiated part can be removed by solvent (example for surface structuring, photoresists)

EVALUATION

- Q1 Characterize the monomer mixture and the resulting polymer by IR spectroscopy to qualitatively determine the conversion of PEG-400-diacrylate ($\nu = 1635$ cm^{-1}).
- Q2 Qualitatively investigate the swelling behavior of the polymer film using different solvents (e.g. THF, toluene, etc.).

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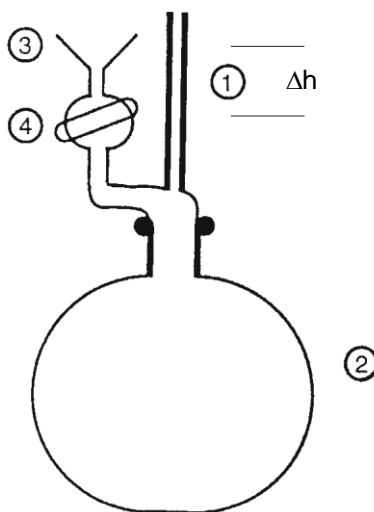
1.1.8. Dilatometry

REAGENTS AND MATERIALS

Name
Styrene
Dibenzoyl peroxide (DBPO)

PROCEDURE

The schematic setup of a dilatometer is shown below:



It consists of a capillary tube (1), the 50 mL round bottom flask (NS 14) (2), the inlet funnel (3) and the stopcock (4).

Put the components of the dilatometer together (capillary tube with funnel and stopcock, reaction flask) thoroughly greasing the stopcock and the joints. Fix the flask with a metal clip and weigh the empty apparatus. Note down the weight of the apparatus and the diameter of the capillary engraved on its top. Take care to not exchange any part of the apparatus after weighing. In the meanwhile, heat up a water bath (15 L beaker) to 50 °C using a thermostat.

The capillary tube has to be equipped with a scale (graph paper) to determine Δh .

After all preparations, use a 100 mL, nitrogen flushed round bottom flask to dissolve different amounts of DBPO (see table below) in 60 mL styrene by shaking carefully to prevent blistering, which would introduce into much oxygen. After completely dissolving the initiator, fill the reaction mixture into the apparatus up to the lower end of the capillary tube. Take care to avoid any bubbles. Close the stopcock and carefully dab away any styrene in the funnel using cellulose and immerse the apparatus into the water bath (50 °C) up to the lower end of the capillary tube.

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Goup	Entry A	Entry B	Entry C
1	1520 mg	1840 mg	2160 mg
2	1600 mg	1920 mg	2240 mg
3	1680 mg	2000 mg	2320 mg
4	1760 mg	2080 mg	2400 mg

CAUTION: Due to the thermal expansion of the styrene, the volume of the reaction mixture exceeds the volume of the apparatus and has to be removed from the upper end of the capillary by dabbing away with cellulose. **WEAR GLOVES!**

After reaching the thermal equilibrium the level of the reaction mixture in the capillary starts to decrease. Note the time and measure the change in height in relation to time. The time interval depends on the initiator concentration and has to be chosen carefully. The measuring points have to be sufficient to draw a regression curve. The measurement is finished when the level approaches the lower end of the capillary. If the reaction is very slow the minimum reaction time will be 90 min. In order to obtain good data, Δh should be checked by the same person!

After the measurement, the apparatus is carefully removed from the water bath. The outside water is wiped off and the weight of the filled dilatometer is determined again. From the difference in weight of the filled to the empty dilatometer, calculate the volume of styrene ($\rho_{20^\circ\text{C}} = 0.9063 \text{ g/ml}$).

Clean the apparatus thoroughly by washing with dichloromethane and acetone.

Measure three initiator concentrations twice each. Check with the other groups that all concentrations are measured in the end and exchange the data.

FUNDAMENTAL EQUATIONS

$$\Delta V_{100} = W \times \left(\frac{1}{\rho_m} - \frac{1}{\rho_p} \right) \quad (\text{Equ. 3})$$

$$\text{conv.} = \frac{\Delta V_t}{\Delta V_{100}} \quad (\text{Equ. 4})$$

$$V_{\text{poly}} = \frac{x/M_M \times 1000}{100/\rho_m \times 60} \quad (\text{Equ. 5})$$

$$\Delta v = \frac{\pi d^2}{4} \Delta h \quad (\text{Equ. 6})$$

$$V_{\text{Poly}} = \frac{\Delta C \rho_M}{\Delta t M_p} = \frac{\rho_M}{\rho_M - \rho_P} \frac{1}{v_0} \frac{\Delta v \rho_M}{\Delta t M_P} \quad (\text{Equ. 7})$$

ΔV_{100} : volume contraction at 100% conversion of styrene

W : weight of monomer

x : conversion speed of monomer per minute

M_M : molecular weight of the monomer

$\rho_{m,p}$: density of the monomer and polymer

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EVALUATION

Q1 Determine the rate of polymerization for the different initiator concentrations.

For the determination of polymerization rate, calculate $\Delta h = h_{max} - h_t$ for every t . h_{max} is measured from the level of the reaction mixture after the thermal expansion of styrene.

Make a plot Δh vs. t . From the slope of the graph, calculate the polymerization rate (V_{poly}) using the equations 1 – 7.

Q2 Why is there a deviation from a straight line in the beginning of the polymerization?

Plot the polymerization rates for different initiator concentrations vs. $[I]$ on a double logarithmic paper. Discuss the plots.

1.2. Anionic Polymerization

1.2.1. Synthesis of Isotactic and Syndiotactic PMMA

REAGENTS AND MATERIALS

Name
Methyl methacrylate (MMA), dry
n-BuLi (1.6M in hexane)
Dimethoxyethane (DME), dry
Toluene, dry
Dichloromethane
Methanol
Pyridine, dry
dry ice/ethanol, dry ice/acetone

PROCEDURE

The initiator mixture is prepared by mixing 6.4×10^{-3} mol of n-BuLi (solution in hexane) with 1.5 equivalents of dry pyridine in a well dried, nitrogen flushed Schlenk tube closed with a septum, using a syringe.

Two polymerizations are carried out in parallel (1.2.1.1 and 1.2.1.2).

15 mL of dry DME is added into one of two completely dried, nitrogen flushed 25 mL Schlenk flask (NS 14, equipped with a magnetic stir bar) (1.2.1.1) and 15 mL of dry toluene into the other (1.2.1.2). The tubes are closed with septa under a slight nitrogen stream.

Inject about 0.5 mL of the initiator to each of the tubes and cool them down to -78°C (1.2.1.2), -50°C (1.2.1.1). Under vigorous stirring, add 9.39×10^{-3} mol MMA to each tube. The reaction mixture should turn red. If there is no change in color, there must have been some moisture in the reaction mixture. Try to add another 0.5 mL of the initiator mixture. After 20 min the tubes are replaced from cooling and the polymerizations are stopped by slowly adding about 1 mL methanol.

Work up: The polymer from 1.2.1.1 (DME) is precipitated by dropping into 75 mL of stirred methanol (beaker equipped with magnetic stir bar), whereas the polymer from 1.2.1.2 (toluene) is diluted with 10 mL DCM prior to precipitation into 150 mL methanol. The polymers are filtered with suction, washed with methanol and dried overnight at 50°C in a vacuum oven. The next day determine the yield and the melting points of the polymers.

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Experiments – Anionic Polymerization

EVALUATION

Store the polymers for IR and ¹H-NMR analysis for the determination of their tacticity.

The table below gives the wave numbers of the IR spectra which are sensitive to the tacticity of the polymers (+ indicates the relative intensity).

cm-1	677	790	808	945	1035	1100	1212	1240	1338
syndiotactic	++++	++++	++++	++++	++++	++++	++++	++++	++++
atactic	+++	++++	+++	+++	+++	+++	+++	+++	+++
isotactic	0	++++	++	0	+	0	0	+	++

- Q1 Compare the IR Spectra of the polymer **1.2.1.1** and **1.2.1.2** with the spectrum of the PMMA synthesized by free radical polymerization (**1.1.1**). By comparison with the IR spectrum of the atactic PMMA (**1.1.1**), make a qualitative conclusion to the structure of **1.2.1.1** and **1.2.1.2**. Also compare the ¹H-NMR of syndiotactic and isotactic PMMA.
- Q2 Explain the different tacticity of **1.2.1.1** and **1.2.1.2** with the polarity of the solvents and the structure of the transition state.
- Q3 Why do you add dry pyridine to the initiator mixture?
- Q4 Why is it essential to exclude moisture from the reaction mixture?

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Experiments – Anionic Polymerization

1.2.2. Anionic Copolymerization of MMA and Styrene

PROCEDURE

Take 5 ml of the monomer mixture prepared in **1.1.5** and transfer to a well dried and nitrogen flushed 50 mL Schlenk tube equipped with a magnetic stirring bar. Add 10 mL of dry toluene. Close the tube with a septum under a small stream of nitrogen. Cool it to -50 °C using a dry ice/ethanol bath (carefully control the temperature). To the cooled mixture, 2 mL of phenyl magnesium bromide (1M in THF) is added via a syringe. After 90 min the flask is removed from the cooling bath. The reaction is quenched by dropping into a stirred mixture of 200 mL methanol and 10 mL 2M HCl. Afterwards, the polymer is isolated by filtration with suction, washing with n-hexane and drying at 50 °C *in vacuo* overnight. Determine the yield and store the polymer for IR and NMR analysis.

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Experiments – Anionic Polymerization

1.2.3. Block copolymerization of Styrene and MMA

REAGENTS AND MATERIALS

Name
Styrene, dry
Methyl methacrylate (MMA), dry
Toluene, dry
Dimethoxyethane (DME), dry
1,1-Diphenyl ethylene
n-BuLi (1.6M in hexane)
dry ice
Methanol
Ethanol

PROCEDURE

Two polymerizations are carried out in parallel:

1.2.3.1: anionic block copolymerization of styrene and MMA

1.2.3.2: anionic homopolymerization of styrene

All operations have to be carried out under a thoroughly exclusion of moisture and air!

10 mL of dry toluene is injected into each of two completely dried, nitrogen-flushed 25 mL Schlenk flasks (NS 14), equipped with magnetic stir bars. They are closed under a small stream of nitrogen using septa. In a third well dried and nitrogen flushed Schlenk flask, dissolve 2.22×10^{-3} mol 1,1-diphenyl ethylene in 5 mL of toluene.

The two toluene filled Schlenk tubes are cooled down to -78 °C using a dry ice/acetone bath. Afterwards, 8.73×10^{-3} mol of dry styrene is transferred into one of the flasks (**1.2.3.1**) and 1.75×10^{-2} mol of dry styrene into the other (**1.2.3.2**) using a syringe. Under vigorous stirring, the polymerization is initiated by injecting 5 mol% of n-BuLi and 4 mL of dry DME in quick succession. It is important to use the same amount of initiator for both polymerizations. After 30 min, 1.5 equivalents (referring to the amount of initiator) of the 1,1-diphenyl ethylene solution is injected into entry **1.2.3.1**. Note down your observation.

After additional 10 min of vigorous stirring, inject 8.73×10^{-3} mol of dry MMA to entry **1.2.3.1**. Note down your observations.

Both reactions are quenched after additional 60 min by injecting 3.94×10^{-3} mol trimethylsilyl chloride. Each of the polymers is isolated by precipitation in 150 mL methanol, filtration under suction and washing with methanol. If the precipitate is too small to filter, use the centrifuge to separate it from the solution. Drying is performed at 50 °C *in vacuo* overnight. Determine the yields of the polymers.

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Experiments – Anionic Polymerization

EVALUATION

- Q1 Calculate the molecular weights of the polymers from GPC/SEC analysis and $^1\text{H-NMR}$ spectrum (end-group analysis with the TMS-group). Compare these results with the calculated degree of polymerization from the initiator/monomer ratio and comment this.
- Q2 Why it is possible to calculate the degree of polymerization from the initiator/monomer ratio?
- Q3 How would you prove having a block copolymer from entry **2.2.3.1** instead of a mixture PS and PMMA (polymer blend)?
- Q4 Why do you add 1,1-diphenyl ethylene?

Copolymerization parameters: $r_{\text{Styrene}} = 0.12$, $r_{\text{MMA}} = 6.4$

1.3. Cationic Polymerization

1.3.1. Cationic Copolymerization of Styrene and MMA

PROCEDURE

To prepare the initiator, equip a well dried 100 mL Schlenk flask with a magnetic stirring bar and a column with vacuum adapter. Fill in aluminium oxide to a level of ca. 5 cm in the column. Connect the Schlenk flask to the nitrogen and flood the whole apparatus by streaming out the vacuum adapter of the column. Add 60 mL of nitrobenzene in the column and let it drop into the flask. There should be ca. 50 mL of dry nitrobenzene in the Schlenk flask after the procedure. Replace the column with a glass stopper. Add 2.25×10^{-3} mol of dry aluminium chloride to the nitrobenzene quickly and stir for complete dissolution.

The polymerization is carried out by adding 5 mL of the monomer mixture prepared in **1.1.5** to a 100 mL well dried Schlenk flask under a slight nitrogen stream. The flask is closed with a septum. To this monomer mixture 40 mL of the initiator solution is added using a syringe. The reaction mixture is stirred until a homogeneous solution is obtained. The polymerization takes place at room temperature. After 1 h drop the polymerization is quenched by pouring the reaction mixture into 200 mL of methanol. The polymer is isolated by filtration with suction, washing with n-hexane and drying at 50 °C *in vacuo* overnight. The yield of the polymer is determined.

Copolymerization parameters: $r_{\text{styrene}} = 10.5$, $r_{\text{MMA}} = 0.1$

Polymer Synthesis and Characterization – Basic Laboratory Course
Experiments – Cationic Polymerization

1.3.2. Cationic polymerization of vinyl isobutylether with BF_3OEt_2

REAGENTS AND MATERIALS

Name
Vinyl isobutylether, dry
Pentane, dry
BF_3OEt_2 , dry
Potassium hydroxide
Dry ice
Acetone
Cyclohexylamine

PROCEDURE

A well dried 50 mL three-neck flask (NS 29) equipped with a magnetic stir bar, a septum, a glass stopper and a nitrogen inlet is cooled down to $-70\text{ }^\circ\text{C}$ using an dry ice/acetone bath. The stopper is exchanged by a funnel and ca. 6 mL dry pentane is added to the reaction vessel. Afterwards the funnel is exchanged against the glass stopper again and secured with a metal clamp.

The apparatus is kept under a constant nitrogen flux throughout the whole polymerization process. 1.5×10^{-2} mol vinyl isobutylether is added using a syringe. Under vigorous stirring 3.9×10^{-5} mol dry BF_3OEt_2 is added drop wise and the reaction mixture is kept at $-70\text{ }^\circ\text{C}$ for 30 min, before another 2.44×10^{-4} mol BF_3OEt_2 is added drop wise. The temperature is kept constant for another 90 min.

Quenching is performed by the addition of cyclohexylamine and increasing the temperature to ambient conditions (remove acetone/dry ice bath). The solvent pentane is evaporated at the evaporator. The polymer is dried in at $50\text{ }^\circ\text{C}$ *in vacuo* overnight and the yield is determined.

EVALUATION

Q1 Why do you add BF_3OEt_2 in two separated portions?

1.4. Polyaddition

1.4.1. Synthesis of Polyurethane Foams

REAGENTS AND MATERIALS

Name
Polyol (<i>Polyolkomponente 1066-139</i> or <i>Elastoflex W5526-101</i>)
Poly(isocyanate) (<i>Lupramat</i> or <i>ISO 145</i>)

PROCEDURE

Prepare four mixtures (20 g) with different ratios of the polyol and the isocyanate compound (e.g. 4:1, 2:1, etc). First add the polyol in a container (single use cup) followed by the required amount of the isocyanate compound. Use a single use syringe to stir until you obtain a homogeneous mixture. The reaction starts after 30 to 90 s under the formation of heat and the volume starts slowly to increase. Let the reaction proceed.

ALWAYS WEAR GLOVES WHEN WORKING WITH THE ISOCYANATE COMPOUND!!!

EVALUATION

- Q1 Explain your observations regarding the structures of the components, e.g. functionality).
- Q2 Why do you use polymers to synthesize polyurethane foams?
- Q3 Which components are required to obtain a foam?
- Q4 Compare the rigidity and the bubble sizes of your different polymers and explain the properties with the structure of the starting compounds.

1.5. Polycondensation

1.5.1. Interfacial Polycondensation of PA 6,10 using hexymethylenediamine and sebacic acid chloride

REAGENTS AND MATERIALS

Name
Sebacic acid chloride
Hexamethylenediamine
Dichloromethane (DCM)
distilled water
Phenolphthalein solution
Ethanol (50 Vol%)
Acetone
Sodium carbonate (Na ₂ CO ₃)

PROCEDURE

Prepare a solution of 1.4×10^{-3} mol sebacic acid chloride in 10 mL DCM in a 25 mL beaker (**solution 1**). Use a separate beaker to prepare a solution of 3.8×10^{-3} mol hexamethylenediamine in 5 mL distilled water (**solution 2**). Further add 1.4 equivalents of Na₂CO₃. Carefully cover **solution 1** with a layer of **solution 2** using a Pasteur pipette (for better recognition of the top layer, color the water phase with a few drops phenolphthalein solution. The polymer film which is formed immediately at the interfacial layer is extracted with tweezers and put over a glass bar. Now it is possible to further extract the polymer strand by rolling the bar. The polymerization stops immediately after stopping the polymer extraction.

The polymer strand is now washed with ethanol, acetone, water using a Büchner funnel and a suction flask. The final polymer is dried at 50 °C *in vacuo* overnight. Determine the melting point of the polymer (Lit.: 228 °C).

EVALUTION

Q1 Why does the polymerization stop when stopping the polymer film extraction?

Q2 Why do you add sodium carbonate?

1.6. Insertion Polymerization

1.6.1. Ring Opening Metathesis Polymerization (ROMP) of Norbornene

REAGENTS AND MATERIAL

Name
Norbornene, dry
Grubbs Catalyst
Dichloromethane (DCM)
Methanol
Phenol

PROCEDURE

6.27×10^{-3} mol Norbornene is dissolved in 2 mL DCM in a well dried 25 mL Schlenk-flask (equipped with a magnetic stir bar) under inert atmosphere. After adding 6.2×10^{-6} mol Grubb's Catalyst, the polymerization starts immediately and the flask is closed with a stopper. After stirring for 1h at r.t. 2 mL DCM, one drop conc. HCl and one drop Phenol are added (quenching). The resulting polymer is stirred for another 20 min. until the color changed from brown to green. The polymer is worked up by filtering and precipitated in 40 mL acidic methanol using a Büchner funnel and a suction flask.

EVALUATION

- Q1 What is important for the monomer selection? Which properties are required?
- Q2 What types of copolymers are possible?

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Experiments – Insertion Polymerization

1.6.2. Synthesis of High Syndiotactic Polystyrene by Homogeneous Ziegler-Natta Catalysis

APPARATUS

Name	Amount	Name	Amount
250 mL three-neck flask	1	oil bath	1
250 mL two-neck flask	1	Büchner funnel	1
magnetic stir bar	2	rubber gasket	1
magnetic stirrer	1	500 mL filtering flask	1
dropping funnel	1	500 mL beaker	2

REAGENTS AND MATERIALS

Name
Styrene, dry
$(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_3$
Ethyl aluminium dichloride $((\text{C}_2\text{H}_5)_2\text{AlCl}_2)$
Toluene, dry
Methanol

PROCEDURE

A well dried 250 mL three-necked flask equipped with a magnetic stir bar is used for the polymerization. 10 ml toluene, 7.5×10^{-4} mol $(\text{C}_2\text{H}_5)_2\text{AlCl}_2$, 1.25×10^{-6} mol $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_3$ and 1.4×10^{-1} mol of dry styrene are charged into the flask in this order under inert atmosphere. The addition of styrene is marked as the starting point of the polymerization, which is kept at 50 °C for 2 h. Quenching is performed by adding methanol and one drop conc. HCl ('acidified methanol'). The resulting polymer is washed with methanol for several times and dried at 50 °C *in vacuo* overnight.

EVALUATION

Q1 Determine the yield of the polymer (Lit.: 7.64 g).

REFERENCES

N. Ishihara, M. Kuramoto, M. Uoi, *Macromolecules* **1988**, *21*, 3356-3360
R. Po, N. Cardi, *Prog. Polym. Sci.* **1996**, *21*, 47-88

2. Polymer Characterization

2.1. Viscosimetry

APPLICABILITY

The dilute solution viscosity measurement is applicable to all polymers, which dissolve to give solutions at a temperature between ambient and about 150 °C. Special techniques, beyond the scope of this experiment, are required in the measurement and data treatment for polyelectrolytes or for polymers of sufficiently high molecular weight that their solution viscosity depends upon the rate of shear in the viscometer.

SAFETY CONSIDERATIONS

Care must be taken in the use of organic solvents such as chloroform and toluene, both of which are highly toxic; toluene is also flammable. Use these and other solvents only in small quantities in well ventilated areas. Avoid the use of flames or sources of electric sparks. Safety glasses must be worn in the laboratory at all times.

APPARATUS

1. Constant temperature bath, capable of maintaining $\pm 0.01^\circ\text{C}$ at 25.0°C .
2. Viscometers with efflux times greater than 100 sec for the solvent (Ubbelohde viscometer).
3. Timer, graduated 1 0.1 sec or less.
4. 25 ml volumetric flasks, stoppered.
5. Pipettes as required.
6. Source of filtered dry nitrogen at low pressure.
7. Fine fritted glass or $1.0\mu\text{m}$ "Millipore" filter in suitable holder.

REGENTS AND MATERIALS

1. Poly (methyl methacrylate) or polystyrene samples prepared in former experiments.
2. Chloroform or toluene, reagent grades.

PREPARATION

Prepare ahead of time solutions of PMMA in chloroform at a concentration of 0.5 g/dl or of polystyrene in toluene at a concentration of 1.0 g/dl. Use 25 ml volumetric flasks to make the solution: After filling the flask with toluene, stopper and agitate gently; do not shake, as particles of polymer may adhere to the walls above the liquid level and fail to dissolve. Repeat agitation from time to time until polymer is completely dissolved. Allow at least 24 hours.

PROCEDURES

1. Rinse the viscometer with solvent and let it drain. Then place the viscometer in the constant-temperature bath, securely fastened and with the upright tubes exactly vertical. Check the bath is regulating properly at the desired temperature.
2. With a pipette or syringe, transfer exactly 10.0 ml filter solvent to the viscometer. If you have to filter your polymer solution use a glass pipette equipped with cotton wool.
3. After temperature equilibrating has been achieved (a minimum of 10 min), bring the liquid level in the viscometer above the upper graduation mark of bulb C as follows:

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Close tube 3 with one finger, and apply a low pressure of filtered nitrogen to tube 1. When the desired liquid level (in bulb D) is reached, open both tube 1 and 3. Bulb A will now drain, establishing the “suspended level” at the bottom of the capillary. Allow the liquid to drain down the capillary. Start the timer exactly as the meniscus passes the upper graduation mark, and stop it exactly as the meniscus passes the lower mark.

4. Determine the efflux time at least three times. The readings should agree within 0.1 sec or 0.1% of their mean, whatever is larger. If they do not, repeat and apply the above test until three satisfactory readings or a total of six readings are obtained. Accept the mean of three readings agreeing as indicated above; if they cannot be obtained, it is likely that the variation results from foreign material in the capillary or inadequate temperature control. Locate and remedy before proceedings.
5. Add exactly 5.0 ml filtered polymer solution to bulb B through tube 1. Mix the solution well by closing tube B and applying nitrogen pressure alternately through tubes 1 and 3.
6. Repeat steps 2 - 4. Add another aliquot of solution as in step 5, and repeat until at least five solutions have been measured.
7. Remove the viscometer from the bath, empty it, and rise all parts of it (including capillary and bulbs C and D) with filtered solvent. Drain the viscometer and blow it dry with the stream of filtered nitrogen.

FUNDAMENTAL EQUATIONS

$$\eta_r = t/t_o \quad (8.15)$$

$$\eta_{sp} = (t - t_o)/t_o \quad (8.16)$$

$$\eta_{inh} = (\ln \eta_r)/C \quad (8.17)$$

$$\eta_{sp}/C = [\eta] + k' [\eta]^2 C \quad (8.18)$$

$$(\ln \eta_r)/C = [\eta] + k'' [\eta]^2 C \quad (8.19)$$

CALCULATIONS

1. Calculate η_r by Eq. 8.15, η_{sp} by Eq. 8-16, and η_{inh} by Eq. 8.17.
2. Plot on the same piece of graph paper, η_{sp}/C versus C and η_{inh} versus C . Read $[\eta]$ as the common intercept at $C = 0$ of the best straight lines through the two sets of points.
3. Calculate the Huggins constant k' from Eq. 8.18 and the Kraemer constant k'' from Eq. 8.19. As an additional check on the accuracy of your work, check to see that $k' - k'' \cong 0.5$.

QUESTIONS:

Q.8.2.1 Include a table of values of C , η_r , η_{sp} , η_{sp}/C , and η_{inh} , and the graph prepared. Report $[\eta]$, k' , k'' the solvent, and the temperature of measurement.

Q8.2.2 Calculate the average molecular weight using the Mark-Houwink equation (search for literature values for K and a)

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COMMENTS

Several variations are possible in the schedule of concentrations to be measured in this experiment. For example, instead of adding five aliquots of 5 ml each to 10 ml solvent, the following schedules are suggested:

- a. Add 10 ml stock solution to 10 ml solvent, then successively dilute with further additions of solvent.
- b. Start with stock solution, and successively dilute with solvent. Determine the efflux time of the solvent separately.

3. References

In general, the references are drawn from:

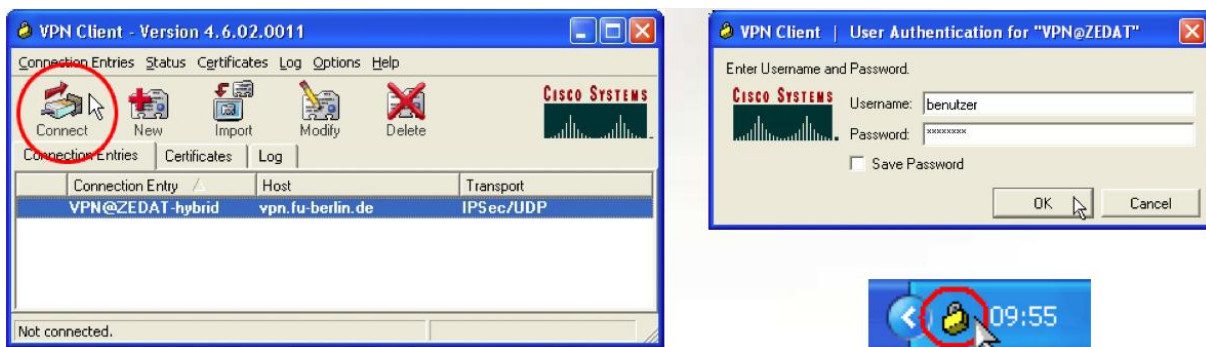
D. Braun, H. Cherdrón, M. Rehahn, H. Ritter, B. Voit, **Polymer Synthesis: Theory and Practice: Fundamentals, Methods, Experiments 4th Ed.**, Springer 2004

Additional references are listed below the experiment description.

4. FU Network Access

In order to use the internet resources provided by the Freie Universität Berlin, such as WLAN or the databases for literature search, the first step is to open an email account at the university computer center, the ZEDAT. In the case you enrolled at the FU Berlin, you should already have such an account. Students, who did not enroll at the FU Berlin should contact our polymer science tutor. He is going to assist you in opening an email account.

To get access to the wireless network on the campus or to use the internet resources outside the university, you have to install the Cisco VPN software on your computer, which is available for downloading at <https://portal.zedat.fu-berlin.de/services/vpn/> for all common operating systems. After installation, start the VPN client, and choose the entry "VPN@zedat-hybrid", press "connect", and enter your zedat-username and password. When the connection is established a small icon should appear in the system tray.

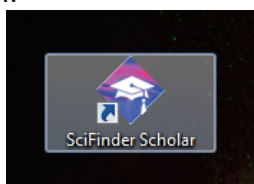


5. Literature Search

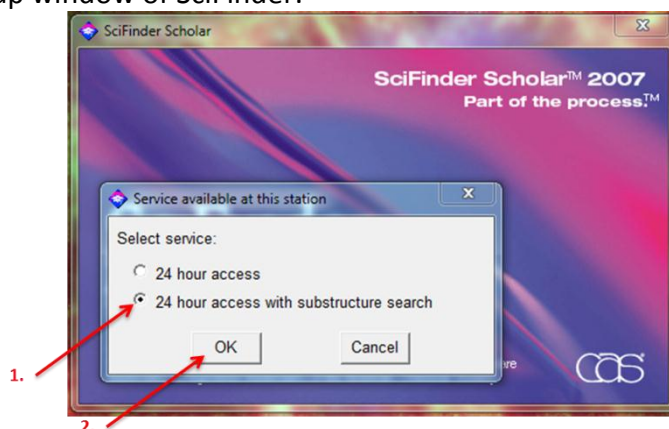
5.1. SciFinder

With SciFinder Scholar you can search various databases for literature, substance properties, reactions, etc. If you do not have SciFinder installed on your computer you can download it from <http://www.chemie.fu-berlin.de/fb/news/sfschlr.html>. To install, follow the installation instructions there.

Make sure that you are connected to the FU network (WLAN or LAN). To start SciFinder Scholar double click the desktop icon:



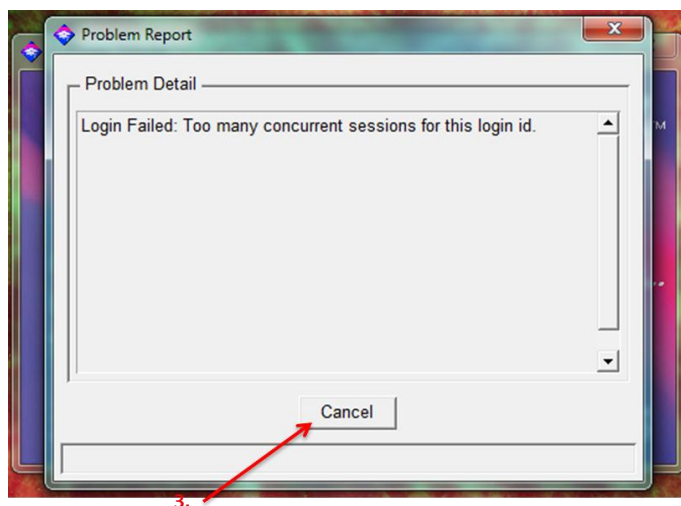
This opens the startup window of SciFinder:



1. Choose '24 hour access with substructure search'
2. Click 'OK'

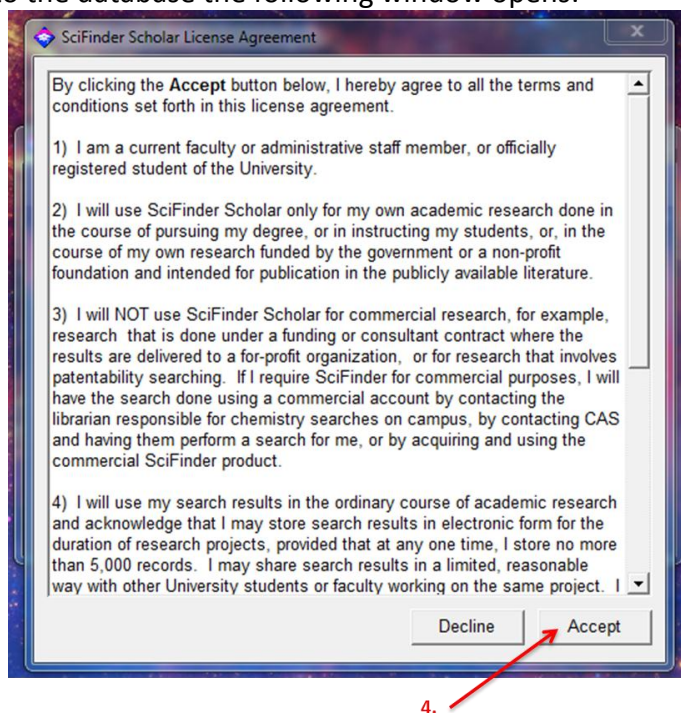
As FU Berlin has only a limited amount of licenses to use SciFinder Scholar and all licenses are already in use the following window opens:

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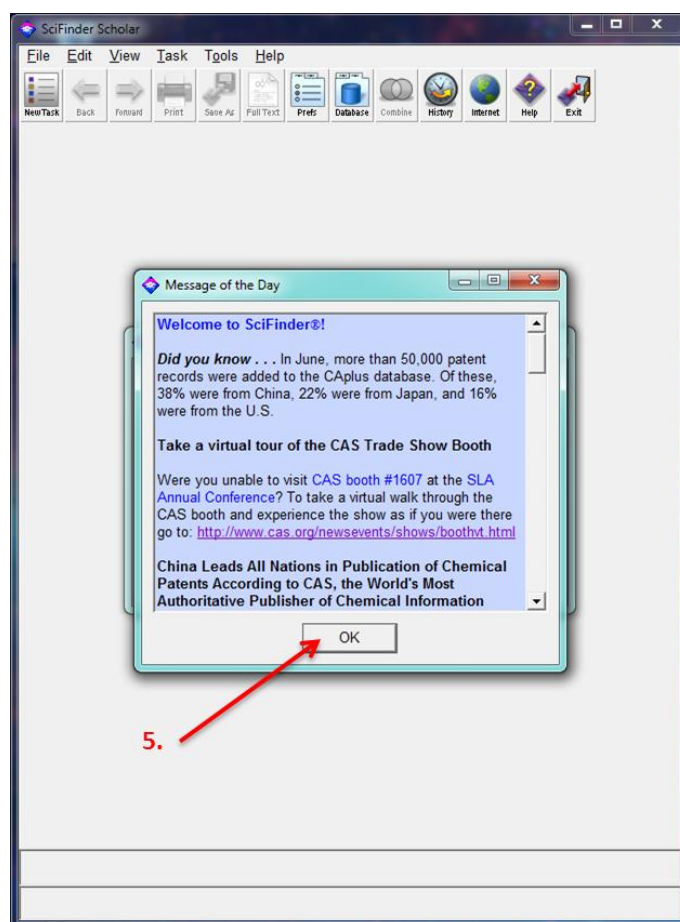
3. Press 'Cancel' and try again later

If you grant access to the database the following window opens:

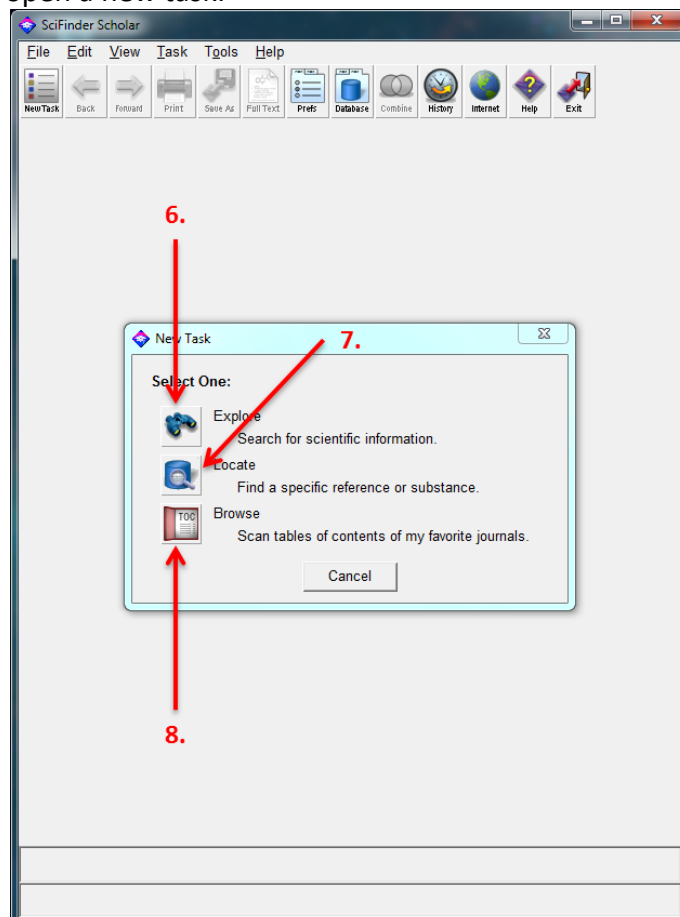


4. Accepting the SciFinder Scholar Agreements (click 'Accept') opens the window 'Message of the day':

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5. Click 'OK' to open a new task:

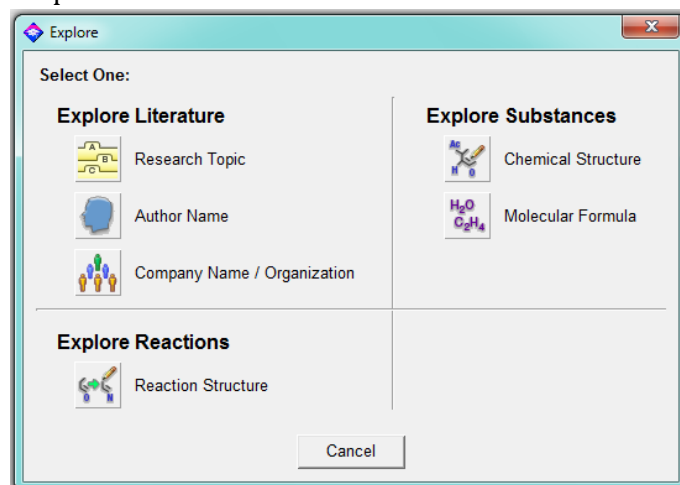


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Starting a new task provides you the following possibilities:

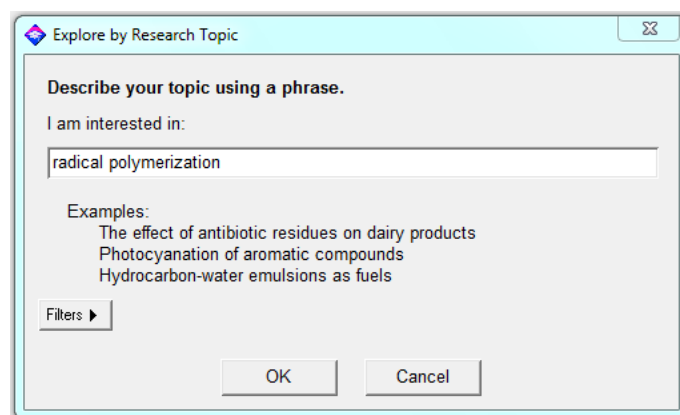
6. 'Explore'
7. 'Locate'
8. 'Browse'

5.1.1. SciFinder 'Explore'



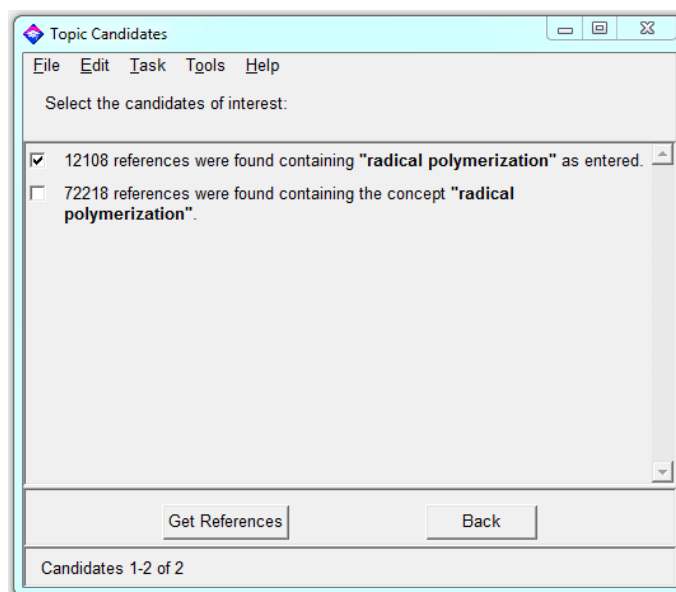
Explore Literature

You can explore the literature by search for a specific topic, an author name or by company name/organization. The following example shows how to search for the topic 'radical polymerization':

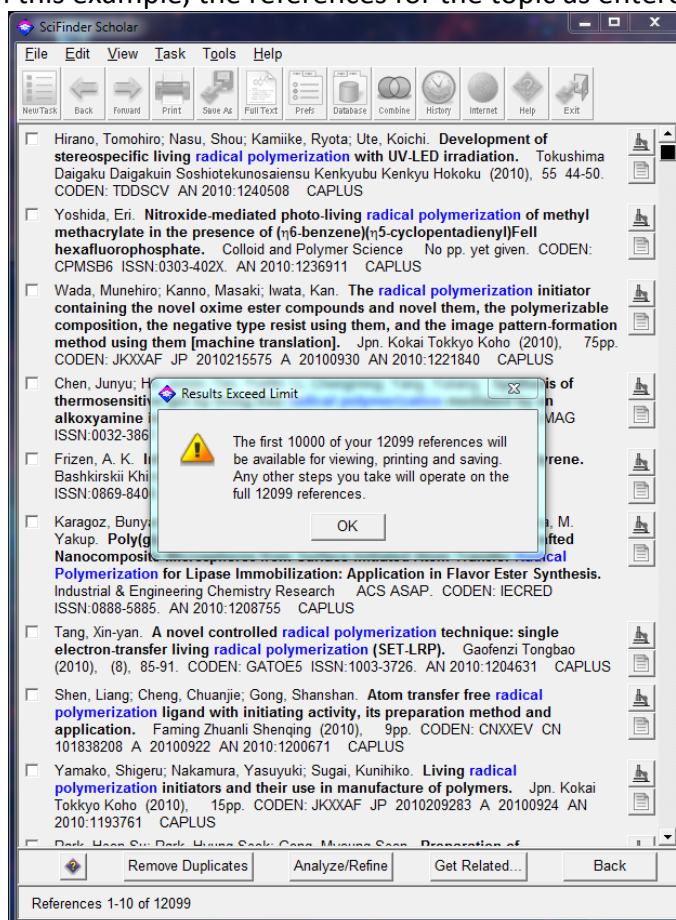


- Enter radical polymerization into the topic field and press 'OK':

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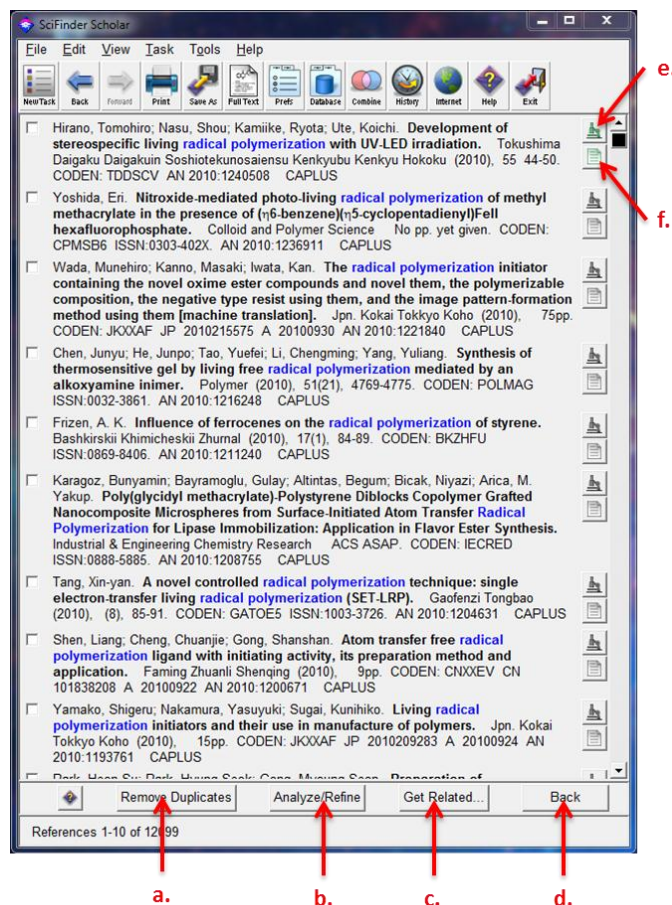


- You can select between candidates of interest by ticking the boxes. It is recommended to get the references containing the topic as entered. If you want to know more about general concepts to the entered topic, select the second possibility. In this example, the references for the topic as entered are selected:



- Due to the large number of references available, SciFinder Scholar reduces the amount of references for viewing, printing and saving to 10000. However, all actions you take will be executed to all the references available:

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In the references window you can process search result further or view a reference you find interesting:

- Some references are shown twice as they are accessible on two or more databases. By pressing 'Remove Duplicates' you can remove them.
- By pressing 'Analyze/Refine' you can further decrease the number of references by further analyzing in terms of e.g. author name, publication year, chemicals of interest, etc.
- By pressing 'Get related...' you can get related information about citing/cited references, chemicals, reactions. However, this can be only performed with a total number of 500 references. Therefore the number of references has to be decreased by 'Analyze/Refine' or by selecting references (ticking the boxes).
- Get back to the topic candidates window.
- Get more details about the reference.
- Search the ChemPort/SFX library of the FU Berlin for the selected literature.

Explore Substances

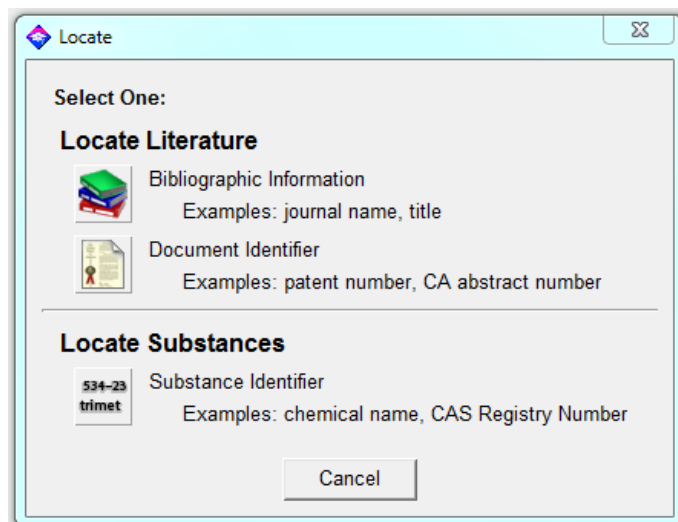
If you are searching for a specific substance you can search by drawing the chemical structure (e.g. if you do not know the correct name) or by entering the molecular formula.

Explore Reactions

If you want to search references/literature for a specific reaction (e.g. if you want to search for reaction conditions) you can enter the reaction here.

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5.1.2. SciFinder 'Locate'



Locate Literature

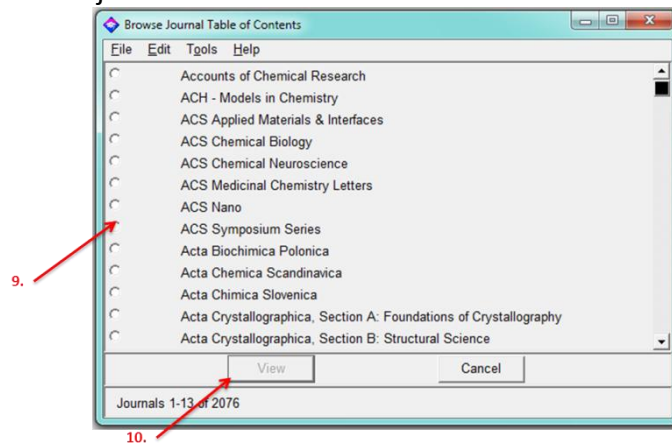
If you are searching for specific literature, use this tool to search for publications and patents.

Locate Substances

Use this tool to search for substance properties and publications applying this substance.

5.1.3. SciFinder 'Browse'

Use this tool to browse the journal table of contents:



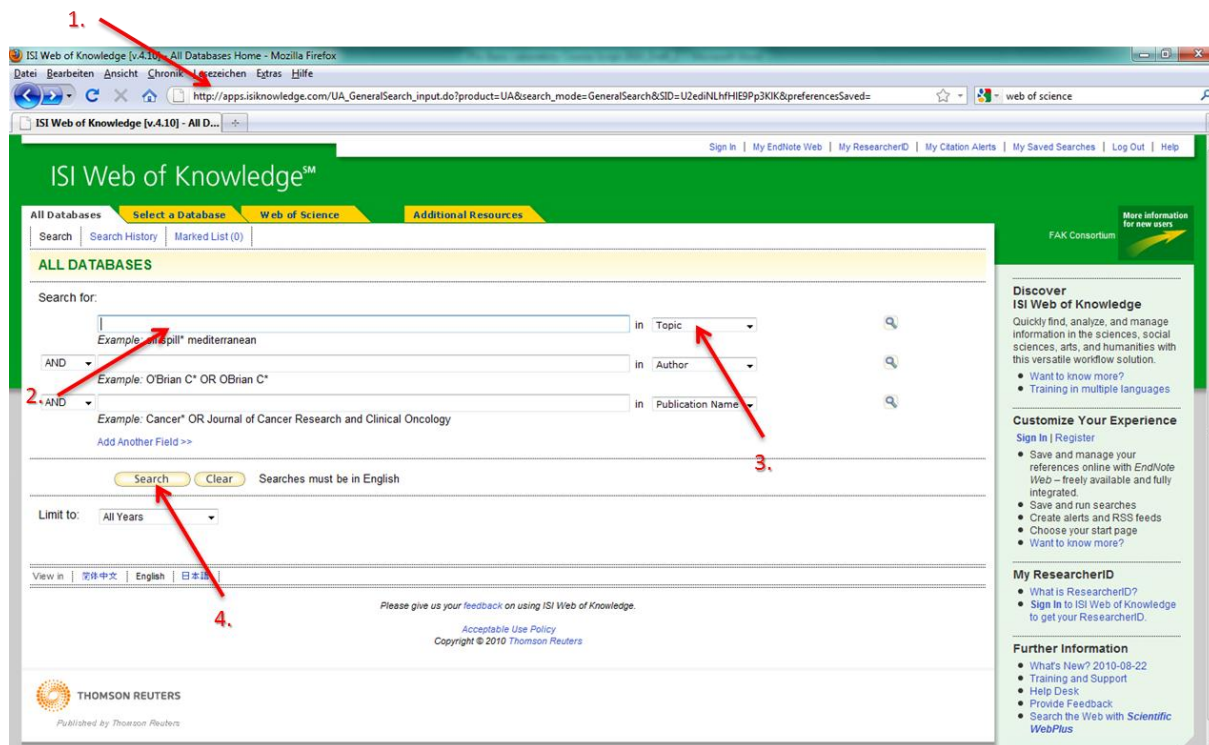
9. Select your journal of interest

10. Click 'View' to watch the current table of contents of your selected journal

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5.2. ISI Web of Knowledge

The following part describes briefly how to use/find literature with 'ISI Web of Knowledge':



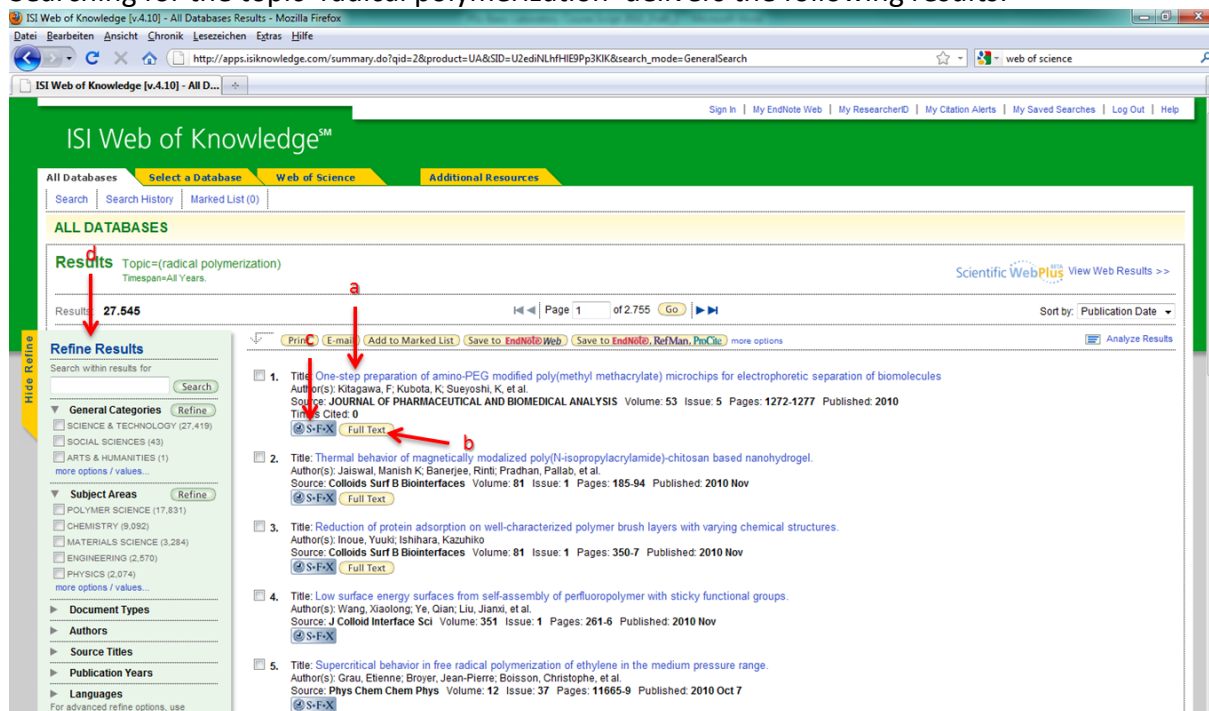
11. Go to: <http://isiknowledge.com>

12. Type in the topic you want to search for, you can also directly refine it by adding further key words

13. Vary the fields in which you want to search for (dependent on your key word)

14. Click 'search'

Searching for the topic 'radical polymerization' delivers the following results:



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Literature Search

Now there are several possibilities to continue:

- a. Go directly to the abstract provided by 'ISI Web of Knowledge':

The screenshot shows the ISI Web of Knowledge interface. The search results for the article "One-step preparation of amino-PEG modified poly(methyl methacrylate) microchips for electrophoretic separation of biomolecules" are displayed. The article is from the Journal of Pharmaceutical and Biomedical Analysis, Volume 53, Issue 5, Special Issue: Sp. Iss. SI, Pages 1272-1277, published in December 2010. The abstract describes a method for chemical surface modification of poly(methyl methacrylate) (PMMA) microchips with amino-poly(ethylene glycol) (PEG-NH₂) by nucleophilic addition-elimination reaction. The article has 37 references and 0 citations. The authors listed are Fumihiko Kitagawa, Kei Kubota, Kenji Sueyoshi, and Koji Otsuka.

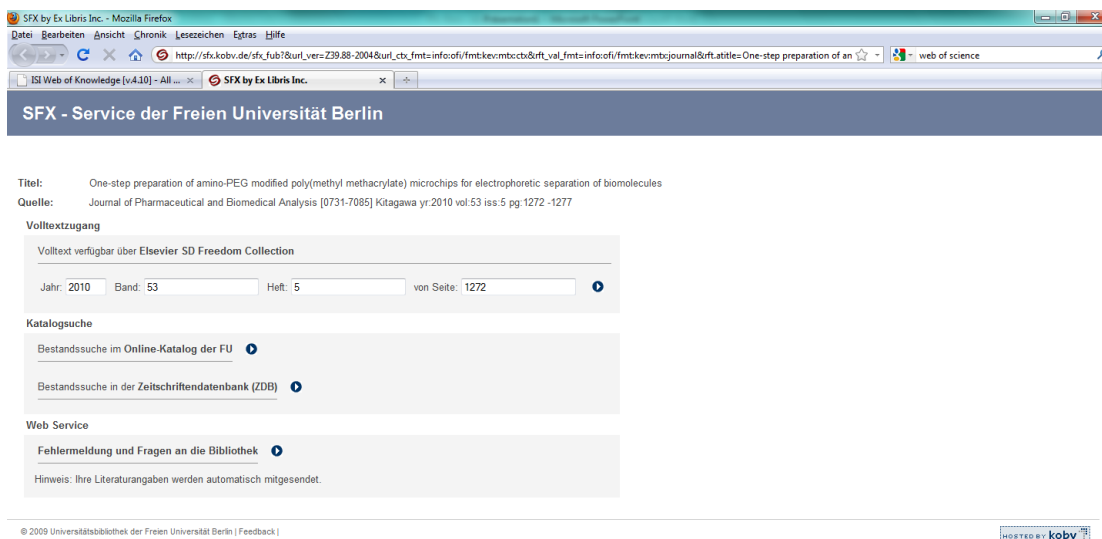
- b. Directly go to the abstract/full text provided by a second database:

The screenshot shows the ScienceDirect interface. The search results for the article "One-step preparation of amino-PEG modified poly(methyl methacrylate) microchips for electrophoretic separation of biomolecules" are displayed. The article is from the Journal of Pharmaceutical and Biomedical Analysis, Volume 53, Issue 5, Pages 1272-1277, published in December 2010. The abstract describes a method for chemical surface modification of poly(methyl methacrylate) (PMMA) microchips with amino-poly(ethylene glycol) (PEG-NH₂) by nucleophilic addition-elimination reaction. The article has 37 references and 0 citations. The authors listed are Fumihiko Kitagawa, Kei Kubota, Kenji Sueyoshi, and Koji Otsuka.

To access the full text, you have to be connected to the FU network (WLAN or LAN).

- c. You can use the ChemPort/SFX library to search for alternative sources:

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The screenshot shows a web browser window with the SFX by Ex Libris Inc. interface. The browser's address bar contains the URL: [http://sfx.kobv.de/sfx_fub?url_ver=Z39.88-2004&url_ctb_fmt=info:ofi/fmt:kev:mtx:ctx&ft_val_fmt=info:ofi/fmt:kev:mtx:journal&ft_title=One-step preparation of an amino-PEG modified poly\(methyl methacrylate\) microchips for electrophoretic separation of biomolecules](http://sfx.kobv.de/sfx_fub?url_ver=Z39.88-2004&url_ctb_fmt=info:ofi/fmt:kev:mtx:ctx&ft_val_fmt=info:ofi/fmt:kev:mtx:journal&ft_title=One-step%20preparation%20of%20an%20amino-PEG%20modified%20poly(methyl%20methacrylate)%20microchips%20for%20electrophoretic%20separation%20of%20biomolecules). The page title is "SFX - Service der Freien Universität Berlin".

Titel: One-step preparation of amino-PEG modified poly(methyl methacrylate) microchips for electrophoretic separation of biomolecules
Quelle: Journal of Pharmaceutical and Biomedical Analysis [0731-7095] Kitagawa yr.2010 vol:53 iss:5 pg.1272-1277

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Fehlermeldung und Fragen an die Bibliothek
Hinweis: Ihre Literaturangaben werden automatisch mitgesendet.

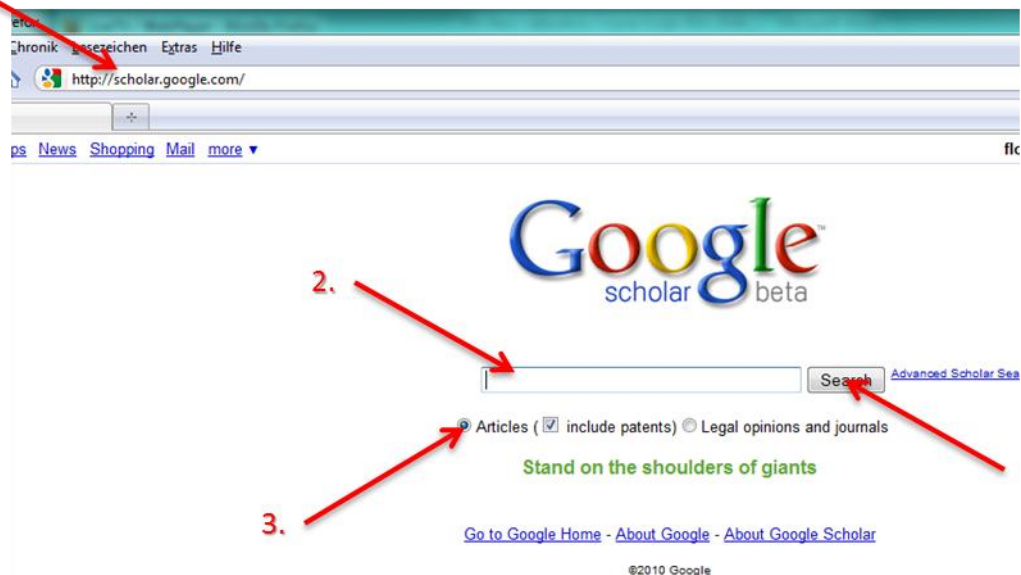
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- d. Refine your search by altering various aspects of your search.

5.3. Google Scholar

The following part describes briefly how to use/find literature with 'Google Scholar':

1.



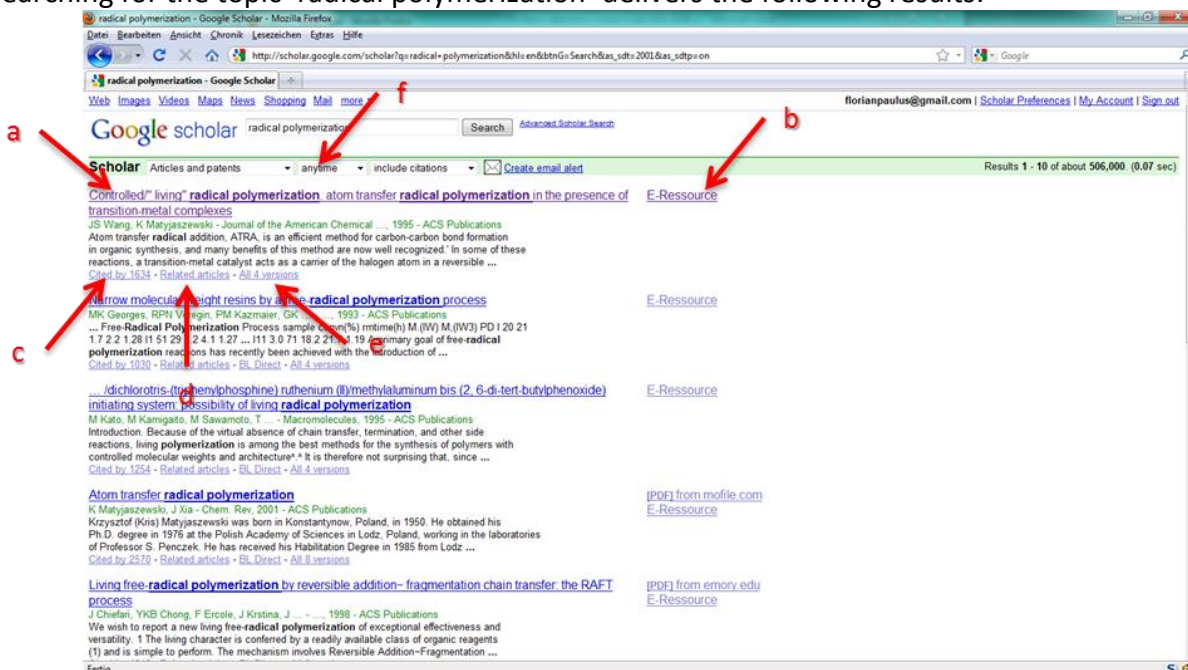
15. Go to: <http://scholar.google.com>

16. Type in the topic you want to search for

17. Vary the type of article you search for (recommended as shown)

18. Click 'search'

Searching for the topic 'radical polymerization' delivers the following results:



Polymer Synthesis and Characterization – Basic Laboratory Course Literature Search

Now there are several possibilities to continue:

a. You can directly go to the article, provided by a certain journal:

The screenshot shows the ACS Publications website interface. The main article title is "Controlled/living radical polymerization. atom transfer radical polymerization in the presence of transition-metal complexes" by Jin-Shan Wang and Krzysztof Matyjaszewski. The article is from the Journal of the American Chemical Society (JACS), published in 1995, volume 117, issue 20, pages 5614-5615. The DOI is 10.1021/ja00125a035. The page includes a search bar, navigation tabs, and a sidebar with related content and tools.

To gain access to the full articles you have to be connected to the FU network (WLAN or Lan).

b. You can use the SFX library to search for alternative sources:

The screenshot shows the SFX library search results page. The search criteria are: Title: "Controlled/living radical polymerization. atom transfer radical polymerization in the presence of transition-metal complexes" and Quelle: "Journal of the American Chemical Society [0002-7863] Wang yr:1995 vol:117 iss:20 pg:5614". The page displays the full text availability, catalog search options, and web service information.

- See all articles referring to this article.
- See all articles having related topics.
- Look at different versions of the article (different language, journal, etc.).
- If you are searching for a certain article but you cannot find it, it is possible to refine your search by altering:
 - Type of article
 - Publication year
 - Complexity of the article

5.4. Further Sources & Information

In order to get an overview over the available ebooks use the search function of the FU catalog. You can restrict your search to the category of ebooks, by marking the button "E-Bücher". The FU catalog can be found on the link below.

http://sf4.ub.fu-berlin.de/F?func=file&file_name=find-b&local_base=fub01



The Royal Society of Chemistry offers also a broad range of ebooks. Therefore, click the following link:

<http://pubs.rsc.org/en/Ebooks?key=Title&value=All> (connection via the VPN client required).

You can also use the old school way of getting information by using the library in the chemistry department. A short list of relatively new educational books is available on the link below:

http://www.bcp.fu-berlin.de/chemie/bibliothek/ressourcen/buecherliste_theke_mai_2009.pdf

For an extensive literature search in all libraries of the FU Berlin, please use the FU catalog:

http://sf4.ub.fu-berlin.de:80/F/4QP8HMYD77RB8YA8R98MYXYKY1XJAQQCF3BJIXSMKL3M5Y8IT-11429?func=option-update-Ing&file_name=find-b&F2=pc-latin&P_CON_LNG=ENG&DOC_LNG_00=ALL&x=50&y=14

For using the printer and copier in the chemistry library you have to purchase a copy card on the right side of the main entrance of the chemistry department.

Comprehensive information for the safe handling of hazardous substances and other chemical substances are available on the GESTIS-Substance Database. Furthermore this database offers you information upon physical and chemical properties of these compounds.

<http://www.dguv.de/ifa/en/gestis/stoffdb/index.jsp>

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Literature Search

Information with respect to physical properties and safety data sheets are also available on the catalogs of the big chemical suppliers, e.g. Sigma-Aldrich:

<http://www.sigmaaldrich.com/catalog/AdvancedSearchPage.do>

6. Preliminary Discussion & Report

In order to understand what you are doing during the laboratory course and not only follow the recipes from the script, you need to prepare every experiment. This includes:

- Safety aspects (toxicity of reagents/solvents, etc.)
- Apparatus setup
- Reaction mechanism
- Be able to answer the questions to the reaction
- Think about difficulties and possible questions/problems regarding the experiment

The tutors will check your preparation by an oral exam before you are allowed to start the experiment. If you are not prepared, you are NOT ALLOWED to conduct the experiment and you will have to repeat it during the catch up week.

Every student has to write a report for each experiment which has to be handed in before starting the next experiment at the latest. Each day the report is delayed your mark will automatically downgrade by 0.3. If you hand in the experimental report IN TIME, you will have the chance to correct it and improve your mark.

If you quote literature or any work which is not your one: REFERENCE IT!!! Be aware of that it is easy to check whether you copied something from the internet or your colleagues. There is help for literature search provided in this script. WIKIPEDIA IS NOT A SCIENTIFIC DATABASE!

The preliminary discussion will make up 1/3 of the mark for the experiment. So it is worth preparing it!

GOOD LUCK!



Sample Report

Anionic Ring Opening Copolymerization of Glycidyl Ethers



Report

Basic Laboratory Course
for Polymer Science
M.Sc. Program

John Smith

Berlin, 11 November 2010

1. Introduction

Poly(glycidyl ether)s (see Figure 1 a) are an interesting class of polymers since several poly(glycidyl ether)s were found to exhibit a thermo-responsive behavior in aqueous media.^[1] Quite contradictory to the commonly observed trend that solutes become more easily dissolved with increasing temperature, thermo-responsive polymers that exhibit a lower critical solution temperature become less soluble and finally precipitate at the LCST (see Figure 1 b). The phase separation at the LCST is generally ascribed to a negative value of the entropy of mixing ($\Delta S < 0$), which becomes according to the Gibbs free energy ($\Delta G = \Delta H - T\Delta S$) more and more important with increasing temperature, thereby overcoming the negative enthalpy of mixing ($\Delta H > 0$) and causing a phase separation.^[2]

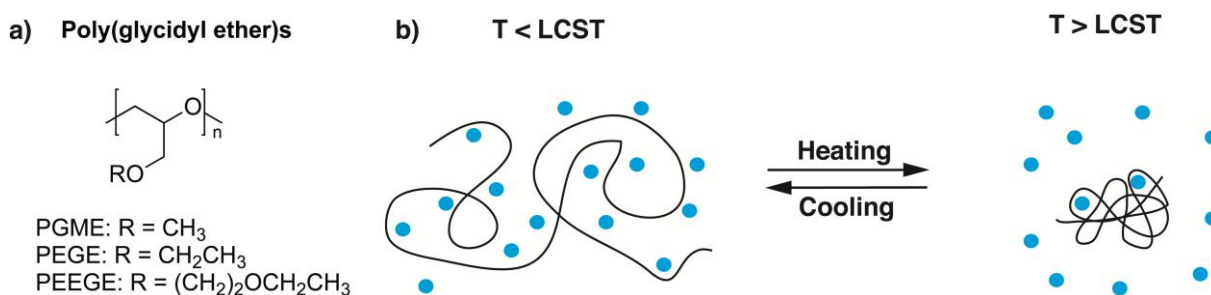


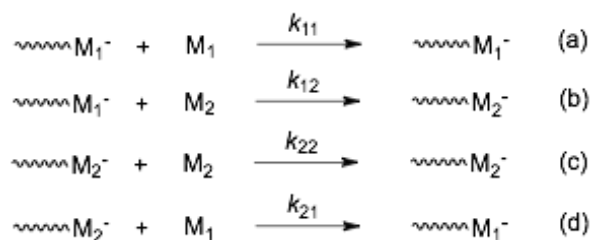
Figure 1: a) Molecular structure of various poly(glycidyl ether)s. b) Entropically induced phase separation of aqueous poly(glycidyl ether)s solution. Blue dots represent water molecules. On the left-hand side the system is depicted in its hydrated state. On the right-hand side the system is shown separated in two phases.

The LCSTs of the poly(glycidyl ether) homopolymers is determined by the nature of the alkoxide group. The greater the number of carbon atoms the lower the LCST. So far, three poly(glycidyl ether)s homopolymers have been found to exhibit thermo-responsive properties, namely poly(glycidyl methyl ether) (PGME), poly(ethyl glycidyl ether) (PEGE), and poly(ethoxyethyl glycidyl ether) (PEEGE) which have LCSTs of 57.7, 14.6, and 40.0 respectively (see Figure 1).^[1] However, the LCST can be finely adjusted by copolymerization of comonomers bearing different alkoxide groups. Since the LCST depends on the solubility of the copolymer, the LCST can be adjusted by varying the monomer feed ratio and thereby the hydrophilicity to hydrophobicity ratio.^[3]

A copolymer is a polymer that is made up of at least two different types of monomer. The distribution of the comonomers in the polymer depends on both the monomer feed ratio

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Preliminary Discussion & Report

and the reactivity ratios r_1 and r_2 , which represent the reactivity of the reactive chain ends towards the same kind of monomer relative to the other kind. The definitions of the reactivity ratios r_1 and r_2 and are based on the following considerations: A copolymerization of two different comonomers M_1 and M_2 encompasses four possible propagation steps: Step (a) and (c) constitute homopolymerization steps of M_1 and M_2 , respectively. Step (b) and (d) constitute heteropolymerization steps (see Scheme 1).



Scheme 1: Possible propagation steps of a copolymerization. k_{xy} denote the respective reaction rates.

According to the reactions in Scheme 2 the reactivity ratios r_1 and r_2 are given as:

$$r_1 = \frac{k_{11}}{k_{12}} ; r_2 = \frac{k_{22}}{k_{21}}$$

The reactivity ratios r_1 and r_2 are the parameters which determine the monomer distribution along the copolymer chain. In order to obtain a random copolymer the reactivity ratios must be almost equal and close to 1. The reactivity ratios of GME and EGE for KOtBu as initiator were determined as $r_{GME} = 1.42$ and $r_{EGE} = 0.53$,^[3] indicating a slight preference for the incorporation of GME into the polymer chain. Hence, the copolymer should exhibit a small compositional gradient along the polymer chain.

The objective of this experiment was the synthesis of a statistical methanol initiated copolymer, comprising GME and EGE units using a comonomer feed ratio (GME/EGE = 3/1) of 3.

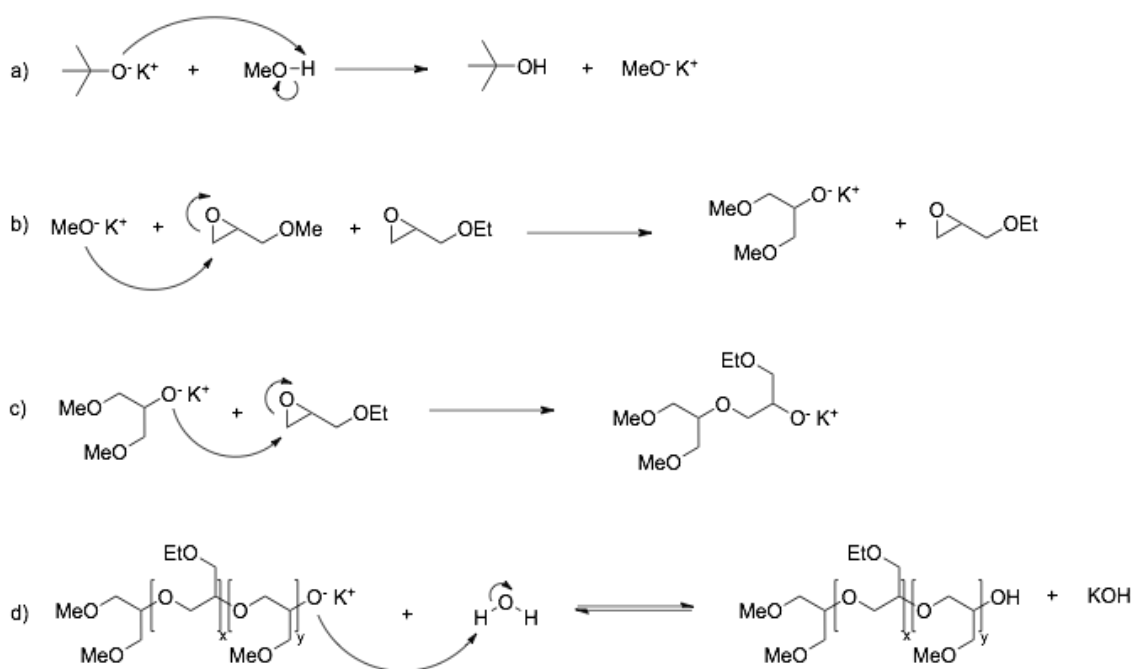
2. Results and discussion

The copolymer poly(GME)₁₅-stat-Co-(EGE)₅ was prepared via anionic ring opening polymerization of GME and EGE and the molecular weight was adjusted by the monomer/initiator ratio [(GME+EGE)/MeOH] = [20]. In order to prevent termination reactions of water impurities the reaction was carried out in flame-dried glass-ware under

argon atmosphere. Methoxide initiated poly(GME)₁₀-stat-Co-(EGE)₁₀ was obtained with 80% yield.

2.1. Reaction mechanism

In the first step MeOH was deprotonated by applying KOtBu as base (see Scheme 2 a). Step (b) and (c) constitute the propagation steps in which a nucleophile, namely the alkoxide, attacks the less substituted carbon of the epoxide ring because it is less sterically hindered. The propagation step is a pure S_N2 reaction. Finally, KOH is formed in an equilibrium chain transfer reaction when water is added.



Scheme 2: Reaction mechanism of the anionic ring opening copolymerization of GME and EGE.

3. Experimental Part

The reaction was carried out in flame-dried glassware under argon atmosphere. KOtBu (0.208 g, 1.857 mmol) was dissolved under dry conditions in a small amount of MeOH. The reaction mixture was heated to 80 °C and stirred for at least 1 h until deprotonation of the alcohol initiator was completed. Subsequently the generated tert-butanol and excess methanol were removed by means of distillation under HV. To the remaining methoxide DME was added (3 mL) and the solution was heated to 110 °C. Then GME (1.16 mL, 13 mmol) and EGE (4.21 mL, 39 mmol) were added simultaneously by syringe and the reaction

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mixture was stirred for 24 h. After cooling down to room temperature the reaction was quenched by the addition of water. The mixture was concentrated under reduced pressure and dried in HV. The residue was dissolved in diethyl ether and precipitated salts were removed by centrifugation. The residue was again concentrated under reduced pressure and dried in HV to yield 3.78 g of a yellowish oil (91%).

4. Literature

- [1] S. Aoki, A. Koide, S. Imabayashi, M. Watanabe, *Chem. Lett.* **2002**, 1128.
- [2] J.-F. Lutz, O. Akdemir, A. Hoth, *J. Am. Chem. Soc.* **2006**, *128*, 13046.
- [3] S. Reinicke, J. Schmelz, A. Lapp, M. Karg, T. Hellweg, H. Schmalz, *Soft Matter* **2009**, *5*, 2648.

Remarks

1. Line spacing 1.5 in order to be able to add remarks directly.
2. Draw the complete mechanism with chemical structures, i.e. each reaction step with the moving electrons (draw arrows).
3. Note references in the text with superscripted numbers.