Preparation of nylon 6,6 by interfacial polymerization

João P. Telo[a]

Supplementary Material

This experiment was performed for high-school students visiting our lab and by under-graduate students of chemistry and polymer sciences. This has been described in many sources using different solvents for the acid chloride, but most of the alternatives are well described in the original paper.[1] Dichloromethane can be replaced by several chlorinated solvents, 1,1,1-trichloroethane being the less toxic. Alternatively, hexane, petroleum ether or the less toxic cyclohexane can be used as a solvent, but in this case the organic solution must be placed over the aqueous solution, since these solvents are less dense than water. A web search of "nylon rope trick" provides useful information and several pictures (below, one taken in our lab).[2,3]

Picture SM 16.1.1 Pulling the nylon rope

Hints to the questions:

Proteins are natural polyamides. Polyamides are very strong polymers due to N-H⋯O=C hydrogen-bonds between the polymer chains.

[1] P. W. Morgan, S. L. Kwolek, *J. Chem. Ed.*, 1959, **36**, 182.
[2] http://www.rsc.org/learn-chemistry/resource/res00000755/making-nylon-the-nylon-rope-trick?cmpid=CMP00000834
[3] https://www.chem.umn.edu/services/lecturedemo/info/Nylon_Rope_Trick.html

Synthesis of Copolymer from Acrylamide (AA),

2-acrylamido-2-methyl-propane-sulfonic acid (AMPS) and

N,N-methyleno-bis-acrylamide (BA)

Supplementary Material

This experiment proposal was developed by the author in his research work and adapted to be carried out by both high-school and university students due to its simple and fast procedure. This work was tested by 3th undergraduate students, where the radical polymerization concepts are known and both polymerization techniques and swelling capacity are taught. This experiment illustrates a free-radical polymerization to obtain a superabsorbent copolymer by solution and inverse emulsion technique. Three different monomers are used: Acrylamide (AA); 2 acrylamido-2-methyl propane sulfonic acid (AMPS) and as crosslinker, N,N-methyleno-bis-acrylamide (BA); Tween 85 (Polyoxyethylene sorbitan trioleate) is used as emulsifier; and Isopar M (Isoparaffinic hydrocarbon solvents) as organic solvent. The measurement of the absorption capacity of the synthesized copolymer in water allows decide on the method of polymerization to use depending of the desired features of the output copolymer, high or lower swelling capacity.

Additional notes on the preparation of the copolymer AA/AMPS/BA by free radical solution polymerization technique

Synthesis can be successfully completed in a glass reactor (250 mL) equipped with a stirrer, a reflux condenser, a thermometer, a dropping funnel and a gas inlet tube. Inert atmosphere is essential to the success of copolymerization. The apparatus for the synthesis of the copolymer is shown in Scheme **SM 16.2.1**.

Scheme **SM 16.2.1 –** The apparatus for the synthesis of the copolymer

Temperature reaction should be 50-60ºC. Higher temperatures lead to copolymer with low swelling

capacity. To precipitate all the copolymer, a total volume of 60 mL of acetone should be added. In

general, 1 volume of copolymer to 4 volumes of acetone is used. Students typically obtain 8-9g of

dried copolymer. Scheme **SM 16.2.2** shows the aspect of the copolymer synthesized when dried and

ground.

Scheme **SM 16.2.2 –** Dried and ground copolymer

Additional notes on the preparation of the copolymer AA/AMPS/BA by free radical inverse emulsion polymerization technique

This polymerization technique origin similar results according copolymer mass.

The swelling equilibrium is measured by placing 0.01 g of copolymer into a tea bag and then immersing it in a beaker with 100mL deionized water as demonstrated in Scheme **SM 16.2.3**.

Scheme **SM 16.2.3 –** Copolymer before and after immersion in deionized water

The equilibrium swelling is reached after 15 minutes. The water absorbed by the copolymer was obtained by removing the sample from the water shaking the excess water and weighing the copolymer. Results show that inverse emulsion polymerization technique leads to better swelling capacity (water increment, 400). With solution polymerization technique the water increment is lower, (c.a. 200).

FT-IR spectra

The FT-IR spectroscopy can be used to confirm the polymerization reaction and that the copolymer's structure shows no change attributable to the copolymerization technique. The FT-IR spectra of the AA monomer and that of the copolymer synthesized are shown in **Error! Reference source not found.**, which allows compare the two spectra and confirm the polymerization reaction. The C=C absorption band of the vinyl monomer (upper curve), at around 980 cm^{-1} is expectedly absent in the spectrum of the polymer (lower curve), as this bond is key to the propagation step of the polymerization reaction. The remaining absorption bands, for both the monomer and the polymer, can be found in the appropriate ranges.
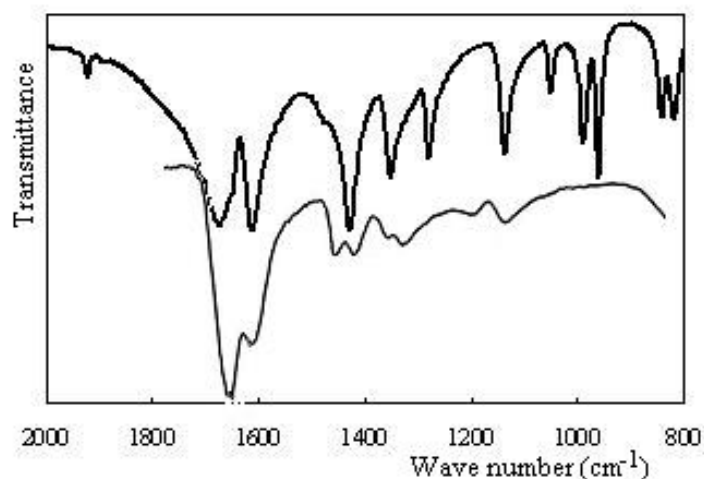
Scheme **SM 16.2.4** – FT-IR spectra of the acrylamide monomer (upper curve) and that of the synthesized   copolymer (lower curve)

Typical absorption bands of the amides may be observed, namely: C=O, in the range 1650–1680 cm^{-1}, in agreement with the reported range[1-2] 1630–1700 cm^{-1}; NH$_2$ deformation, 1610 cm^{-1}, in the reported range[3] 1500–1690 cm^{-1}; primary amides, 1426 cm^{-1}, generally not well resolved but in the reported range[3] 1420–1400 cm^{-1}.

[1] C. Erbil, C. Cin, A. B. Soydan, A. S. Saraç, *Journal of Applied Polymer Science*, 1993, **47**, 9, 1643-1648.

[2] T. W. G. Solomons, *Organic Chemistry*, 6th ed., John Wiley and Sons, New York, 1995.

[3] C. N. R. Rao, *Chemical Applications of Infrared Spectroscopy*, Academic Press Inc., New York, 1963.

Multi-step Synthesis of Nylon from Cyclohexene

Supplementary Material

This experiment uses basic chemical transformations learned in introductory organic chemistry courses to illustrate how a simple commercially available compound can be used to make a material in the organic chemistry laboratory setting.

Course Audience

This laboratory has been used in the second quarter introductory organic chemistry laboratory. The students taking this course are usually second year students majoring in chemistry, biology or biochemistry. The course is taught four quarters a year with a minimum of 8 and maximum of 16 sections, each containing 18 students. This amounts to 288 students in the most demanding quarter. The students work in pairs to decrease the need for space and allow collaborative efforts.

Common Results

Students usually complete the entire reaction process with successful results. Student yields of the oxidation of cyclohexene to adipic acid are usually 80%, but do range from 50% to quantitative, with some rare instances of milligram quantities of product obtained. The acid chloride formation is fairly quick and successful, but enough oxalyl chloride equivalents must be used to obtain good results. In the final polymerization step, it can be difficult to obtain a good strand, but usually a matter of patience. Most students obtain a strand that is 25 cm for the stretch test, but the majority of students obtain strands that are much longer, with the longest strand to date being over 7.6 m.

Melting Point of Adipic Acid: 152.1 °C

IR Spectrum of Adipic Acid:

Adipic Acid   10/15/2014

Page 1/1
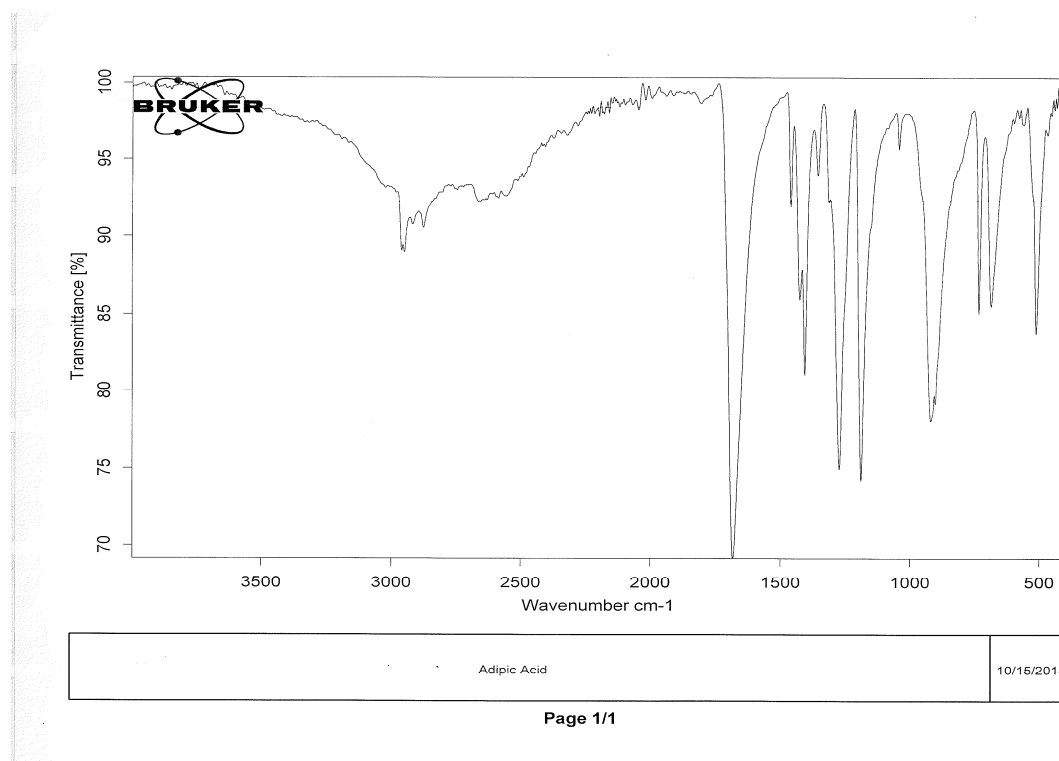
Time Requirements & Adaptations

Two laboratory sessions (4 hours each) are usually allotted for this experiment. In most cases, the first session takes prepared students 3 hours and the second session takes prepared students 2 hours, but some students take the full time. In the second session, the shortened time requirement allows the instructor to discuss determination of yield (of polymer) over multiple steps to obtain overall % yield. The oxidation using potassium permanganate was chosen since the oxidant is often introduced in introductory organic lectures courses. However, the oxidant itself is rather caustic and "greener" processes and reaction adaptations are known.[1] If the instructor can only allow 1 laboratory session, commercial adipic acid may be used to form adipoyl chloride subsequent to the polymerization reaction. This single session can still be used to convey the desired message and introduce some common transformations. In this case, the instructor may introduce a question or class exercise on how to obtain adipic acid from other commercial reagents.

Laboratory Set-Up & Equipment

The laboratory set-up is performed for all of the sections by the undergraduate laboratory stockroom.

The preparation notes included here are for sections of 18 students that work in pairs. The amounts

included allot enough supplies and reagents to run 9 experiments in a laboratory section. The items

included in these preparation lists are in addition to the common equipment students have in assigned

lockers from a microscale equipment kit and that are generally included in undergraduate organic

chemistry laboratory lockers.

Session 1: Oxidation of cyclohexene to adipic acid

CHEMICALS		AMT/LAB (9 pairs)
Reagents:		
Cyclohexene	[110-83-8]	20 mL
Potassium Permanganate	[7722-64-7]	84 g
Sodium Hydroxide, 1%	[1310-73-2]	250 mL
Hydrochloric Acid, 12M	[7647-01-0]	40-50 mL
Hydrochloric Acid, 6M*	[7647-01-0]	~5 250ml wash bottles
Common Chemicals:		
Methanol	[67-56-1]	10 mL

EQUIPMENT & SUPPLIES

250mL Beakers	10
250mL Erlenmeyer Flask	10
500mL Filter Flask*	6
Tubing for 500ml Filtering Flask*	6
Büchner Funnels (size 5.5-9cm)*	6
Weighing Boats	4
Scoopulas	4
Filter Papers (for Büchner funnels)*	3 boxes
Filter Paper Strips	1 beaker full
Coffee Filters	1 big stack
#14 Corks	1 beaker full
Permanent Markers	6
PH Paper Strips	1 box

WASTE

Potassium Permanganate Waste*	3
Acidic Waste	1
Basic Waste	1
Organic Waste	1

NOTES:

1) Set up three **labeled** vacuum filtration stations in each lab. Line each station with Bytak liner cut to the appropriate size and include all items with an (*) in the hood.

2) Set two separate bins of (10x) 250mL beakers and (10x) 250mL Erlenmeyer flasks in each. Place in front of lab near TA.

3) Make three separate solid waste containers for potassium permanganate sludge; Place one in each vacuum filtration station hood. Add an acidic waste container for waste from cleaning.

4) At each filtering station, put 250ml wash bottles of 6M HCl for glassware cleaning.

Session 2: Acid chloride formation and polymerization

CHEMICALS   **AMT/LAB (9 pairs)**

        Reagents:

Adipic Acid	[124-04-9]	10 g
Oxalyl Chloride	[79-37-8]	20-30 mL
DMF		~10 mL
5% Hexamethylenediamine/5% NaOH		100 mL
Hexamethylenediamine	[124-09-4]	
Sodium Hydroxide	[1310-73-2]	
Sodium Hydroxide, 20%	[1310-73-2]	10-20 mL

Common Chemicals:

Hexanes		250 mL
Methanol	[67-56-1]	250 mL

EQUIPMENT & SUPPLIES

150 mL Beakers	10
25/50 mL RB Flask	10
15 cm Piece of Heavy Gauge Copper Wire	1 beaker
Bunsen Burner	1
Yardstick	2

WASTE

Acidic Waste	1
Basic Waste	1
Organic Waste	1

NOTES:

1) Make up a stock solution of the following:
    5% hexamethylenediamine / 5 % sodium hydroxide in water
    20% sodium hydroxide in water

Experiment Photos
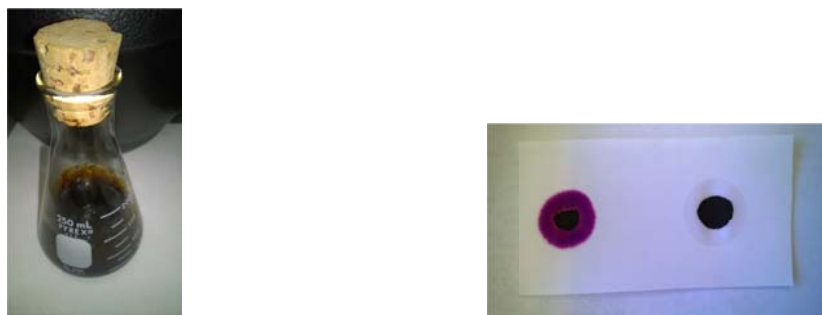
Figure SM 16.3.1: Stoppered reaction flask with all reagents and filter paper indicating reaction (A) incomplete and (B) complete.
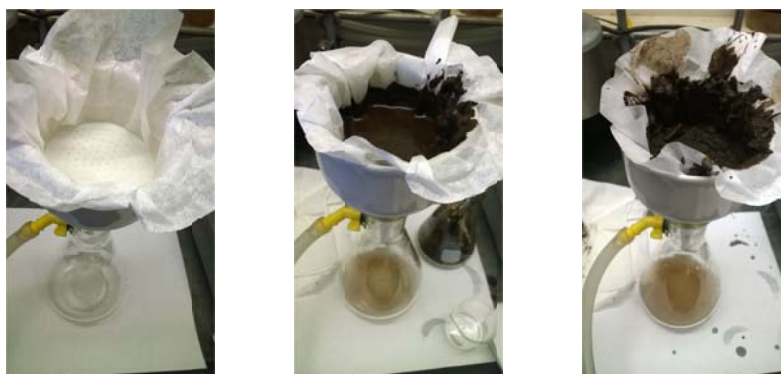

Figure SM 16.3.2: Filtration set-up and process to remove MnO$_2$ produced during reaction.

Figure SM 16.3.3: (A) Honey colored adipic acid (B) crystallization from hydrochloric acid solution and (C) product filtration.

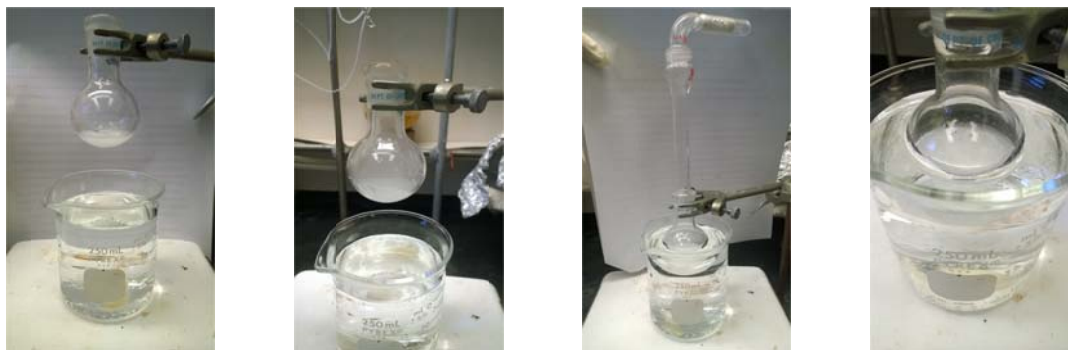**Figure SM 16.3.4: Reaction set-up before addition of oxalyl choride.**

Figure SM 16.3.5: Addition of oxalyl chloride (A) and dimethylformamide (B) followed by appending an air condenser and drying tube.
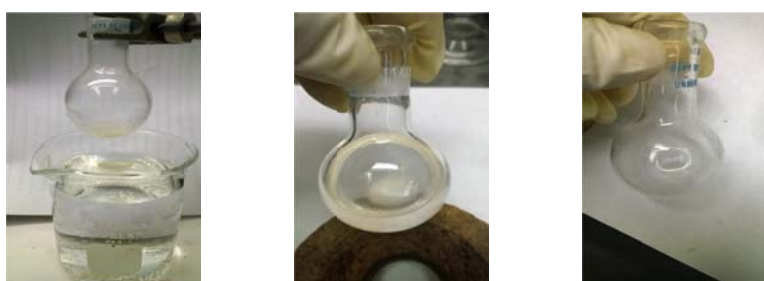
Figure SM 16.3.6: (A) Crude adipoyl chloride and (B) crude adipoyl chloride in hexanes (notice solids on flask and slight yellow color).

Figure SM 16.3.7: Adipoyl chloride and basic diamine solution (2 phases) and removal of Nylon strand using a copper wire hook.

Figure SM 16.3.8: Stretch test before (A) and after (B).

Additional Questions (Including Answers)

Step 1: Oxidation

1. Why is methanol added if the reaction contains unreacted KMnO$_4$? (Think about the mechanism).

The methanol is oxidized by unreacted KMnO$_4$ and results in the formation of formic acid.

2. What formed from the reduction of KMnO$_4$? *Manganese dioxide (MnO$_2$) is formed.*

3. Draw a balanced chemical equation to illustrate the purpose of using concentrated HCl for the

reaction work-up?. *The hydrochloric acid ensures protonation of the adipic acid so it can be isolated.*

Hydrochloric acid is also able to react with the MnO$_2$ by-product as outlined below.

$$MnO_{2\,(s)} + 4\,HCl_{\,(aq)} \rightarrow MnCl_{2\,(aq)} + Cl_{\,2\,(g)} + 2\,H_2O_{\,(l)}$$
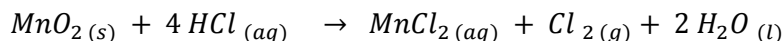
Step 2: Acid Chloride Formation

1. What product do you anticipate can form if oxalyl chloride and adipic acid sit at room temperature?
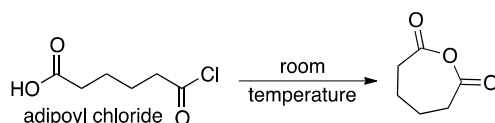
2. How could the adipoyl chloride be purified? *The reactive species can be purified by distillation.*

Step 3: Polymerization

1. Why must the polymerization step have a basic solution? (Consider how it would affect your yield).

The polymerization solution must be basic so that the diamine is not protonated and is nucleophilic.

The amine must be able to add to the carboxylic acid and form the amide bond. If the solution is not

basic, or not basic enough, there will not be enough of the nucleophilic amine to react with the acid

chloride and form polymer product. This would result in a lowered product yield.

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[1] (a) Reed, S. M.; Hutchinson, J. E. *J. Chem. Ed.* **2000**, *12*, 1627-1629. (b) Sato, K.; Aoki, M.; Nyori, R. *Science* **1998**, *281*, 1646-1647. (c) Deng, Y.; Ma, Z.; Wang, K.; Chen, J. *Green Chemistry* **1999**, *1*, 275-276. (d) Usui, Y.; Sato, K. *Green Chemistry* **2003**, *5*, 373-375.

Copolymerisation of styrene and methyl methacrylate: an introduction to radical polymerisation and monomer reactivity ratios
Supplementary Material

Experiment Notes

    Background information

    Copolymer composition analysis from FT-IR data

    Table **SM 16.4.**1 – Calibration data for polystyrene–poly(methyl methacrylate) mixtures

    Typical student results

Figures

    Photo of a polymerisation tube

    Example of an IR spectrum of a styrene-rich copolymer

    Example of an IR spectrum of a methyl methacrylate-rich copolymer

    Typical copolymer composition diagram and best-line fit

    95% joint confidence limits for the reactivity ratios

    ^{1}H NMR spectrum of a copolymer

This experiment has been used for over 10 years in a dedicated Polymer Chemistry lab course for Year 3 Chemistry students. The experiment is typically carried out in groups of 8 or more students where each student prepares and analyses his or her own copolymer. The results are then combined into a copolymer composition diagram from which the reactivity ratios are extracted using non-linear curve fitting. It is possible to complete the experiment in a single 3-hour lab session, but in such a case students should best be provided with monomers where the inhibitor has already been removed prior to the lab class.

Table SM 16.4.1 – Suggested compositions for a series of monomer mixtures ranging from 10 to 90% styrene monomer and methyl methacrylate

Sample	S/mL	MMA/mL	S/mmol [a]	MMA/mmol [a]	f_S
1	9.0	1.0	78.6	9.3	0.89
2	8.0	2.0			
3	7.0	3.0			
4	6.0	4.0			
5	5.0	5.0			
6	4.0	6.0			
7	3.0	7.0			

8	2.0	8.0
9	1.0	9.0

Students are only given a partially completed Table **SM 16.4.**1 showing the proposed compositions of the monomer mixtures and the calculated results for sample 1. Sample 9 can be omitted if only 8 students are doing the experiment. Students first need to complete the table.

Example calculation (sample 2):

Amount of styrene used $= \dfrac{8.0\ mL \cdot 0.909 g \cdot mL^{-1}}{104.15 g \cdot mol^{-1}} \cdot 1000 = 69.8$ mmol

Amount of methyl methacrylate $= \dfrac{2.0\ mL \cdot 0.93 g \cdot mL^{-1}}{100.12 g \cdot mol^{-1}} \cdot 1000 = 18.6$ mmol

$f_S = \dfrac{69.8}{69.8+18.6} = 0.79$

More recently, the experiment has been incorporated into a more open-ended miniproject for Chemistry Masters students (Year 4) who, again, work in small teams to determine the copolymerisation reactivity ratios for various styrene–methacrylate and styrene–itaconate mixtures. Students are allowed to choose which analytical technique they want to use (FT-IR or ^{1}H NMR or both). The copolymer composition tends to be obtained more easily (and more cheaply) by analysing IR spectra of the copolymers.

Students then blend their copolymers with a strongly interacting [poly(4-hydroxystyrene)] and a weakly interacting homopolymer [e.g. polystyrene, poly(ethyl methacrylate) or poly(ethylene oxide)]. Differential scanning calorimetry is then used to test whether blends are miscible (in which case they show a single glass transition) or immiscible (in which case two glass transitions are seen, one for each of the components).

Photos of the experiment

Radical polymerisations are routinely carried out under inert gas atmosphere. Traces of oxygen are not a problem, but too much oxygen present can inhibit the polymerisation.

Yields of copolymer tend to be in the range of 0.15 − 0.70 g (1.5 − 7.5%). Yields >10% are undesirable since it is important that the monomer composition does not change significantly during the copolymerisation.
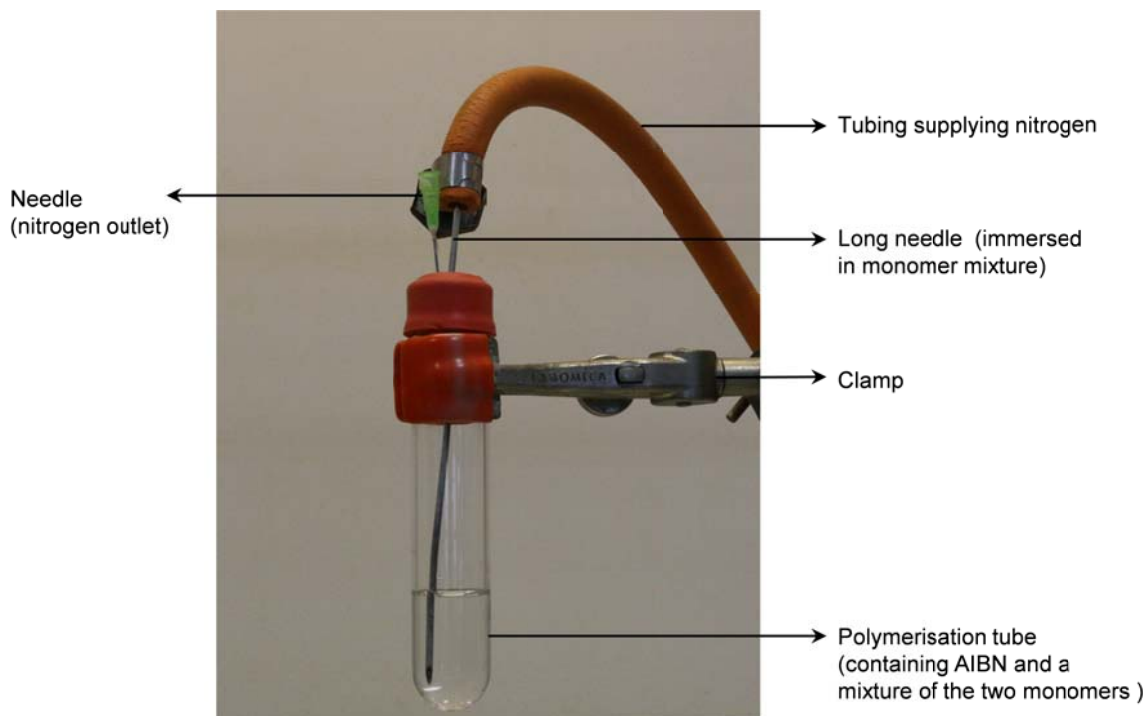
Figure SM 16.4.1 – Photo of a polymerisation tube showing the flushing the monomer mixture with N_2 prior to the copolymerisation.

Copolymer composition analysis from FT-IR data

Copolymer compositions can be determined using a procedure similar to that reported by M. K. Bellamy for an ethylene/vinyl acetate copolymer (*J. Chem. Educ.*, 2010, **87**, 1399).

Two typical FT-IR spectra for styrene/methyl methacrylate copolymers are shown in Figures **SM 16.4.**2 and **SM 16.4.**3. To determine the copolymer composition for this copolymer system, students will need to record the two values of absorbance at 1730 cm^{-1} and 700 cm^{-1}, A_{1730} and A_{700}, corrected for any baseline contribution. The structural units absorbing at 1730 cm^{-1} and 700 cm^{-1} belong, respectively, to the C=O stretch of the methacrylate's ester group and the mono-substituted benzene deformation mode of the styrene repeat units.
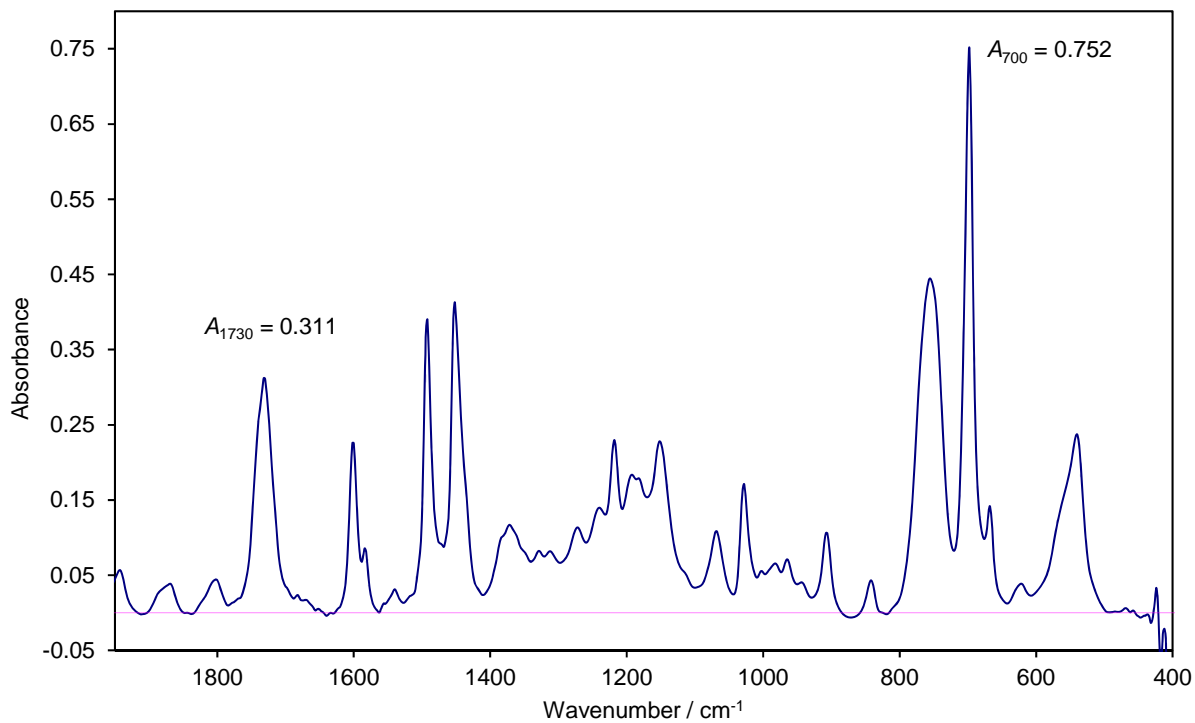
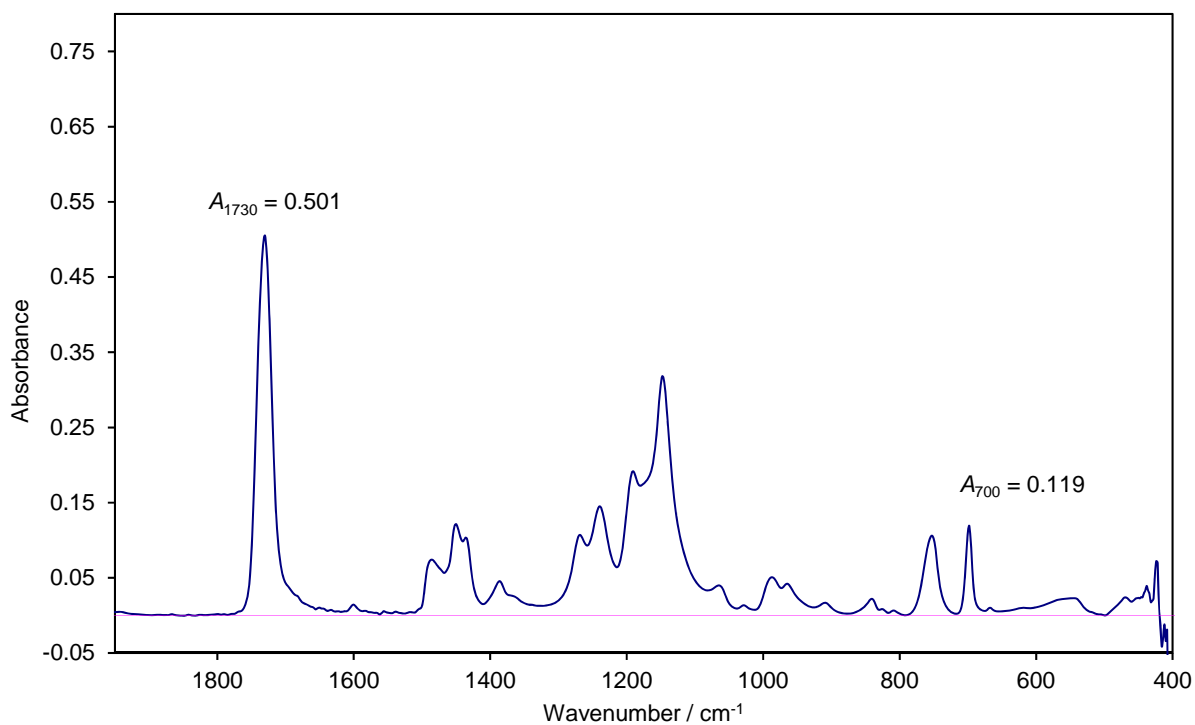**Figure SM 16.4.2 –** Example of an IR spectrum of a styrene-rich copolymer.

Figure SM 16.4.3 – Example of an IR spectrum of a methyl methacrylate-rich copolymer.

To determine the fraction of styrene in the copolymer (F_S) from the IR absorbance values students will need to prepare a calibration curve first. If students have only a 3-hour session to complete the experiment, they are provided with the calibration data (Table **SM 16.4.**2) and asked to calculate the A_{700}/A_{1730} and $\varepsilon_S/\varepsilon_{MMA}$ ratios. In a more open-ended lab project, they can be asked to prepare their own calibration curve.

A calibration curve is easily obtained by first making blends of the two homopolymers, polystyrene and poly(methyl methacrylate), by dissolving the mixture in a suitable solvent (e.g. chloroform) and making a film of the blend by allowing a drop of the solution to evaporate on an NaCl plate or an ATR crystal. A minimum of four samples of different compositions are needed, covering the composition range of your copolymer.

The Beer-Lambert law applies to both absorbances at 1730 cm^{-1} and 700 cm^{-1}

$$A_{700} = \epsilon_S \cdot c_S \cdot d$$

$$A_{1730} = \epsilon_{MMA} \cdot c_{MMA} \cdot d$$

Dividing the two equations gives

$$\frac{A_{700}}{A_{1730}} = \frac{\epsilon_S \cdot c_S}{\epsilon_{MMA} \cdot c_{MMA}}$$

where the sample thickness d cancels since both components are part of the same film. Since the ratio c_S/c_{MMA} is known from the blend composition, the ratio $\varepsilon_S/\varepsilon_{MMA}$ can then be determined from the IR data. The completed results of such a calibration are shown in Table **SM 16.4.**2.

Table SM 16.4.2 – Calibration data for polystyrene/poly(methyl methacrylate) mixtures of the two homopolymers.

c_S/c_{MMA}	A_{700}	A_{1730}	A_{700}/A_{1730}	$\varepsilon_S/\varepsilon_{MMA}$
3.20	0.540	0.257	**2.101**	**0.657**
1.44	0.437	0.458	**0.954**	**0.663**
0.642	0.207	0.529	**0.391**	**0.610**
0.236	0.108	0.754	**0.143**	**0.607**

A simple average gives $\varepsilon_S/\varepsilon_{MMA} = 0.634$ (the least squares result[1] is 0.656 ± 0.003).

Knowing $\varepsilon_S/\varepsilon_{MMA}$ makes it possible to determine the concentration ratio, c_S/c_{MMA}, for a sample from an FT-IR measurement of A_{700} and A_{1730}.

$$\frac{c_S}{c_{MMA}} = \frac{A_{700}}{A_{1730}} \cdot \frac{\epsilon_{MMA}}{\epsilon_S}$$

The mole fraction of S units in the copolymer is then:

$$F_S = \frac{c_S}{c_S + c_{MMA}} = \frac{\dfrac{c_S}{c_{MMA}}}{\dfrac{c_S}{c_{MMA}} + 1}$$

Example calculation

The copolymer composition F_s can now been determined. Example calculation using the data from

Figure **SM 16.4.**2 with $A_{1730} = 0.311$ and $A_{700} = 0.752$, and $\varepsilon_S/\varepsilon_{MMA} \dfrac{\epsilon_{MMA}}{\epsilon_S} = \dfrac{1}{0.634} = 1.577$:

$$\frac{A_{700}}{A_{1730}} = \frac{0.752}{0.311} = 2.42$$

$$\frac{c_S}{c_{MMA}} = \frac{A_{700}}{A_{1730}} \cdot \frac{\epsilon_{MMA}}{\epsilon_S} = 2.42 \cdot 1.577 = 3.81$$

$$F_S = \frac{c_S}{c_S + c_{MMA}} = \frac{\dfrac{c_S}{c_{MMA}}}{\dfrac{c_S}{c_{MMA}} + 1} = \frac{3.81}{3.81 + 1} = 0.79$$

Typical student results

IR absorbances vary with the thickness of the film and should be preferably in the range of 0.2 –
0.8 for the two key IR bands at 1730 cm^{-1} and 700 cm^{-1}. If necessary, students need to adjust the
amount of their sample. A typical list of absorbances for the copolymer samples is shown in Table
SM 16.4.2.

Table SM 16.4.2 – Typical absorbances and calculated compositions of copolymer samples

Sample	f_S	A_{700}	A_{1730}	A_{700}/A_{1730}	F_S
1	0.89	0.2661	0.1271	2.094	0.77
2	0.79	0.1904	0.1284	1.483	0.70
3	0.69	0.3522	0.3309	1.064	0.63
4	0.58	0.171	0.1995	0.857	0.57
5	0.48	0.3461	0.559	0.619	0.49
6	0.38	0.2018	0.3328	0.606	0.49
7	0.29	0.1606	0.3389	0.474	0.43
8	0.19	0.1993	0.4792	0.416	0.40

Figure **SM 16.4.**4 shows typical student results for this experiment fitted to the theoretical equation

$$F_A = \frac{r_A \cdot f_A{}^2 + f_A \cdot (1 - f_A)}{r_A \cdot f_A{}^2 + 2 \cdot f_A \cdot (1 - f_A) + r_B \cdot (1 - f_A)^2}$$

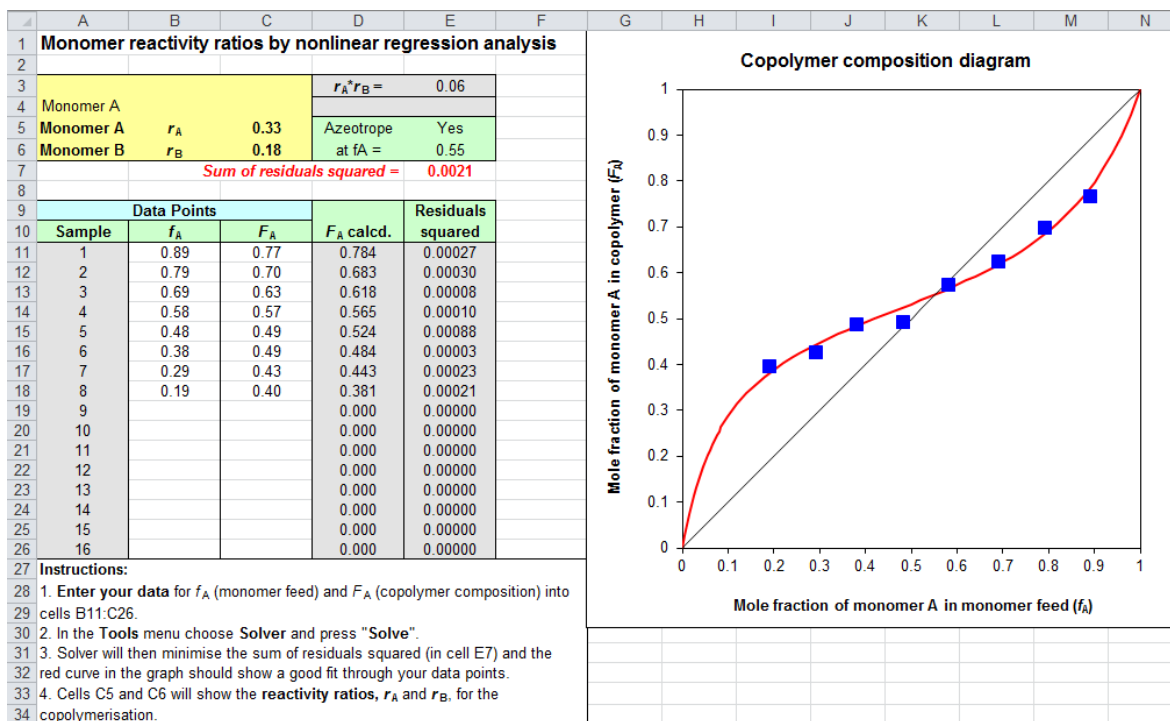by non-linear regression using the Solver tool in Excel.[2]

Figure SM 16.4.4 – Excel spreadsheet analysis showing a typical copolymer composition diagram and the best-line fit through the data points for reactivity ratios r_S = 0.33 and r_{MMA} = 0.18. The calculations used data derived from IR analysis of a series of copolymers.[3] The general appearance of the copolymer composition diagram is *S*-shaped. The point where the *S*-shaped curve crosses the diagonal (here at f_S = 0.55) and the monomer feed mixture does not give rise to a composition drift during the polymerisation is called the azeotrope (in analogy to mixtures of two or more liquids whose composition cannot be changed by simple distillation).
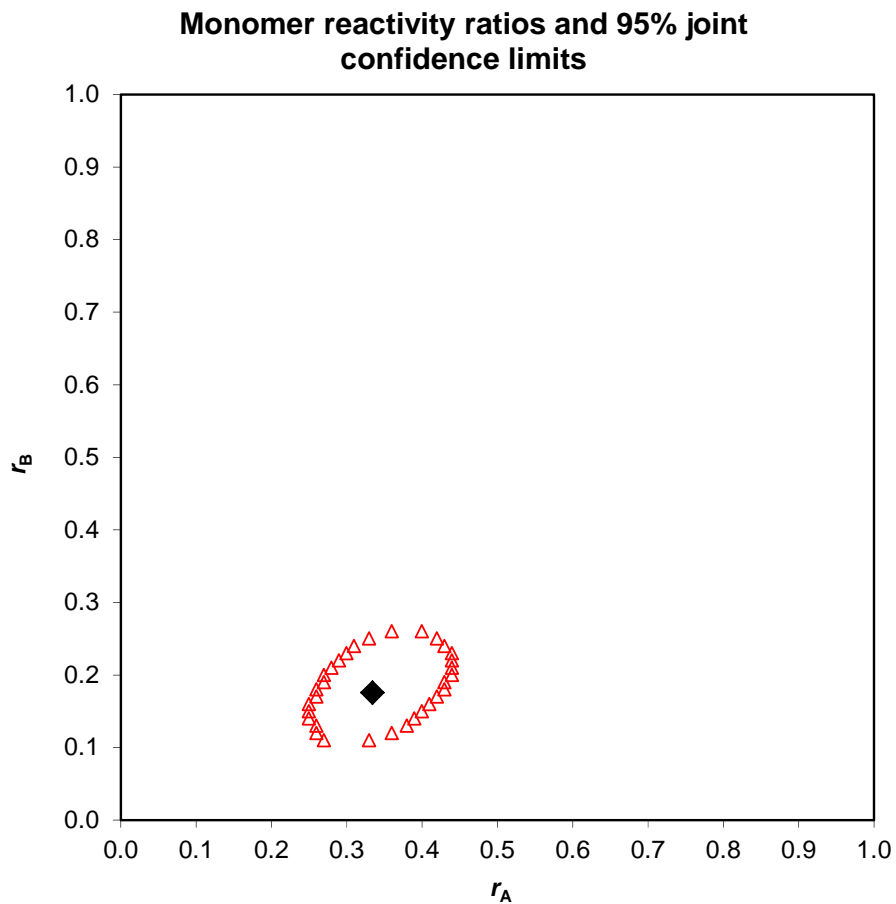
Figure SM 16.4.5 – 95% joint confidence limits for the reactivity ratios.[4]
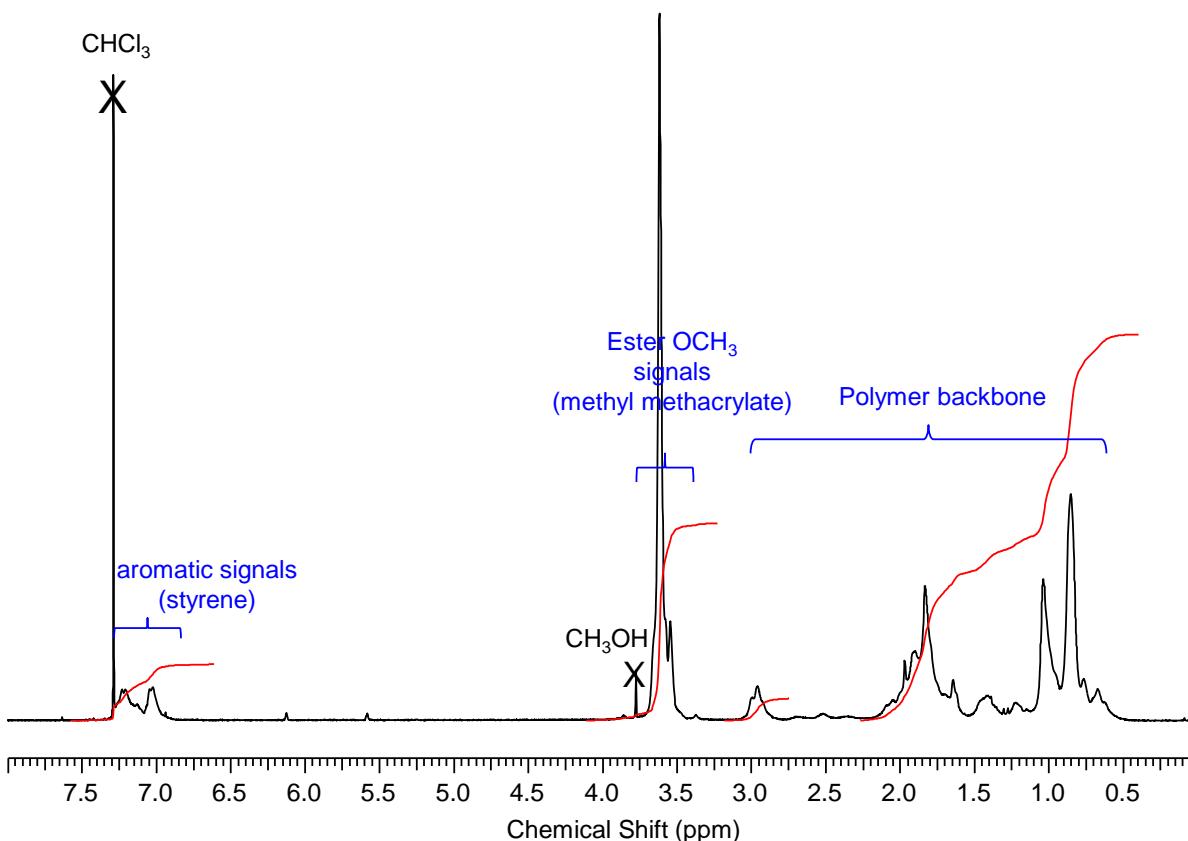
Figure SM 16.4.6 – ^{1}H NMR spectrum (300 MHz, CDCl$_3$) of a methyl methacrylate-rich copolymer (f_s = 0.10). Using ^{1}H NMR for analysing the composition of the copolymer requires care since integrals need to be corrected for contributions by residual solvents (CHCl$_3$, methanol, acetone) left over from the purification procedure and cleaning the NMR tube.
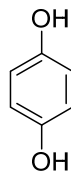
Answers to questions

1. A common stabiliser for styrene is 4-*tert*-butylcatechol, whereas hydroquinone is used for methyl methacrylate monomer. Inhibitors are added to the monomer to prevent accidental polymerisation triggered by adventitious radicals. Both stabilisers are weakly acidic phenols and can be removed by extraction with NaOH.

    Alternatively, monomers could be stored at low temperature since this slows down reactions (including polymerisations). Moreover, in a fridge, the monomer is also kept in the dark so that even light won't be able to generate radicals and thus initiate a radical polymerisation.
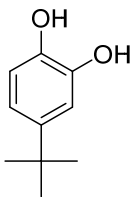
4-*tert*-Butylcatechol   Hydroquinone
(stabiliser in styrene)   (stabiliser in MMA)

2. After one half-life, half the AIBN will be left:

$$\frac{1}{2} = e^{-k_d \cdot t_{1/2}}$$

$$ln\frac{1}{2} = -k_d \cdot t_{1/2}$$

$$-ln2 = -k_d \cdot t_{1/2}$$

$$t_{1/2} = \frac{ln2}{k_d} = \frac{ln2}{k_d} \approx 22 \ hours$$

This calculation emphasises to students that during the 40 minutes reaction time hardly any of the AIBN was consumed.

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[1] From plotting A_{700}/A_{1730} against c_S/c_{MMA}. The value for $\varepsilon_S/\varepsilon_{MMA}$ can then be determined from the slope of a trendline.

[2] E. J. Billo, *Excel for Chemists: A Comprehensive Guide*, 3rd ed., Wiley 2011, Chapter 15, pp. 463-488.

[3] Literature values are variable and depend on temperature. For an atom-transfer radical polymerisation of styrene and methyl methacrylate they tend to be around $r_S = 0.60 \pm 0.10$ and $r_{MMA} = 0.43 \pm 0.05$, see: M.A. Semsarzadeh and M. Abdollahi, *Polymer* **2008**, *49*, 3060.

[4] For estimating the 95% confidence limits in the reactivity ratios the following procedure was used: A. M. van Herk, *J. Chem. Educ.*, 1995, **72**, 138.

Polymerization of ε-caprolactone using a ruthenium(II) mixed metallocene catalyst

Supplementary Material

Experiment Notes

This experiment aims at the synthesis of an organometallic catalyst that will be further used to the polymerization of -caprolactone.

Concerning the ruthenium catalyst synthesis, since the precursor tris(acetonitrile)cyclopentadienylruthenium(II) hexafluorophosphate is an yellowish/orange powder and the resulting product of the reaction is white/beige and toluene insoluble, the reaction can be followed easily by the disappearance of the starting material.

The reproducibility of the experiment was assessed by 3rd year Chemistry Graduation students from *Faculdade de Ciências, Universidade de Lisboa* that have had some prior experience with *Schlenk* techniques (a total of 6 students for the organometallic synthesis and *ca.* 20 students for the polymerization). The yields obtained for the organometallic syntheses are in the 80-90% range while for the polymerization are in the 80-90% range (as expected for 24 h polymerization). The polymerization procedure can be given to students with less experience, however the catalyst synthesis does need more caution due to some intermediaries unstable to air that might be formed during the reaction.

The use of dried solvents and reactants in the synthetic procedure is absolutely mandatory. To successfully complete this experiment during 2 laboratory classes, all the solvents and reactants must have been carefully dried previously. One cannot discard these steps otherwise the organometallic compound might not be formed, and the presence of water molecules during the polymerization will significantly decrease the molecular weight of the final polymers.

The polymerization reaction can be performed in shorter times, however one should expect a lower yield. The order by which the reactants are introduced in the polymerization procedure <u>is very important and should not be changed</u>; the amounts of reactants and solvents indicated are the result of an optimization of the reaction and should not be changed either.

Results interpretation and additional questions

For NMR chemical shifts discussion on the $^6-{}^4$ slippage on the coordination mode of the toluene ring in the catalyst during the polymerization procedure, it is expected to observe a shielding on the protons of the arene ligand, relatively to the catalyst alone, during polymerization. After quenching the reaction at 24 h with methanol, the ^{1}H NMR spectrum should become almost identical to that of the original complex (see below).

In relation to question **7**, students are asked to discuss the ratio between M_n theoretical (calculated in question 6) and M_n NMR (calculated in question 5) in terms of initiation efficiency, bearing in mind that total efficiency should lead to five polymer chains per Ru considering the alcohol/catalyst ratio. This value is easily obtained by:

$$\frac{n(isopropyl\ alcohol)}{n(catalyst)} = \frac{230\ \mu mol}{45.1 \mu mol} = 5$$

If total efficiency is achieved five polymer chains per each ruthenium atom would be growing, i.e., all the alcohol molecules would be involved in the polymerization. Thus if, for example, only 72% initiation efficiency is achieved using the expression given in question 7, only 3.6 polymer chains per ruthenium are growing.
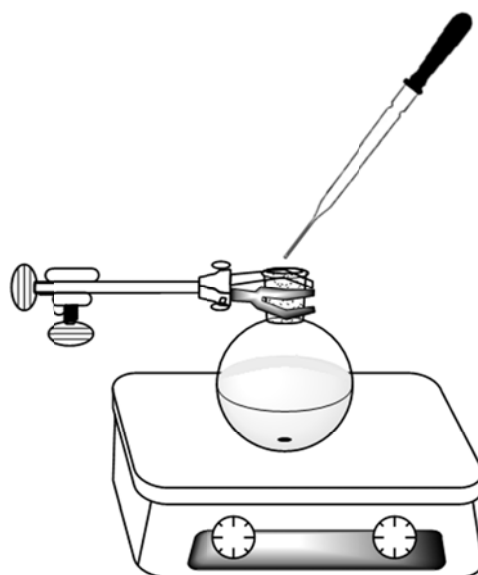
Figures from the reaction setup apparatus needed to perform the experiments
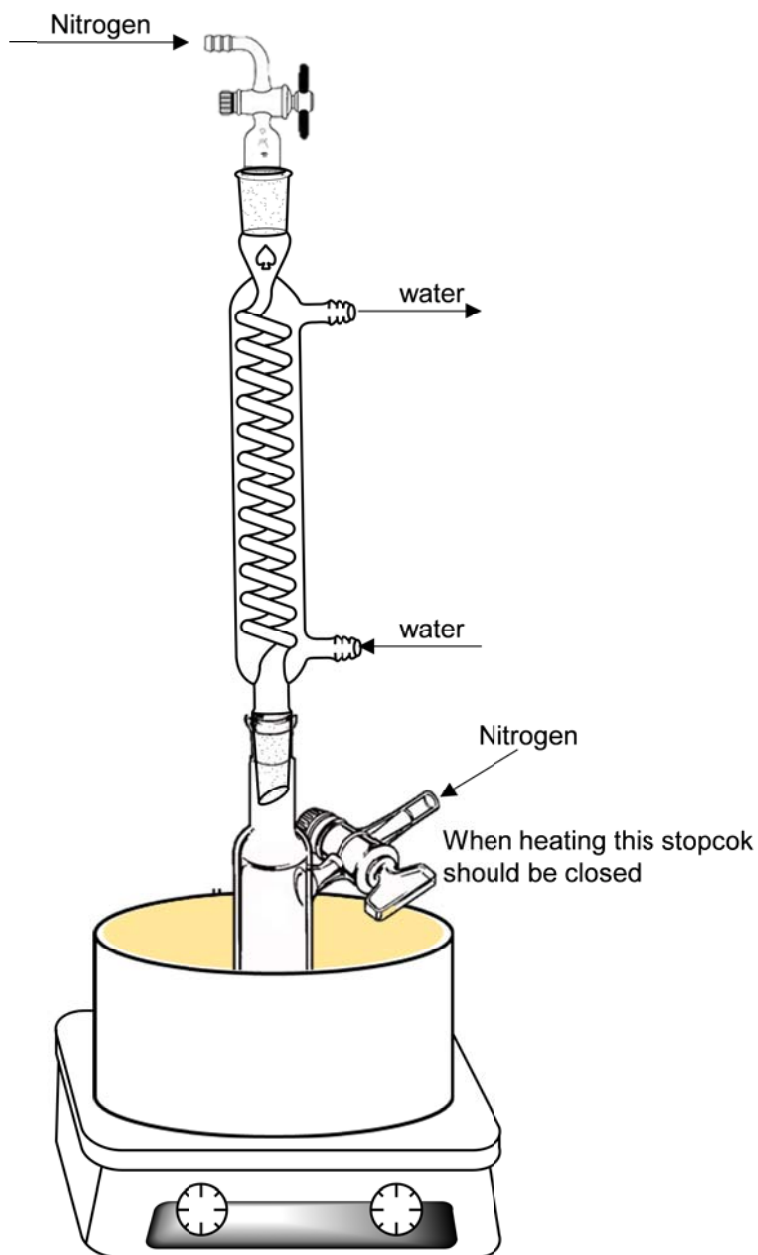
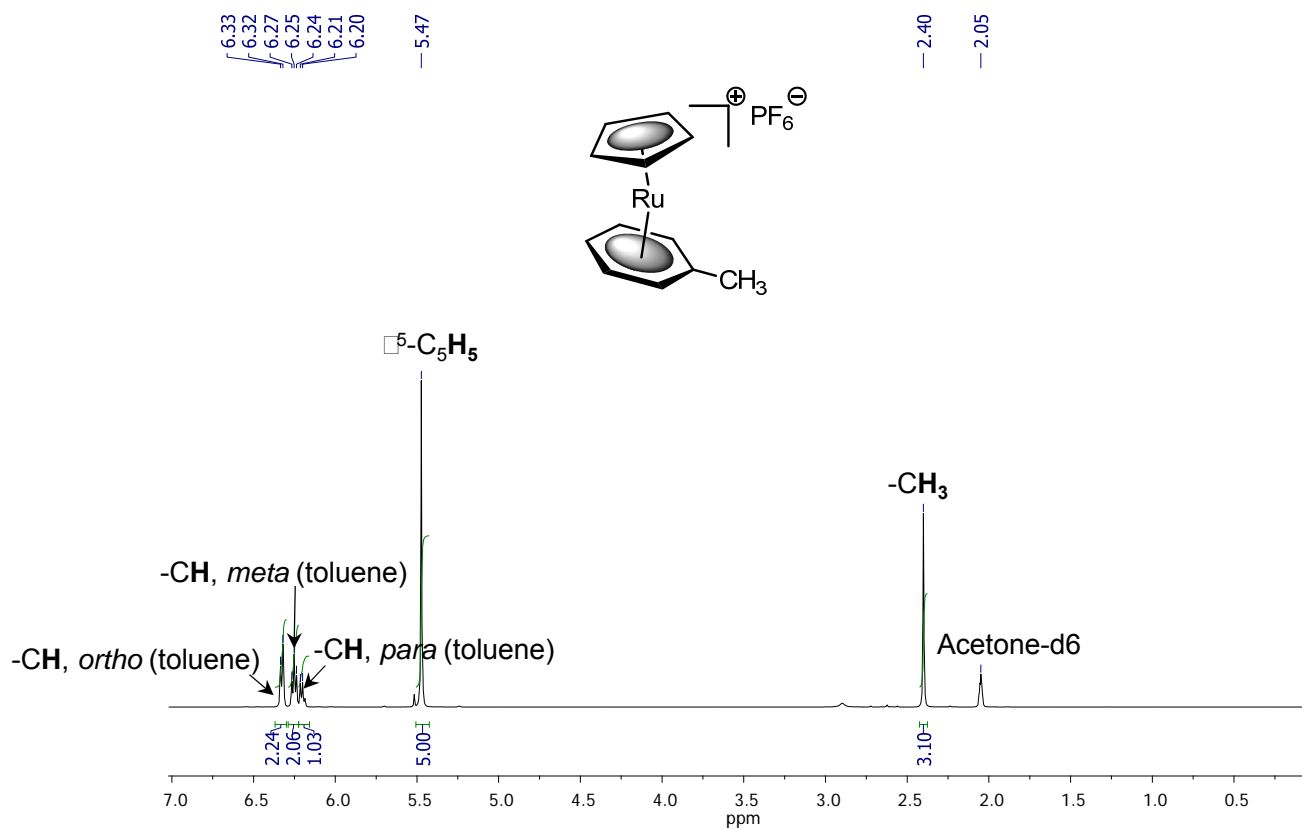**Scheme SM 16.5.1.** Reaction setup apparatus needed to perform the synthesis of the ruthenium catalyst
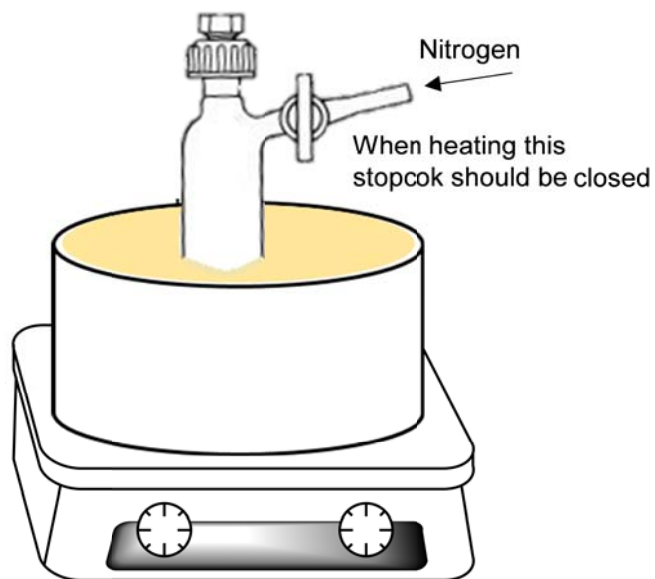
Scheme SM 16.5.2. Reaction setup apparatus needed to perform the polymerization of -caprolactone.
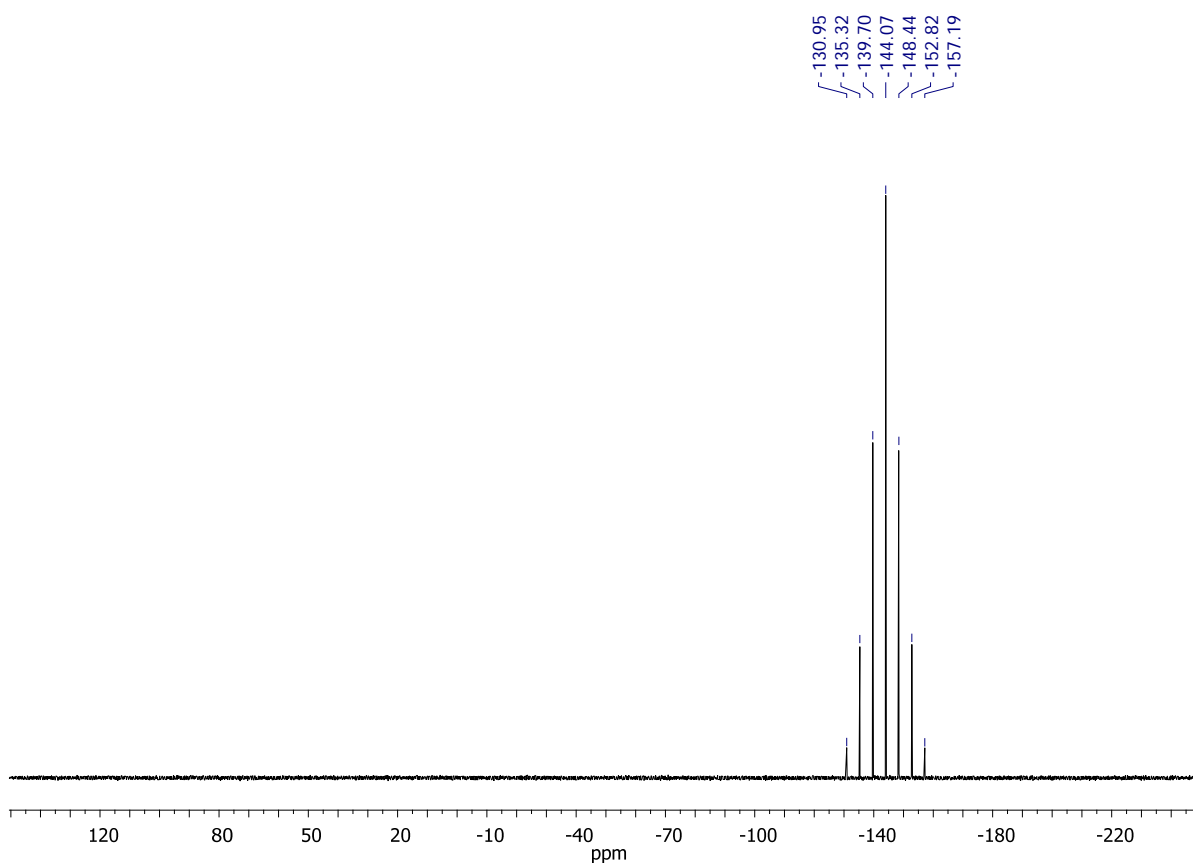

Scheme SM 16.5.3. Reaction setup apparatus needed to quench the polymerization of -caprolactone.
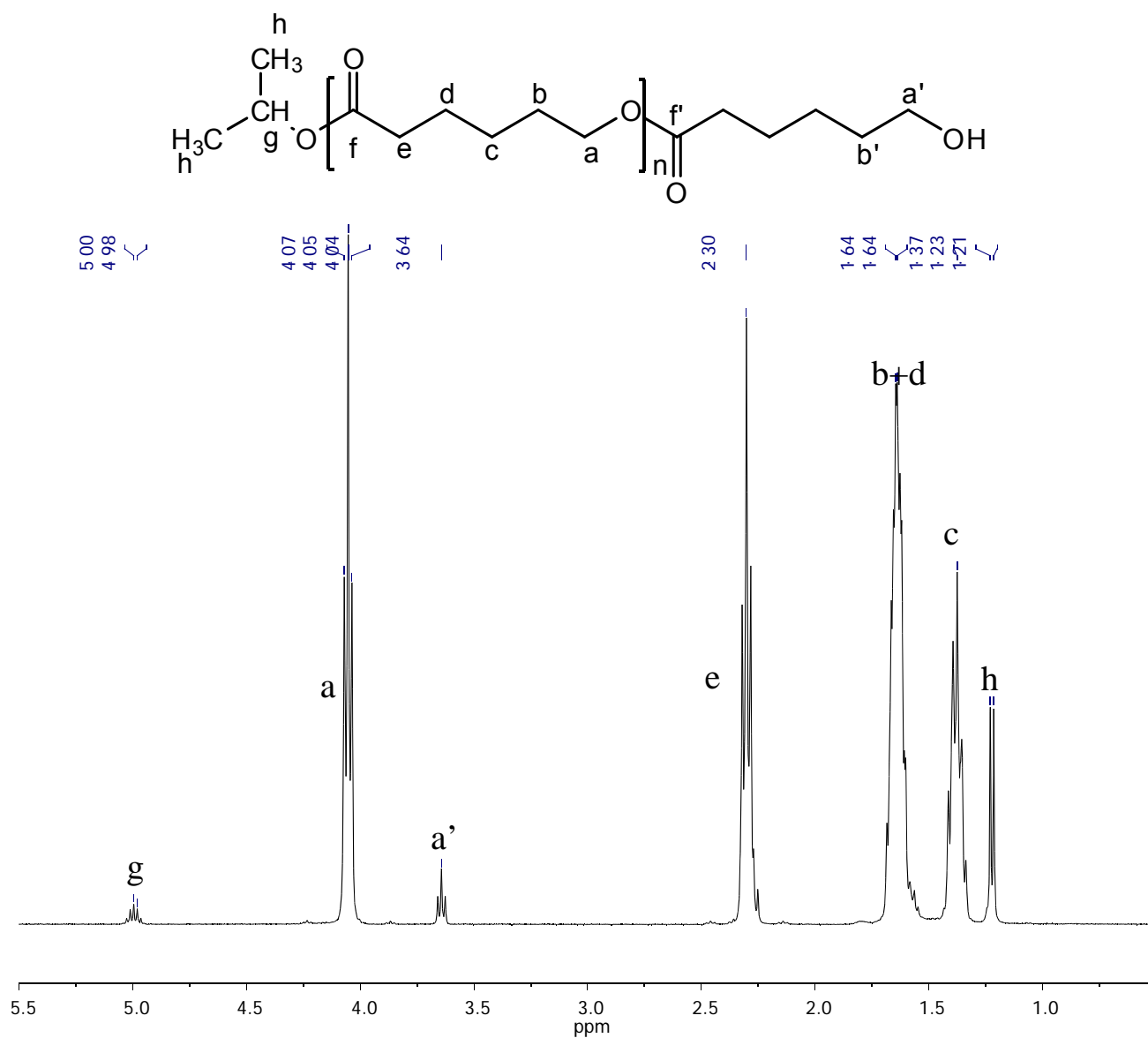
^{1}H and ^{31}P NMR spectra

Scheme SM 16.5.4. ^{1}H NMR (400 MHz) spectrum in acetone-d6 of [Ru(η^5-C$_5$H$_5$)(η^6-toluene)][PF$_6$]

Scheme SM 16.5.5. ^{31}P NMR (161 MHz) spectrum in acetone-d6 of [Ru(η^5-C$_5$H$_5$)(η^6-toluene)][PF$_6$]

Scheme SM 16.5.6. ^{1}H NMR (400 MHz) spectrum in CDCl$_3$ of polycaprolactone