
12 Experimental Protocols

Cellulose triacetate, Dormagen method (adapted from [515, 516])

6 g (37 mmol) cellulose is mixed with 2.1 g (35 mmol) glacial acetic acid and kept for 18 h at RT: 16.5 g (0.162 mol) acetic anhydride, 22.0 ml dichloromethane and 0.03 ml concentrated H_2SO_4 are added and the temperature is kept below 25 °C. The fibre pulp is slowly heated (15 °C per h) under stirring to 40 °C and kept at this temperature until total dissolution of the fibres occurs. 2 g potassium acetate is dissolved in 50% aqueous acetic acid and added to the reaction mixture to decompose the excess H_2SO_4 . 80.0 ml water is added drop-wise in order to convert the acetic anhydride to acetic acid. The methylene chloride is evaporated under vacuum, followed by pouring the residual viscous mass into water. The cellulose acetate is intensively washed with water and finally dried. Solubility, see Table 4.1.

Cellulose-2,5-acetate, secondary acetate (adapted from [516])

6.0 g (37 mmol) cellulose is ground with 2.1 g (35 mmol) glacial acetic acid and kept for 18 h at RT. 16.5 g (0.162 mol) acetic anhydride, 22.0 ml methylene chloride and 0.03 ml concentrated H_2SO_4 are added while the temperature is kept below 25 °C. The fibre pulp is slowly heated (15 °C per h) under stirring to 40 °C, and the temperature is maintained until total dissolution of the fibres. A solution of 0.03 ml concentrated sulphuric acid in 3.0 ml water is added and stirring at 60 °C is continued until the cellulose ester is soluble in acetone. This can be tested by precipitation of a small sample in methanol, washing with methanol and then testing the solubility. When the cellulose ester is acetone soluble, a mixture of 0.6 g potassium acetate dissolved in 50% acetic acid is added. After evaporating the dichloromethane under vacuum, the cellulose ester is isolated by precipitation in water, washing and drying. DS 2.38, solubility, see Table 4.1.

Cellulose triacetate, polymeranalogues reaction (adapted from [88])

10 g (62 mmol) cotton linters is placed in a 250 ml conical flask, followed by a mixture of 80 ml (1.4 mol) glacial acetic acid, 120 ml toluene and 2.0 ml 71–73% HClO_4 . The mixture is shaken vigorously for a few minutes, and the excess liquid is decanted into 50 ml (0.529 mol) acetic anhydride. This mixture is swirled and immediately poured back into the flask containing the linters. The purpose of this

procedure is to minimise the possibility of a high initial concentration of acetic anhydride contacting the fibres closest to the flask, and hence generating material that might have higher than average degrees of acetylation. The closed flask is shaken for 8 h at 30 °C. The acetylated linters are removed, and washed three times with ethanol and then several times with water in order to remove residual traces of acid. Washing is continued until the solution is neutral. The cellulose acetate is washed with ethanol and subsequently dried under vacuum overnight at 60 °C. DS 2.93, ^{13}C NMR ($\text{DMSO}-d_6$): δ (ppm) = 171.3, 170.4, 170.1 (C=O), 100.4, 77.0, 73.6, 73.2, 72.9, 63.4 (polymer backbone), 21.2, 20.9 (CH_3).

Cellulose valerate, heterogeneous reaction in Py and activation of the carboxylic acid with TFAA as impeller (adapted from [95])

100 ml (19.4 mol/mol AGU) TFAA and 96 ml (23.9 mol/mol AGU) valeric acid are mixed and stirred at 50 °C for 20 min. This solution is added to 6.0 g (37 mmol) dried cellulose powder and heated at 50 °C for 5 h. The reaction mixture is poured into methanol and the polymer is filtered off, washed repeatedly with methanol and dried. DS 2.79.

Hemicellulose acetate, synthesis in DMF and activation with NBS (adapted from [98])

0.66 g dry hemicellulose powder dispersed in 10 ml distilled water is heated to 80 °C under stirring until complete dissolution (~ 10 min). 5 ml DMF is added and the mixture stirred for 5 min. The water is removed from the swollen gel by repeated azeotropic distillation under reduced pressure at 50 °C for 0.5 h. In this case, about 12 ml solvent is recovered. 30 ml acetic anhydride and 0.3 g (1.3 mmol) NBS are added and the homogeneous reaction mixture is heated at 65 °C for 5 h. After cooling to RT, the mixture is slowly poured into 120 ml ethanol (95%), with stirring. The product is filtered off, washed thoroughly with ethanol and acetone, and dried initially in air for 12 h and subsequently for 12 h at 55 °C. DS 1.15. FTIR (KBr): 1752 ν (C=O), 1347 ν (C- CH_3), 1247 ν (C-O) cm^{-1} .

Dextran palmitate, heterogeneous synthesis in Py/toluene with palmitoyl chloride (adapted from [92])

20 g (123 mmol) dextran, 100 g (363 mmol) palmitoyl chloride, 75 g Py and 75 g toluene are heated under reflux with vigorous agitation at 105–110 °C for 1.5 h. The mixture is cooled rapidly to RT and washed with 250 ml water. About 100 ml of chloroform is added to the residue, followed by shaking. The resulting solution is poured into 1 l methanol to precipitate the ester. The ester is filtered off, redissolved in a mixture of 75 ml toluene and 100 ml chloroform, reprecipitated in methanol, collected and dried. DS 2.9. The product is soluble in chloroform, carbon tetrachloride, benzene, toluene and xylenes.