3.5.3.3 Unseeded Experiments

The procedure for unseeded crystallisation experiments is similar to that for the seeded ones, except that (a) cooling was from 50 to 15 °C without seeds, giving a supercooling of 35 °C; (b) 446.8 g $NaClO_3$ and 400 g of distilled water were used for each experiment; (c) cooling profiles were linear and four cooling rates were used of 0.04, 0.1, 0.2 and 0.4 °C min^{-1}. The fully dissolved and filtered solution was added to the crystalliser and held at 50 °C for a further hour prior to the experiment. A pre-calibrated FTIR spectrometer probe (Shimadzu IR-Prestige 21), a stainless steel turbidity probe (HEL Crystaleyes DMS-2) with a Hastelloy mirror and a stainless steel PT100 thermocouple were inserted in the crystallisers to measure the profiles of solute concentration (peak area), solution turbidity and temperature as a function of time during the experiments. Three runs were undertaken at each cooling rate, ensuring a good repeatability.

The data in Table 3.7 indicate that crystals in the STC have predominantly a single enantiomeric form, while the EEs in the OBC are significantly less than 100%, with both dextro- and laevorotatory crystals. In our experiments, the supercooling was 35 °C and spontaneous nucleation is expected in both crystallisers, as indicated by Denk and Botsaris (1972),[196,197] leading to close to total symmetry breaking as seen in Viedma's work.[181] It must be noted that our experiments differ from Viedma's trials[181] in that

i. our saturated solution was under constant mixing from the start to the finish, while there was no stirring in Viedma's solution when it was cooled from 90 to 20 °C, then sudden and rapid stirring at ~1000 rpm was applied at 20 °C;
ii. our cooling was controlled so that a linear profile was maintained, while natural cooling was used in Viedma's work;
iii. our product crystals were collected and filtered straightaway after each experiment, while Viedma harvested his crystals after two days.

Our data in the STC suggest that controlled cooling at constant mixing contributed to the chiral symmetry breaking, this would be new to Viedma's work. However, is scraping also responsible for the different EEs in the OBC?

Table 3.7 Summary of EE for both the STC and the OBC in unseeded experiments.

	STC				OBC			
Cooling rate (°C min^{-1})	0.4	0.2	0.1	0.04	0.4	0.2	0.1	0.04
EE (%)	99.9	99.5	98.8	96.1	48.8	15.8	31.2	59.4
Standard Deviation (SD)	0.07	0.42	0.7	3.07	13.21	9.94	11.72	17.02