Introduction

Poly(ethylene oxide) (PEO), a widely used polymer in industry, biology and medicine, has one of the most promising applications as electrolyte material in lithium ion batteries, because of its excellent ion conductivity. However, the linear structure of PEO leads to high crystallinity, which restrains ion transportation especially at low temperatures. Thus, there is a high demand for PEO based materials with low crystallinity or low melting points, so to achieve a good performance of the batteries at room temperature.

PEO molecule adopts a linear structure, which makes it easily crystallize. Similarly to many other semicrystalline polymers, PEO crystallizes into lamella layers according to the folded chain model, with the chains folded and aligned perpendicular to the lamella surface. The typical thickness of a PEO crystal lamella is within the nanometer scale, composed of several monomers. With increasing degree of polymerization, N, chains get longer and need to fold more times during crystallization. Within the nanoscale, lamella thickness has a huge impact on crystallization properties. For example, Gibbs Thomson relation describes how the melting point of the crystal lamella changes with the lamella thickness because of the interfacial energy between crystalline and amorphous phases. Apart from N, polydispersity index (PDI) also has an effect on polymer properties. Synthesized polymers contain a distribution of different molecular weights. Even the most monodisperse synthetic polymers have a polydispersity index (PDI) of about 1.01, which still contain many different N values. Particularly for crystallization of PEO oligomers, it has been suggested by Yeates et al. that there is a significant difference in melting points between monodisperse samples and commercial polydisperse samples. In order to understand this phenomenon, and investigate the N dependence of crystallization, highly monodisperse PEO samples with different N values are needed. In this research, we aim to first produce monodisperse PEO oligomers, and then explore the mechanism through which N influences oligomeric PEO crystallization properties, including chain folding and crystallinity.

Methodology

Production technique: We applied thermal evaporation to obtain highly monodisperse PEO oligomers. The neat sample (PEO 600) as purchased was heated on the bottom substrate, transformed into gas phase, and condensed onto a cold top substrate. When the material stops coming off at a certain temperature, we level up the temperature of bottom plate, and replace the top plate. The evaporation was carried out in nitrogen atmosphere, with the pressure kept at around 847 mbar, and the evaporation temperature was raised progressively from 393K to 493K. We expected that each temperature would correspond to a specific N, and thus different Ns are separated.

MALDI-TOF measurements: With Matrix-Assisted Laser Desorption/Ionization - Time Of Flight mass spectrometry, we analyzed the distributions of N values in our isolated products from different evaporation temperatures and compared them with the neat sample.

DSC measurements: With Differential Scanning Calorimetry, we performed some analysis on the crystallization behaviours of our products. DSC measures the heat flow during controlled temperature change in the sample, and the running process for each sample was as follows: equilibrate to 353K; isothermal for 10min; ramp 10K/min to 173K; ramp 10K/min to 353K; isothermal for 10min; ramp 10K/min to 173K; ramp 10K/min to 353K. Based on DSC data, we analyzed their melting point, enthalpy of melting, crystallinity, etc.

Crystal growth rate measurements: Under optical microscope, we observed the crystallization of isolated products, and measured the crystal growth rate.

Results and Discussion
Regarding the distribution of N values, with the increasing evaporation temperature, the peaks are shifted to higher Ns as expected (Fig. 1). From the MALDI data, we calculated their number average molecular weight, weight average molecular weight, and polydispersity index. The lowest PDI we achieved (1.005) is significantly better than the neat sample (1.032).

![MALDI spectrum of products.](image)

From DSC data, the plot of $T_m$ vs $\bar{N}$ (calculated from MALDI) was obtained (Fig. 2). The general upward trend with increasing $\bar{N}$ is as expected from Gibbs Thomson equation. To explain the double melting points of some fractions, we propose that the higher $T_m$s correspond to extended chain crystals, and the lower $T_m$s correspond to once-folded chains. By fitting the higher $T_m$s with Gibbs Thomson equation using the interfacial tension for chains ends, and the lower $T_m$s using an average interfacial tension, our assumption was proven by the nice fitting with these two curves.
With one of the fractions that showed two melting peaks, we kept the sample at a temperature between the two peaks for 24 hours, cooled to a much lower temperature, and measured the melting again. This time only one peak was observed. Based on the assumption we proposed, the mechanism is that all the once folded chains were melted, and forced to recrystallize into the other form, therefore on the second run there was only one peak.

Comparing our melting point data with the data from Yeates, we find our melting points agree more with their polydisperse samples, which suggests that the difference between the mono and polydisperse samples is very unlikely to be due to polydispersity. Instead, it could be related to something more particular to the details of the monodisperse sample, such as end group chemistry.

Fig. 3a is our growth rates vs crystallization temperature. Comparing it with the results from the work done by Kovacs\(^6\) (Fig. 3b), we find our data resembles the plateau of their curves, which makes sense because the crystallization temperatures we adopted were quite lower than their melting temperatures, so we have not been able to get to the rapid decreasing regions.
Fig. 3 Measured crystal growth rates with respect to crystallization temperature for four fractions (a). Literature data of growth rates for PEO with five molecular weights (b)⁶. Vertical lines are melting temperatures.

In conclusion, we applied the evaporative purification to get highly monodisperse PEO oligomers, and achieved a significantly improved PDI. With DSC measurements, we obtained the change in $T_m$ with $\bar{M}$, and proposed the extended chain and once folded chain models. In the future, we could try to achieve even lower PDI by applying larger scale and shorter collection intervals. In the crystal growth experiments, we would try to get to near melting temperatures, and we could also use X-ray experiments to get more information about the lamella. With better understanding of our monodisperse PEO products, we would be able to apply such materials in various fields. For example, one possible direction is to produce stable PEO liquids at room temperature, and the first application is highly likely to be polymer batteries.

References