MALDI-TOF spectrum of P2

The sample was dissolved in chloroform at 10 mg/mL and 0.5 mL of sample solution applied to the MALDI target along with 0.5 mL alpha-cyano-4-hydroxycinnamic acid matrix (prepared in 50:50 acetonitrile:ethanol at 10 mg/mL). Spectra were obtained on a Micromass TofSpec 2E instrument (Micromass, Manchester, U.K.), equipped with a 337 nm laser and operated in reflectron mode. The data was calibrated using the tryptic peptides of B-galactosidase (Sigma).

A MALDI-TOF spectrum of P2 (Fig S1) showed the usual emphasis on low molecular weight material, due to its greater volatility. Peaks were observed in repeating patterns for $H[(C_6H_4)(C_{13}H_{10}(C_{6}H_{13})_2)_nX]^+$, $X=H$, Br, $C_6H_5$, $C_6H_4Br$. 

![Fig S1: MALDI-TOF of polymer P2](image-url)
For example, \( n=2 \) gave three main peak clusters at 819 (X=H), then 895 (X=CH₃) overlapping with 897/899 (X=Br), and finally 975 Da (X=CH₂Br). There was also a broader, smaller peak at 1054 Da due to dibrominated Br\([(CH₃)₃(C₆H₄(C₆H₁₃)₂)₂C₆H₄Br]⁺\). There was also a minor peak at 1151 Da due to the member of the family containing one more fluorene group than phenyl group, i.e. \( H(CH₃)₂(C_{13}H₆(CH₃)₂)₃H^+ \). These low molecular weight oligomers are produced on a small scale though end-capping by monobrominated benzene impurity in the starting dibromobenzene comonomer. Brominated oligomers will be produced in even smaller quantities as they can react further. The concentrations of the oligomers will be reduced after the Soxhlet extraction step.

**Fig S2: MALDI-TOF of polymer P2 (880-1100 Da region)**

**Infra-Red Studies**

In order to examine in more detail the origin of the long wavelength peak, a thin film of the all-para polymer P1 was spin coated onto a salt plate used in infra-red spectroscopy. The infra red spectrum for the pristine film was recorded and showed
no carbonyl stretching frequency as anticipated. The film was then annealed in air for 1 h, 24 h, and so on, as was done for the measurement of the PL spectra (Fig. S3).

Figure S3: IR spectra of P1annealed in air

Over this period a small peak at 1740 cm$^{-1}$ emerges which can be attributed to a C=O stretching frequency. Samples annealed under an argon atmosphere at 140 °C for the same periods of time did not display this peak (Fig. S4). This implies that carbonyl moieties are formed only in the presence of oxygen.
Figure S4: IR spectra of $\textbf{P1}$ annealed under argon