Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Quasi-Monodisperse Polymer Libraries via Flash Column Chromatography: Correlating Dispersity with Glass Transition

Joris J. Haven[a] and Tanja Junkers*,[a]

[a] Polymer Reaction Design Group, School of Chemistry, Monash University, 19 Rainforest Walk, Clayton VIC 3800, Australia. E-mail: tanja.junkers@monash.edu; Tel: +61 0399054524

1. Materials

The monomer methyl acrylate (MA, Acros organics, 99%) was deinhibited over a column of activated basic alumina prior to use. 2-2'-azoisobutyronitrile (AIBN, Sigma-Aldrich, 0.2 M in toluene) was recrystallized twice from methanol prior to use. Petroleum spirit (Boiling range 40-60 °C, chem-supply), n-butyl acetate (chem-supply) and ethyl acetate (Merck) were used without further purification. The RAFT agent 2-cyano-2-propyl dodecyl trithiocarbonate (CPD-TTC) was synthesized according to literature procedures.[1]

2. Methods

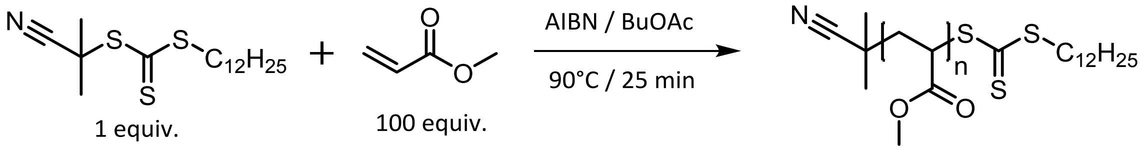
Purification of polymers was performed via Flash Column Chromatography (FCC) on a Puriflash® XS420+ (Interchim®) equipped with Puriflash® Intersoft V5.0 software. Separation were monitored via a diode array detector (range 200-400 nm) at lambda 305 nm and 254 nm. The PMA polymer (1.6 g) was embedded on celite and dry loaded on a pre-column cartridge (Interchim puriflash® F0012). The pre-column was subsequently wetted with eluent and attached to the pre-wetted normal phase silica cartridge (Interchim puriflash® F0040) on the integrated column holder. Polymer separation was performed with an optimized mobile phase (eluent) gradient mixture of ethyl acetate:petroleum spirit (40:60 to 90:10 v/v%) with a flow rate of 25 mL/min. Fraction were automatically collected by a fraction collector in racks with 18 x 150 mm glass tubes.

Analysis of the molar mass (distributions) of the PMA polymer samples was performed on a PSS SECcurity[2] GPC system operated by PSS WinGPC software, equipped with a SDV 5.0 µm guard column (50 x 8 mm), followed by three SDV analytical 5.0 µm columns with varying porosity (1000 Å, 100000 Å and 1000000 Å) (50 x 8 mm) and a differential refractive index detector using THF as the eluent at 40°C with a flow rate of 1 mL·min^{-1}. The GPC system was calibrated using linear narrow polystyrene standards from PSS Laboratories ranging from 682 to 2.52 x 10^6 g·mol^{-1} PS (K = 14.1 x 10^{-5} dL·g^{-1} and α = 0.70). Molar masses of the PMA samples were determined by universal calibration using Mark-Houwink-Sakurada (MHS) parameters for PMA reported literature values (K = 10.2 x 10^{-5} dL·g^{-1} and α = 0.74).[2] With regards to the accuracy of resulting molar masses of fractions, it is important to note that relative accuracy of SEC is much higher than absolute mass accuracy. Due to calibration limitations, absolute accuracy is limited to roughly 10 %. Yet, if measurements are carried out carefully under equal conditions within a single series on a well-calibrated machine, much smaller mass differences between samples are detectable. For this reason it was chosen to discuss M_n data with reported accuracy limits in the range of 10 g/mol, to highlight the differences between samples.

Glass transition of the PMA polymers was analyzed via Differential Scanning Calorimetry (DSC) on a PerkinElmer Instrument model DSC8000 under nitrogen flow and cooled with a PerkinElmer intracooler 2. PMA samples were prepared in aluminum pans and covers (PerkinElmer®). To determine the glass transition temperatures (T_g), the PMA samples were first heated to 100 °C at 50 °C/min, equilibrated at this temperature for 1 min, and subsequently cooled to -50 °C at 150 °C/min. Secondly, the samples were held at -50 °C for 3 min and the then reheated to 30 °C at 10 °C/min, equilibrated at this temperature for 1 min, and subsequently cooled to -50 °C at 150 °C/min. this second cycle was repeated to confirm T_g of the PMA samples.

3. Synthetic procedures

3.1. Synthesis of poly(methyl acrylate)

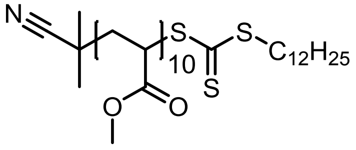


Poly(methyl acrylate). 28.93 mmol (2.50 g, 100 equiv.) of the monomer *methyl acrylate*, 0.015 mmol (2.37 mg, 0.05 equiv.) of 2-2'-azoisobutyronitrile (AIBN), 0.289 mmol (0.1 g, 1 equiv.) of 2-cyano-2-propyl dodecyl trithiocarbonate (CPD-TTC) and 1.25 mL of butyl acetate were added into a glass vial with a magnetic stirrer. The glass vial was sealed by a rubber septum. The solution was degassed for 10 min by N_2 purging and the mixture was subsequently reacted in a preheated oil bath for 25 min at 90 °C. Number average molar masses and dispersities of the polymer were measured by SEC (7840 Da, *Đ* = 1.130).

3.2. ESI-MS analysis of monodisperse oligo(acrylate) with chain length 10.

Synthesized according to literature procedure.[3] Oligo(methyl acrylate) was obtained via RAFT homopolymerization of methyl acrylate and purification via flash column chromatography.

ESI-MS: $[1228.51]^{Na+}$



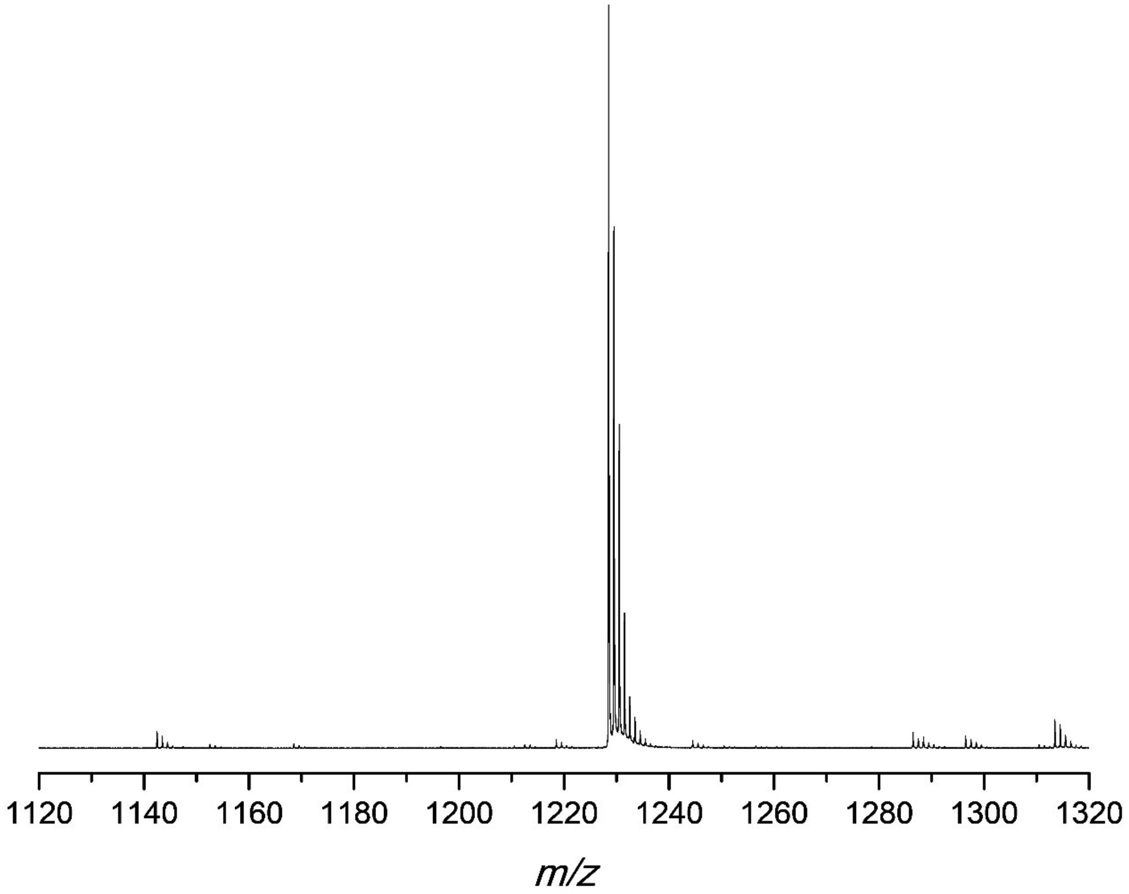


Figure S1. Electrospray ionisation mass spectrometry (ESI-MS) spectrum of the monodisperse oligo(methyl acrylate) (chain length 10) obtained via RAFT homopolymerization of methyl acrylate and purified via flash column chromatography.

4. Glass transition temperatures of PMA samples A and B7

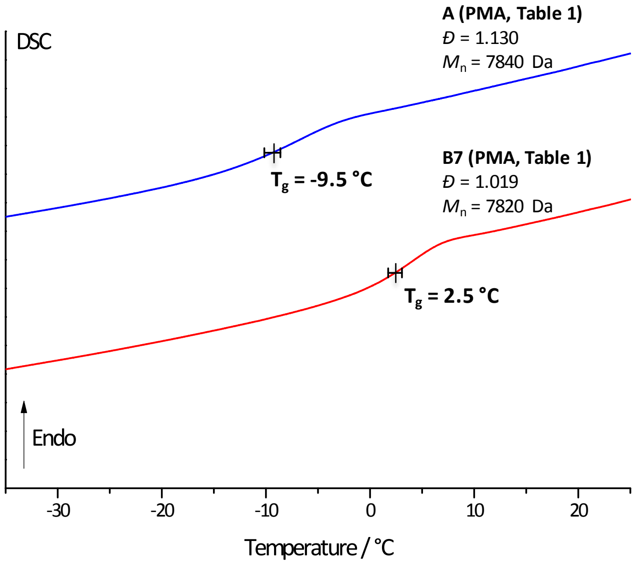


Figure S2. Differential scanning calorimetry (DSC) thermograms of the crude PMA polymer (A, Table 1) and a quasi-monodisperse PMA polymer (B7, Table 1). A Tg shift from -9.5 °C (blue trace, Đ = 1.130) to +2.5 °C (red trace, Đ = 1.019) was observed.

5. References

1. Y. K. Chong, G. Moad, E. Rizzardo and S. H. Thang, *Macromolecules*, 2007, **40**, 4446-4455.
2. C. Barner-Kowollik, S. Beuermann, M. Buback, P. Castignolles, B. Charleux, M. L. Coote, R. A. Hutchinson, T. Junkers, I. Lacík, G. T. Russell, M. Stach and A. M. van Herk, *Polymer Chemistry*, 2014, **5**, 204-212.
3. J. De Neve, J. J. Haven, L. Maes and T. Junkers, *Polymer Chemistry*, 2018, **9**, 4692-4705.