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Electronic Supplementary Information for:

Synthesis of crystallizable poly(behenyl methacrylate)-based block and statistical copolymers and their performance as wax crystal modifiers

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Contents

Experimental Section

Materials

All reagents purchased were used as received, unless stated otherwise. Behenyl alcohol (1-docosanol; $C_{22}H_{45}$-OH; 98%), methacryloyl chloride ($\geq$ 97%), triethylamine (TEA) (dried over activated molecular sieves prior to use), *n*-hexane and chloroform-*d* ($CDCl_3$) were purchased from Sigma-Aldrich (UK). Lauryl methacrylate (LMA; 96%) was also purchased from Sigma-Aldrich and filtered through a column of basic alumina (VWR Chemicals, UK) to remove inhibitor prior to use. Toluene, methanol, ethanol and *n*-dodecane (>99%) were purchased from Fisher Scientific (UK). 2,2′-Azoisobutyronitrile (AIBN) initiator was obtained from Molekula (UK) and *tert*-butyl peroxy-2-ethylhexanoate (T21s; >97%) initiator was purchased from AkzoNobel (The Netherlands). *n*-Octacosane ($C_{28}H_{58}$; 99%) was obtained from Alfa Aesar (UK). Tetrahydrofuran (THF; HPLC grade) was purchased from VWR Chemicals (UK). Dichloromethane-d_2 (CD_2Cl_2) was purchased from Goss Scientific Instruments Ltd (UK). 4-Cyano-4-(2-phenylethane sulfanylthiocarbonyl)sulfanylpentanoic acid (PETTC; >99%) was synthesized according to a previously reported protocol.[1] The synthesis of behenyl methacrylate (BeMA) is described in the *Synthesis Protocols* section of the Electronic Supplementary Information (ESI), while the synthesis of $PBeMA_{37}$ homopolymer was performed by Derry *et al.* in a previous study by our group.[2]

Characterization Techniques

^{1}H NMR Spectroscopy. ^{1}H NMR spectra were recorded in either CD_2Cl_2 (to determine the mean DP for the $PLMA_{98}$ precursor) or $CDCl_3$ (for all other spectra) at 400 MHz using a Bruker Ascend™ 400 spectrometer. Typically, 64 scans were averaged per spectrum.

Size Exclusion Chromatography. Size exclusion chromatography (SEC) analysis was used to assess (co)polymer molecular weight distributions and was performed using an Agilent 1260 Infinity GPC system equipped with an Agilent guard column (PLgel 5 μm) and two Agilent Mixed-C columns (PLgel 5 μm). Detection was conducted using a WellChrom K-2301 differential refractive index (RI) detector operating at λ = 950 ± 30 nm. The eluent was THF (HPLC grade) containing 2.0% v/v TEA and 0.05% w/v butylhydroxytoluene (BHT) with a toluene flow-rate marker at flow rate of 1.0 mL min^{-1} at 30 °C. Number-average molecular weights (M_n), weight-average molecular weights (M_w) and dispersities ($Đ = M_w/M_n$) were calculated using a series of eleven near-monodisperse poly(methyl methacrylate) (PMMA) calibration standards (M_p values ranging from 800 to 988 000 g mol^{-1}).

UV-Visible Absorption Spectroscopy. UV-vis absorption spectra were recorded by Dr. E. J. Cornel between λ = 200 and 800 nm using a PC-controlled UV-1800 spectrophotometer at 25 °C and a 1.0 cm path length quartz cell. A Beer–Lambert calibration curve was constructed using a series of eight PETTC solutions in toluene with the PETTC concentration ranging from 2.9×10^{-3} mol dm^{-3} to 3.5×10^{-2} mol dm^{-3}. The absorption maximum at λ = 448 nm assigned to the n-π transition of the trithiocarbonate group was used to construct this calibration plot. The absorbance of a solution of the PLMA$_{98}$ precursor in toluene at known concentration (389 g dm^{-3}) was recorded and the mean degree of polymerization (DP) was calculated using **Equations S1** and **S2**.

$$MW\ PLMA\ /\ (g\ mol^{-1}) = \frac{[PLMA]/\ (g\ dm^{-3})}{[PETTC]/\ (mol\ dm^{-3})} \quad \textbf{(S1)}$$

$$PLMA\ DP = \frac{MW\ PLMA}{MW\ LMA} \quad \textbf{(S2)}$$

Turbidimetry. Turbidimetry measurements were performed using an Agilent Technologies Cary 300 UV-visible spectrophotometer. Absorbance *vs.* temperature data were recorded at λ = 650 nm, then converted to % transmittance using the formula %T = $10^{(2\text{-}A)}$. Wax-copolymer mixtures were equilibrated at 50 °C for 5 min before three consecutive thermal cycles (from 50 °C to 0 °C to 50 °C) were performed at a constant cooling/heating rate of 1 °C min^{-1}. T_{cool} was taken as the temperature required for zero transmittance on cooling, averaged over the three cooling cycles. During the third thermal cycle, each wax-copolymer mixture was heated from 0 °C to 20 °C at 1 °C min^{-1} for subsequent microscopy analysis at room temperature.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) studies were performed using a TA Instruments Discovery DSC instrument equipped with TZero low-mass aluminum pans and hermetically-sealed lids. All (co)polymer samples were equilibrated at 90 °C for 5 min before two consecutive thermal cycles (from 90 °C to -90 °C to 90 °C) were performed at a constant cooling/heating rate of 10 °C min^{-1}. Two cycles were performed to eliminate any thermal history in each case.

Optical Microscopy. Samples were placed on a glass slide under a coverslip prior to imaging on a Zeiss Axio Scope A1 optical microscope equipped with AxioCam 1Cm1 monochrome and AxioCam

105 color cameras. All images were collected and processed using Zen lite 2014 software supplied with the microscope.

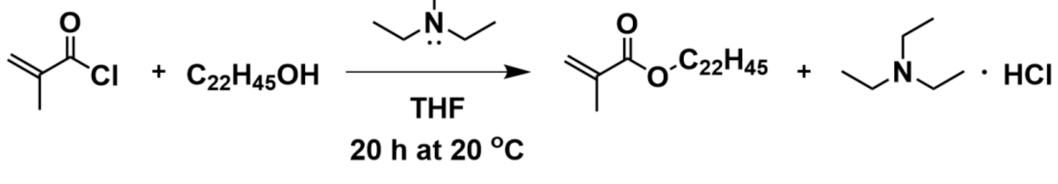
***Scanning Electron Microscopy*.** Scanning electron microscopy (SEM) images were acquired using a field emission FEI Inspect-F instrument at an accelerating voltage of 10 kV. Samples were allowed to dry overnight onto silicon wafers and then sputter-coated with a thin overlayer of gold prior to imaging. Where specified, ImageJ software was used to determine crystal dimensions (mean lengths and widths). A minimum of 50 crystals were counted across multiple images recorded for each sample on the same day.

Synthesis Protocols

Synthesis of behenyl methacrylate (BeMA)

Behenyl methacrylate was synthesised by reacting behenyl alcohol (dried in a vacuum oven overnight) with a 50 mol% excess of methacryloyl chloride in THF in the presence of triethylamine (dried over activated molecular sieves prior to use). A similar protocol was reported for the synthesis of propargyl methacrylate by Ghasdian *et al.*[3] A 500 mL two-neck flask was fitted with a rubber septum and a dropping funnel and purged with nitrogen. To this flask was added anhydrous THF (125 mL), behenyl alcohol (51.1 g, 0.157 mol) and TEA (68.8 mL, 49.9 g, 0.493 mol) and the resulting reaction mixture was stirred at 23 °C (i.e. ambient temperature). The flask was then placed in an ice bath at 0°C with continuous stirring. Methacryloyl chloride (22.9 mL, 24.5 g, 0.235 mol) was added dropwise to the reaction mixture *via* the dropping funnel over 30 min. After stirring for 1 h, anhydrous THF (60 mL) was added to facilitate more efficient stirring. The reaction mixture was stirred for 20 h and allowed to warm up to ambient temperature over this period (**Scheme S1**). The resulting viscous white solution was exposed to air to produce a cloudy yellow solution, which was treated with basic alumina to remove unreacted methacryloyl chloride, methacrylic acid and TEA hydrochloride salt. The purified product was filtered under vacuum to afford a white solid, which was dissolved in *n*-hexane, washed with sodium bicarbonate solution (pH 9) and then passed through a silica column to remove any remaining impurities. Then the THF and *n*-hexane were removed under reduced pressure and the residue was dried overnight in a vacuum oven at 30 °C.

Behenyl methacrylate was obtained as a white solid (26.3 g, 66.6 mmol, 42% yield). Elemental microanalysis: C, 79.35%; H, 12.48%. $C_{26}H_{50}O_2$ requires C, 79.12; H, 12.77%. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ (ppm) 0.88-0.93 (t, 3H, $-COOCH_2CH_2(CH_2)_{19}C\boldsymbol{H_3}$), 1.22-1.44 (m, 38H, $-COOCH_2CH_2(C\boldsymbol{H_2})_{19}CH_3$), 1.64-1.74 (m, 2H, $-COOCH_2C\boldsymbol{H_2}(CH_2)_{19}CH_3$), 1.97 (s, 3H, $HHC{=}C\boldsymbol{H_3}COO-$), 4.13-4.20 (t, 2H, $-COOC\boldsymbol{H_2}CH_2(CH_2)_{19}CH_3$), 5.57 (s, 1H, $\boldsymbol{H}_2C{=}CH_3-$, *cis*), 6.12 (s, 1H, $\boldsymbol{H}_2C{=}CH_3-$, *trans*). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ (ppm) 167.8, 136.7, 125.3, 64.9, 32.0, 29.7, 29.3, 28.6, 26.0, 22.7, 18.4, 14.2 (**Figures S1** and **S2**).



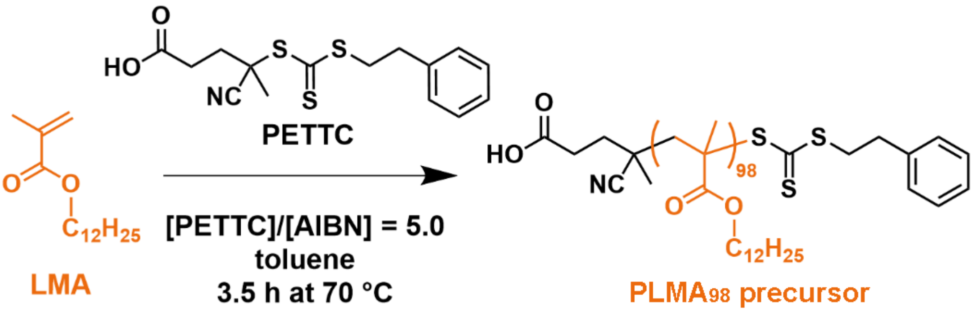
Scheme S1. Synthesis of behenyl methacrylate (BeMA) by reacting behenyl alcohol with excess methacryloyl chloride in THF in the presence of TEA.

Synthesis of the poly(lauryl methacrylate)$_{98}$ (PLMA$_{98}$ or L$_{98}$) precursor *via* RAFT solution polymerization

A typical synthesis of the PLMA precursor was conducted as follows. A 250 mL round-bottomed flask was charged with lauryl methacrylate (LMA; 52.5 g, 206 mmol), 4-cyano-4-(2-phenylethane sulfanylthiocarbonyl)sulfanylpentanoic acid (PETTC; 0.50 g, 1.47 mmol; target DP = 140), 2,2′-azobisisobutyronitrile (AIBN; 47.9 mg, 292 μmol; [PETTC]/[AIBN] molar ratio = 5.0) and toluene (53.0 g; total solids content = 50% w/w). The sealed reaction vessel was purged with nitrogen for 30 min and then placed in a pre-heated oil bath at 70 °C. The polymerization was allowed to proceed for 3.5 h at this temperature (**Scheme S2**). After this period, the polymerization was terminated by removing the flask from the oil bath and cooling to 20 °C, while exposing the reaction solution to air. ^{1}H NMR spectroscopy in CD_2Cl_2 was used to determine an LMA monomer conversion of 57% by comparing the integrated monomer vinyl protons with the integrated oxymethylene signals assigned to the LMA monomer and PLMA homopolymer.

The crude product was purified by precipitating three times into excess methanol and then dried under vacuum. The mean DP of the purified PLMA precursor was determined *via* end-group analysis from ^{1}H NMR spectroscopy in CD_2Cl_2 (**Figure S3**).

A mean DP of 98 was calculated by comparing the integrated signals corresponding to the aromatic protons of the trithiocarbonate-based end-group at 7.2-7.4 ppm with those assigned to the two oxymethylene ester protons of the PLMA repeat units at 3.8-4.2 ppm. A mean DP of 99 was determined using the molar extinction coefficient of 31.64 ± 0.27 mol^{-1} dm^3 cm^{-1} calculated by Dr. E. J. Cornel for the PETTC RAFT agent (**Figure S4**) and **Equations S1** and **S2**. THF SEC analysis indicated a PMMA-equivalent number-average molecular weight ($M_{\mathrm{n,\,SEC}}$) of 18.0 kg mol^{-1} (for comparison $M_{\mathrm{n,\,NMR}}$ = 25.3 kg mol^{-1}) and dispersity ($Đ$,) of 1.20.



Scheme S2. Synthesis of a poly(lauryl methacrylate)$_{98}$ (PLMA$_{98}$) precursor by RAFT solution polymerisation of LMA at 50% w/w solids in toluene at 70 °C, using PETTC as the RAFT agent.

Synthesis of poly(lauryl methacrylate)$_{98}$-poly(behenyl methacrylate)$_x$ (PLMA$_{98}$-PBeMA$_x$ or L$_{98}$-*b*-Be$_x$) diblock copolymers *via* RAFT solution polymerization

The protocol for the synthesis of the PLMA$_{98}$-PBeMA$_{60}$ diblock copolymer *via* RAFT solution polymerization at 80% w/w solids in *n*-dodecane is representative for all of the PLMA$_{98}$-PBeMA$_x$ diblock copolymers (x = 10-60) used in this study and was conducted as follows. PLMA$_{98}$ (1.45 g, 57.0 µmol), BeMA (1.36 g, 3.45 mmol; target DP = 60), and *n*-dodecane (0.672 g) were weighed into a glass vial and heated in an oven at 70 °C to aid dissolution. An aliquot (one droplet, approx. 20 mg) of the reaction solution was extracted for use as a 'zero time' reference point for determination of the BeMA conversion by ^{1}H NMR spectroscopy in $CDCl_3$. After cooling the remaining solution to 20 °C, T21s initiator was added (4.14 mg, 19.2 µmol; 10.0% v/v in *n*-dodecane; [PLMA$_{98}$]/[T21s] molar ratio = 3.0) along with a magnetic stirrer bar and this reaction mixture was purged with nitrogen gas for 30 min. The sealed sample vial was then immersed in a pre-heated oil bath set at 90 °C and the reaction mixture was stirred for 16 h (final BeMA conversion = 98%; M_n = 33.2 kg mol^{-1}; $Đ$ = 1.25). After this period, the polymerization was terminated by removing the vial from the oil bath and cooling to 20 °C, while exposing the reaction solution to air. The resulting PLMA$_{98}$-PBeMA$_{60}$ diblock copolymer was purified by precipitation into excess ethanol at 35 °C (twice) to remove residual BeMA, and then dried under vacuum. In all cases, BeMA conversions were determined *via* ^{1}H NMR spectroscopy in $CDCl_3$ using an additional spectrum recorded at zero time to distinguish between the new oxymethylene signals originating from the PBeMA and those assigned to the PLMA$_{98}$ precursor.

Synthesis of poly(lauryl methacrylate$_{100}$-*stat*-behenyl methacrylate$_x$) (P(LMA$_{100}$-*stat*-BeMA$_x$) or L$_{100}$-*stat*-Be$_x$) statistical copolymers *via* RAFT solution polymerization

The protocol for the synthesis of the P(LMA$_{100}$-*stat*-BeMA$_{60}$) statistical copolymer *via* RAFT solution polymerization at 80% w/w solids in *n*-dodecane is representative of all the P(LMA$_{100}$-*stat*-BeMA$_x$) statistical copolymers (x = 10-60) used in this study and was conducted as follows. PETTC (25.0 mg, 73.6 µmol; total target DP = 160), LMA (1.87 g, 7.36 mmol), BeMA (1.74 g, 4.42 mol), *n*-dodecane (0.40 g) and T21s initiator (5.31 mg, 24.5 µmol; 10.0% v/v in *n*-dodecane; [PETTC]/[T21s] molar ratio = 3.0) were added to a 10 mL round-bottomed flask along with a magnetic stirrer bar and this reaction mixture was purged with nitrogen for 30 min. The sealed flask was then immersed into a pre-heated oil bath set at 90 °C and the reaction mixture was stirred for 64 h (final comonomer conversion = 99%; M_n = 39.6 kg mol^{-1}; $Đ$ = 1.24). After this period, the polymerization was terminated by removing the flask from the oil bath and cooling to 20 °C, while exposing the reaction solution to air. The resulting P(LMA$_{100}$-*stat*-BeMA$_{60}$) statistical copolymer was purified by precipitation into ethanol at 35 °C (twice) to remove residual LMA and BeMA, and then dried under vacuum.

Preparation of wax-copolymer solutions

n-Octacosane (0.188 g; 5.0 % w/w), *n*-dodecane (3.53 g) and each diblock or statistical copolymer (0.26 mM) were weighed into a glass vial and heated in a 70 °C oven to aid dissolution. The resulting solutions were then transferred into glass cuvette cells *via* syringe for variable temperature turbidimetry measurements. A fixed molar copolymer concentration of 0.26 mM (equivalent to 1.0 % w/w PLMA$_{98}$-PBeMA$_{10}$) was used for initial wax crystal modification experiments, which ensured that the number of copolymer chains remained constant. Thus the copolymer concentrations expressed in weight per cent varied from 1.0 % w/w to 1.7 % w/w. For the PBeMA$_{37}$ and PLMA$_{98}$ homopolymers, 0.26 mM corresponded to 0.5 % w/w and 0.9 % w/w, respectively. In subsequent studies, the molar copolymer concentration was varied from 0.06 to 1.03 mM (*i.e.*, a factor of four lower or higher than the initial 0.26 mM value).

Supplementary Characterization Data for BeMA Monomer

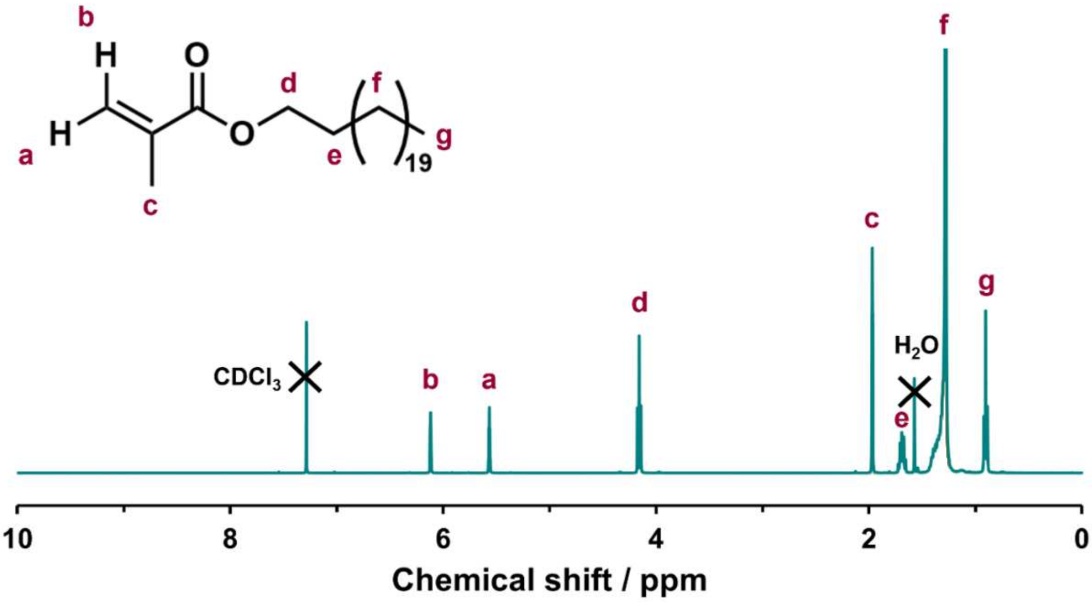


Figure S1. Assigned ^{1}H NMR spectrum obtained for the purified BeMA monomer in CDCl$_3$.

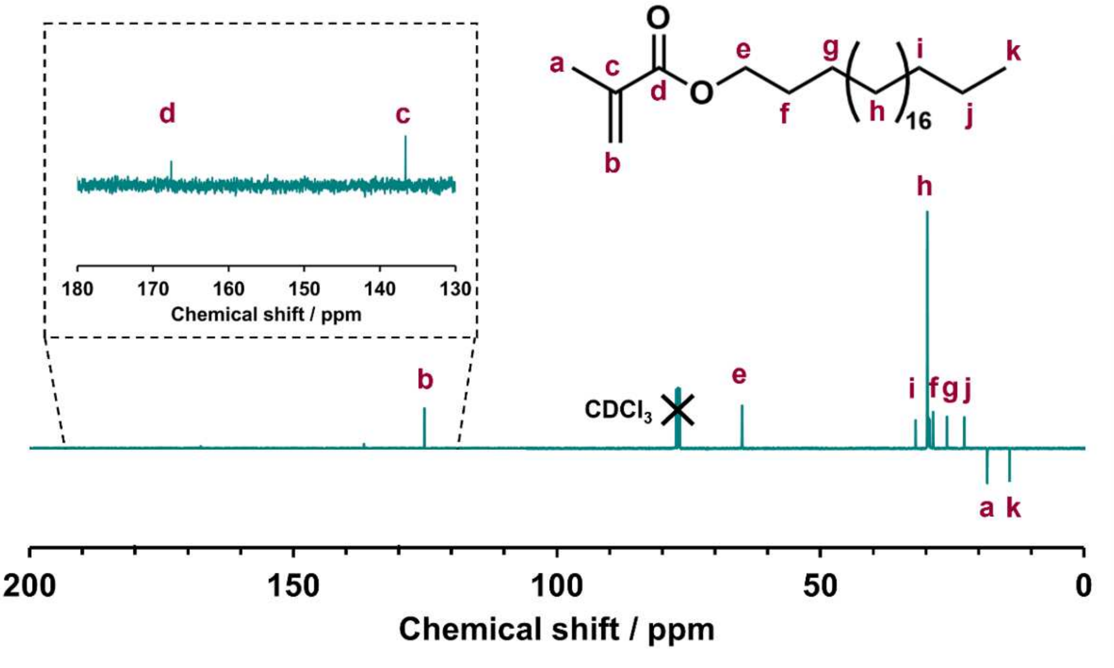


Figure S2. Assigned ^{13}C NMR spectrum obtained for the purified BeMA monomer in CDCl$_3$.

Supplementary Characterization Data for the PLMA98 Precursor

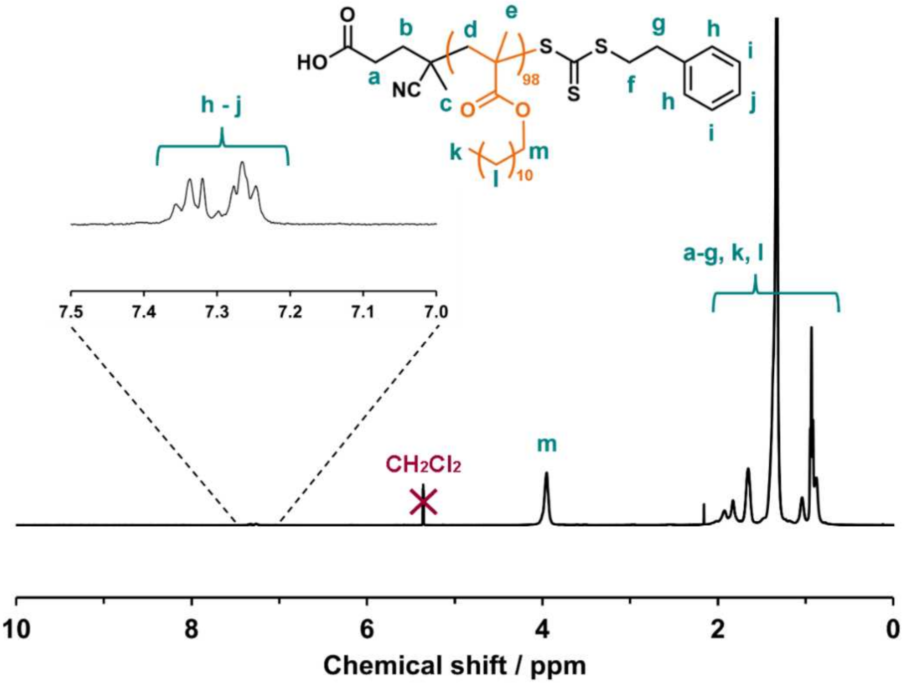


Figure S3. Assigned ^{1}H NMR spectrum obtained for the purified PLMA$_{98}$ precursor in CD_2Cl_2.

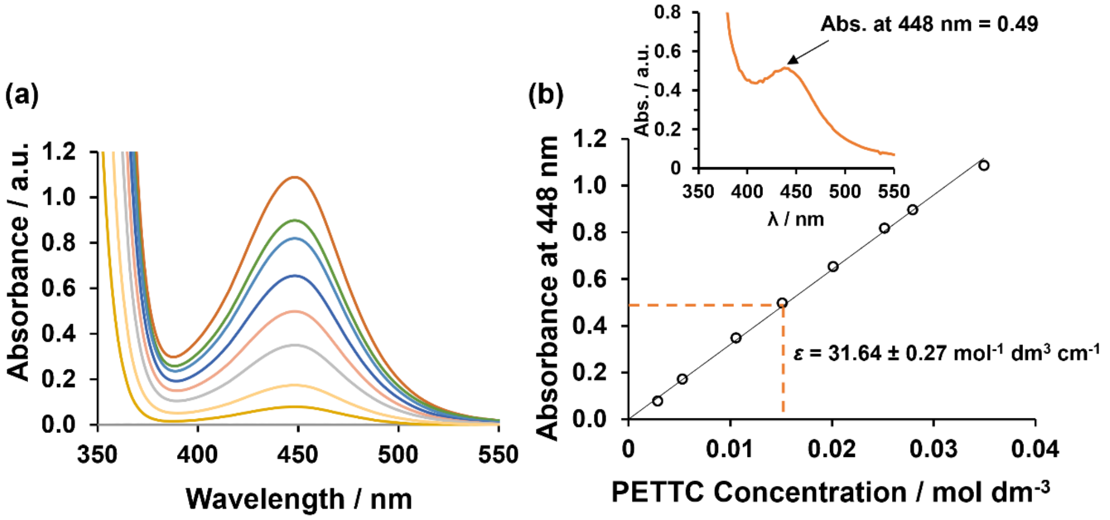


Figure S4. (a) Absorbance *vs.* wavelength spectra recorded for a series of PETTC solutions in toluene ranging from 2.9 to 35 mmol dm^{-3}, and (b) Beer-Lambert linear calibration plot used to calculate the molar extinction coefficient of PETTC (ε = 31.64 ± 0.27 mol^{-1} dm^3 cm^{-1} at λ = 448 nm). Insert shows the absorbance *vs.* wavelength spectrum recorded for a 389 g dm^{-3} PLMA$_{98}$ precursor solution in toluene with absorbance peak maximum at λ = 448 nm recorded at 0.49. Determination of the PETTC concentration of this PLMA$_{98}$ sample (1.55 × 10^{-2} mol dm^{-3}) shown by orange dashed line.

Supplementary Characterization Data for PLMA$_{98}$-PBeMA$_x$ Diblock Copolymers

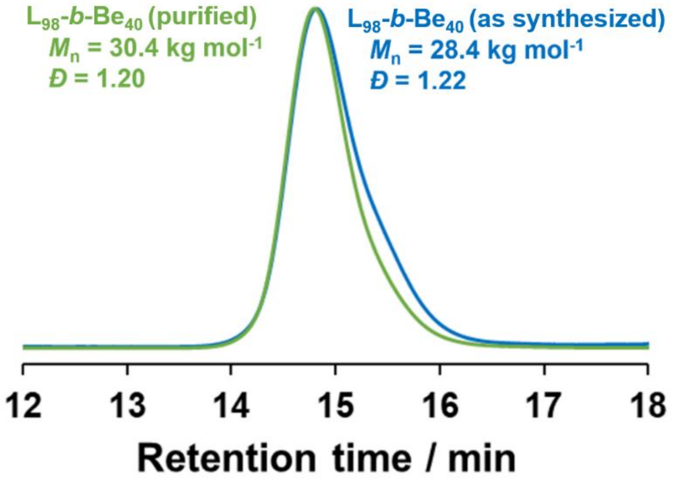


Figure S5. THF SEC curves recorded for a PLMA$_{98}$-PBeMA$_{40}$ diblock copolymer before (blue curve) and after (green curve) its purification *via* precipitation into excess ethanol at 35 °C.

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