Electronic Supplementary Information

Synthesis, Structure and Crystallization Behavior of Amphiphilic Heteroarm Molecular Brushes with Crystallizable Poly(ethylene oxide) and *N*-Alkyl Side Chains

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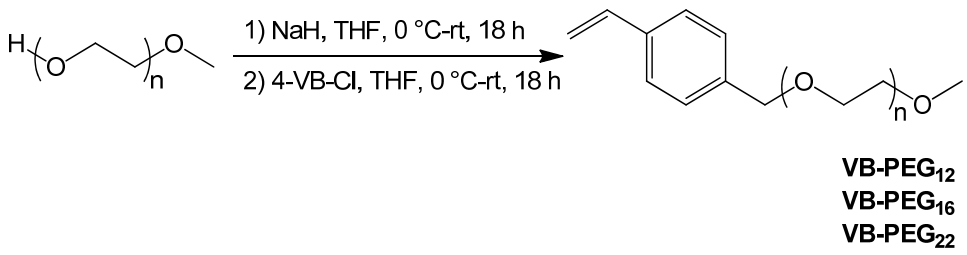
Synthesis of 4-vinyl benzyl-(poly ethylene glycol) methyl ether (VB-PEG$_n$)



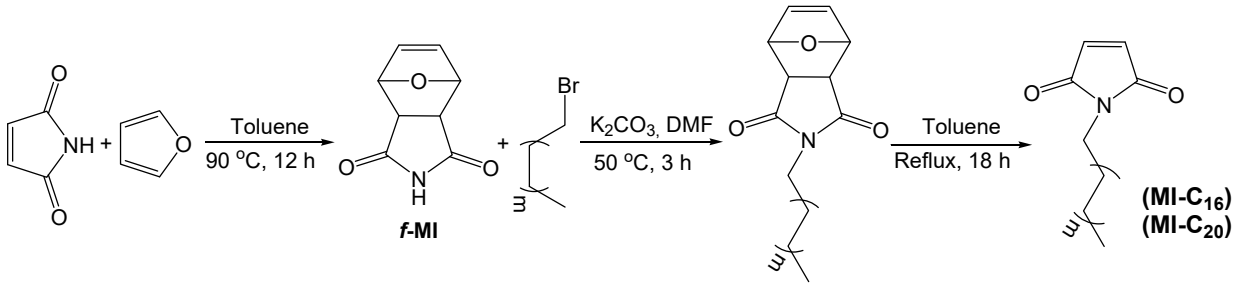
Scheme S1. Synthetic route towards 4-vinyl benzyl-[poly (ethylene glycol)] methyl ether (VB-PEG$_n$).

The monomers were prepared in two steps using different oligo (ethylene glycol) monomethyl ethers.

In a representative reaction, VB-PEG$_{22}$-M was synthesized as follows; sodium hydride (60% in mineral oil, 1.0 g, 41.67 mmol, 2.5 eq) and dry THF (50 mL) was added to a 3-necked flask and cooled to 0 °C under inert conditions. A solution of the azeotropically dried poly (ethylene glycol) monomethyl ether (10 g, 10 mmol, 1 eq) in dry THF (40 mL) was added dropwise over 2 hours. The reaction mixture was stirred overnight at room temperature, thereafter it was cooled with an ice bath and a solution of 4-vinyl benzyl chloride (2.1 mL, 15 mmol, 1 eq) in THF (30 mL) was added dropwise. The reaction mixture was further stirred overnight at room temperature. After cooling the mixture to 0 °C it was carefully quenched with deionised water. The aqueous layer was extracted with DCM (50 mL x 3), and the combined organic layers was dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. VB-PEG$_{12}$, VB-PEG$_{16}$ and VB-PEG$_{22}$ was purified by precipitating the residue from ice cold diethyl ether and leaving it in the freezer overnight (×2). The product VB-PEG$_{12}$ (yield = 70 %,) was isolated as a yellow viscous liquid and VB-PEG$_{16}$ (yield = 80 %,) and VB-PEG$_{22}$ (yield = 80 %,) as a white solid. ^{1}H NMR : **VB-PEG$_{22}$** (400 MHz, $CDCl_3$) δ 7.32 (dd, 4H, C$H_{aromatic}$), 6.67 (dd, J =10.9 and 17.5, 1H, CH_{vinyl}), 5.70 (dd, 1H, CH_{vinyl}), 5.20 (dd, 1H, CH_{vinyl}), 4.52 (s, 2H, benzyl-CH_2O), 3.6-3.65 (m, OCH_2CH_2-PEG), 3.51 – 3.53 (m,

2H), 3.35 (s, 3H, OC*H*$_3$). **VB-PEG$_{12}$** (300 MHz, $CDCl_3$) δ 7.32 (dd, 4H, C*H*$_{aromatic}$), 6.69 (dd, *J* =10.9 and 17.5, 1H, C*H*$_{vinyl}$), 5.72 (dd, 1H, C*H*$_{vinyl}$), 5.22 (dd, 1H, C*H*$_{vinyl}$), 4.54 (s, 2H, benzyl-C*H*$_2$O), 3.6-3.67 (m, OCH_2CH_2-PEG), 3.52 – 3.55 (m, 2H), 3.36 (s, 3H, OC*H*$_3$). **VB-PEG$_{16}$** (300 MHz, $CDCl_3$) δ 7.32 (dd, 4H, C*H*$_{aromatic}$), 6.69 (dd, *J* =10.9 and 17.5, 1H, C*H*$_{vinyl}$), 5.72 (dd, 1H, C*H*$_{vinyl}$), 5.22 (dd, 1H, C*H*$_{vinyl}$), 4.53 (s, 2H, benzyl-C*H*$_2$O), 3.58-3.68 (m, OCH_2CH_2-PEG), 3.50 – 3.57 (m, 2H), 3.36 (s, 3H, OC*H*$_3$). FT-IR (ATR, cm^{-1}): 2883 (aliphatic, -C-H stretching), 1101 (C-O-C), 842 cm^{-1} (para-disubstituted benzene rings (-C-H)).

Synthesis of *N*-alkylmaleimide (MI-C$_m$)



Scheme S2. Synthetic route towards *N*-alkylmaleimides (MI-C$_m$).

Step 1. Maleimide (1.00 g, 10.3 mmol), furan (1.05 g, 15.5 mmol) and 15 mL dry toluene was mixed in a 100 mL round bottom flask and heated to 90 °C for 12 hours. The product, furan-maleimide, (*f*-MI) precipitated out as white crystals that were collected by filtration and washed with cold diethyl ether (3×5 mL). The white crystals were then dried under vacuum for 4 hours and used without further purification (1.32 g, 78 %).

Step 2. The macromonomers were prepared using the following alkyl bromines; 1-bromohexadecane (n=7) and 1-bromoeicosane (n=9). In a representative experiment, *N*-hexadecanemaleimide (**MI-C$_{16}$**) was synthesized as follows. In a dry 100 mL round bottom flask *f*-MI (2.6 g, 15.7 mmol) and K_2CO_3 (5.44 g, 39.4 mmol) were mixed in dry DMF (50 mL) before a solution of 1-bromohexadecane in DMF (12.0 g, 39.4 mmol in 15 mL) was added. The mixture was heated to 50 °C for 6 hours. Thereafter, diethyl ether (80 mL) was added, followed by a careful

addition of 5% HCl (30 mL). The mixture was washed with water (3×80 mL). The organic layer was collected and dried with anhydrous magnesium sulphate and evaporated to dryness to yield a yellow oil. The crude products of furan-protected alkyl-maleimides was purified by column chromatography (EtOAc:Hexane, 2:8) or Kugelrohr distillation.

Step 3. Furan-protected *N*-alkylmaleimide was then dissolved in toluene (50 mL) and heated at reflux under argon flow for 12 hours. After removing most of the toluene by rotavap, the crude product was subjected to a column chromatograph using EtOAc/hexane (2:8 v/v) as the eluent, and after removing the solvents an white solid was obtained. *N*-hexadecylmaleimide (**MI-C16**) (yield = ~75%) and *N*-eicosanemaleimide (**MI-C20**) (yield = ~60%). ^{1}H NMR (400 MHz, $CDCl_3$) **MI-C16** δ =0.87 (t, 3H, C*H*$_3$); 1.24 (m, 26H, C*H*$_2$); 1.57 (m, 2H, C*H*$_2$); 3.50 (t, 2H, N-C*H*$_2$); 6.68(s, 2H, C*H*$_{vinyl}$). **MI-C20** δ =0.87 (t, 3H, C*H*$_3$); 1.24 (m, 34H, C*H*$_2$); 1.57 (m, 2H, C*H*$_2$); 3.50 (t, 2H, N-C*H*$_2$); 6.67(s, 2H, C*H*$_{vinyl}$). FT-IR (ATR, cm^{-1}): 2917 and 2850 (aliphatic, -CH_2 and –CH_3 stretching), 1697 (N-C=O), 1402 (C-N).

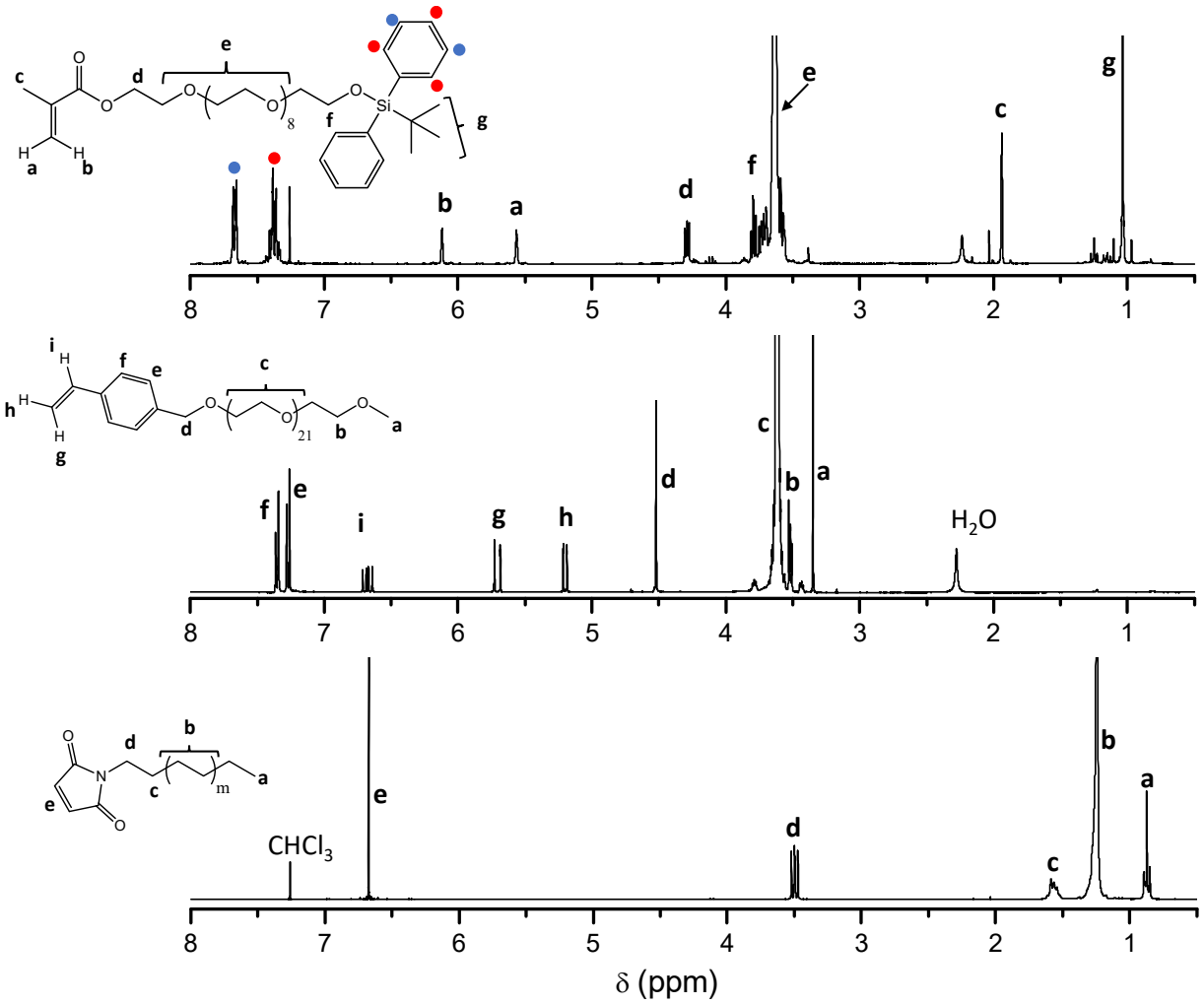


Figure S1. ^{1}H NMR spectra of two of the hydrophilic macromonomers, *tert*-butyl diphenyl silyl poly(ethylene glycol) methacrylate (TBDPS-PEGMA) and 4-vinyl benzyl-(poly(ethylene glycol)) methyl ether (VB-PEG$_{22}$), and hydrophobic macromonomer *N*-alkylmaleimide (MI-C$_{16}$) used for the preparation of the AMBs.

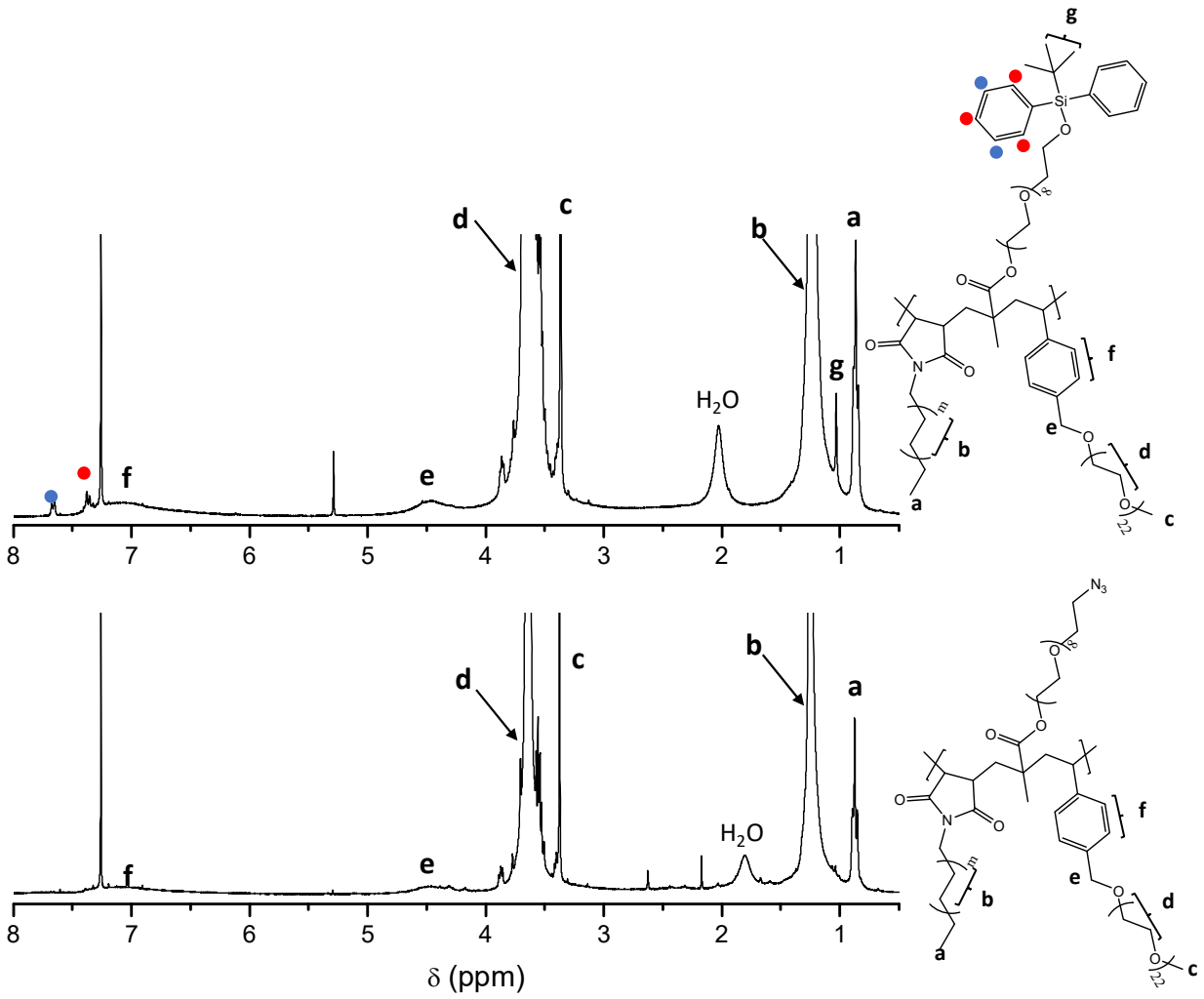


Figure S2. A typical ^{1}H NMR spectra of the hetero-arm amphiphilic molecular brush before (top) and after (bottom) modification of the methacrylate repeat units (TBDPS to azide). Spectra shows characteristic resonances for all three of the macromonomer repeat units.

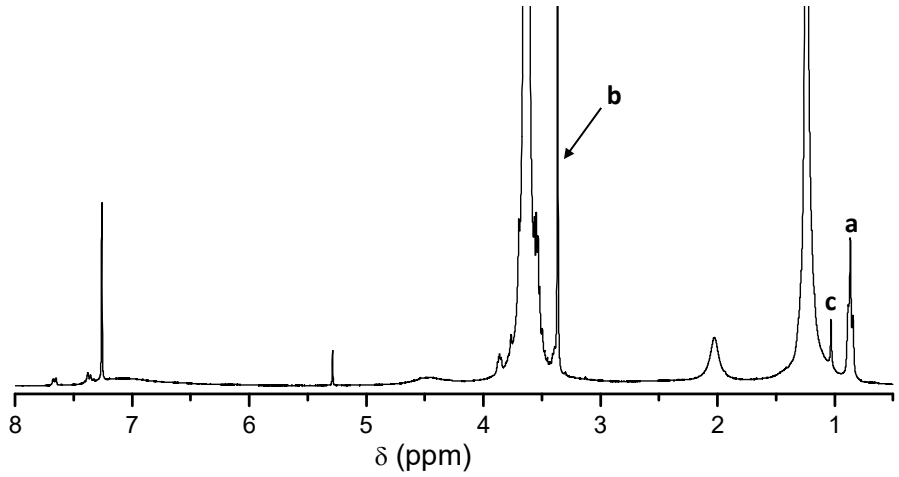


Figure S3. ^{1}H NMR spectrum of AMB-PEG$_{22}$C$_{16}$ showing the peaks integrated for composition analysis of the three repeat units in the AMB. Peak **a** (-C*H*$_3$, *N*-alkylmaleimide), **b** (-C*H*$_3$, VB-PEG$_n$) and **c** (-C(C*H*$_3$)$_3$, TBDPS-PEGMA).

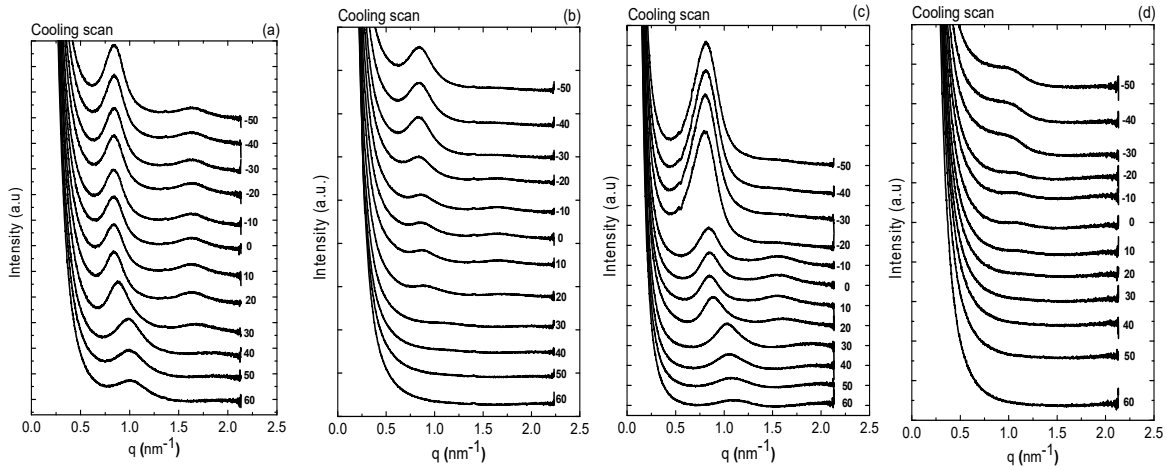


Figure S4. Variable-temperature SAXS pattern taken at different temperatures during cooling from the melt of (a) AMB-PEG$_{12}$C$_{20}$, (b) AMB-PEG$_{16}$C$_{20}$, (c) AMB-PEG$_{22}$C$_{20}$ and (d) AMB-PEG$_{22}$C$_{16}$.

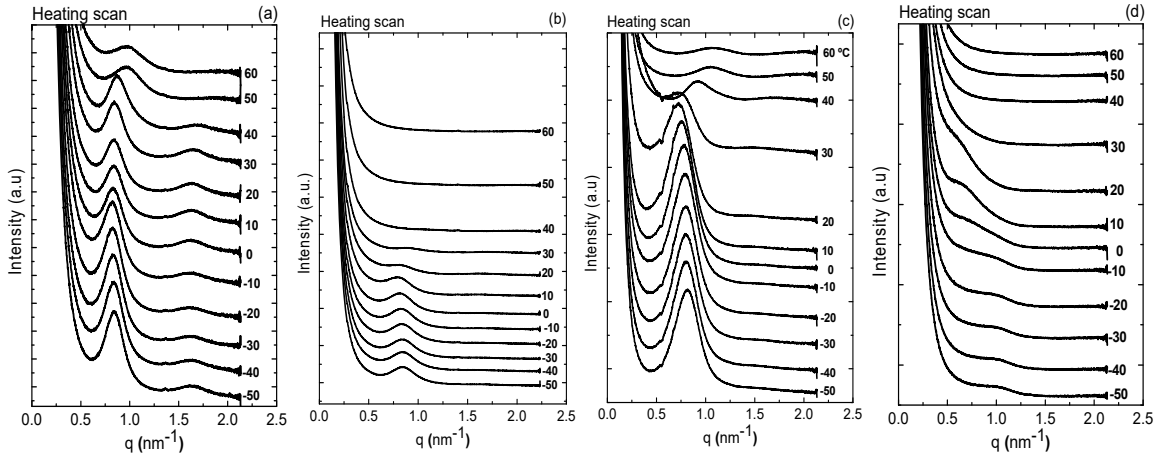


Figure S5. Variable-temperature SAXS pattern taken at different temperatures during heating from the crystalline state of (a) AMB-$PEG_{12}C_{20}$ (b) AMB-$PEG_{16}C_{20}$, (c) AMB-$PEG_{22}C_{20}$ and (d) AMB-$PEG_{22}C_{16}$.

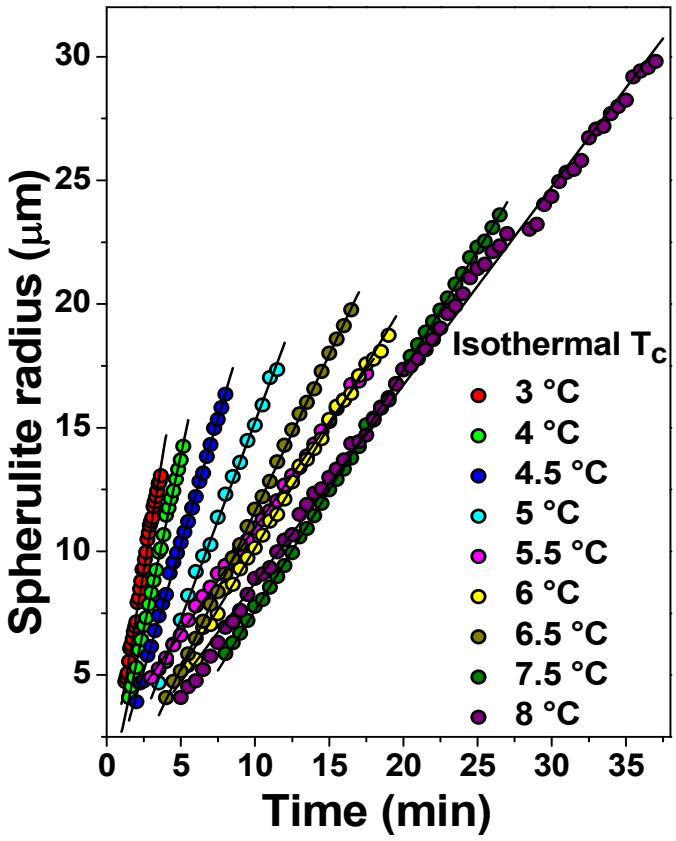


Figure S6: Spherulite radius versus isothermal crystallization time of AMB-$PEG_{22}C_{20}$, at various isothermal temperatures.

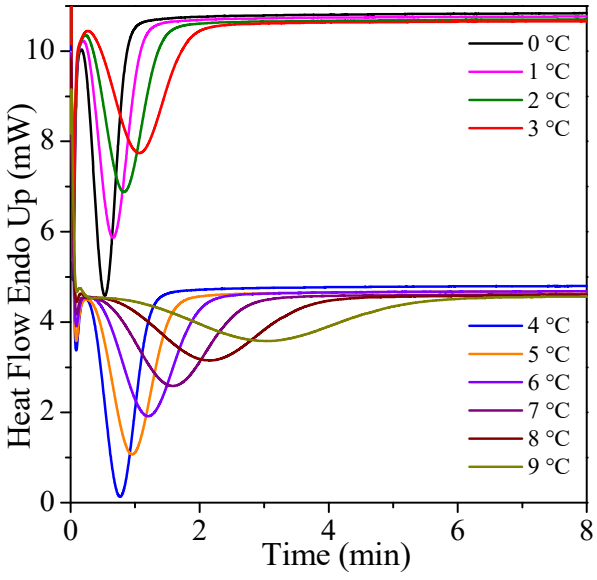


Figure S7: Isothermal crystallization curve of AMB-$PEG_{22}C_{20}$, following isothermal protocol 1a at different crystallization temperatures. Isothermal protocol 1a: Cooling from the melt at 1 °C·min^{-1} to 10 °C, followed by further cooling from 10 °C at 50 °C·min^{-1} to the established crystallization temperature.