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Modulation of side chain crystallinity in alternating copolymers

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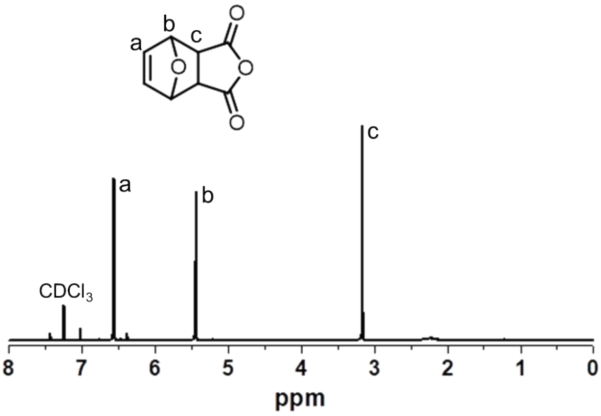


Fig. S1 ^{1}H NMR spectrum of compound **1** in CDCl$_3$.

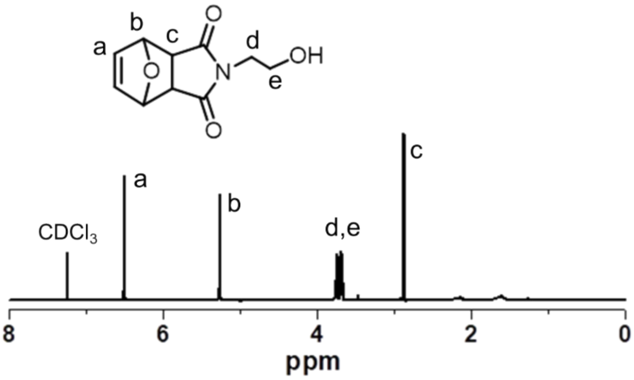


Fig. S2 ^{1}H NMR spectrum of compound **2** in CDCl$_3$.

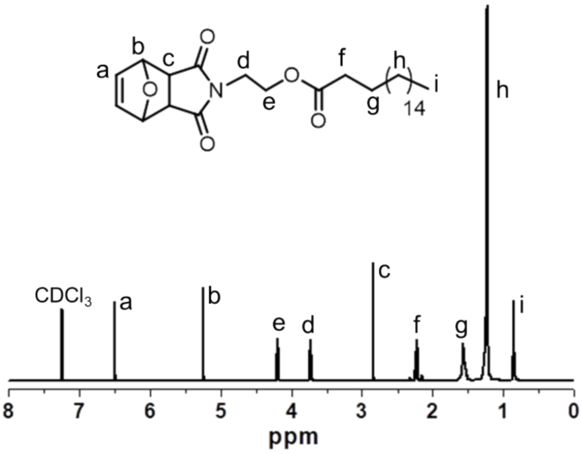


Fig. S3 ^{1}H NMR spectrum of compound **3** in CDCl$_3$.

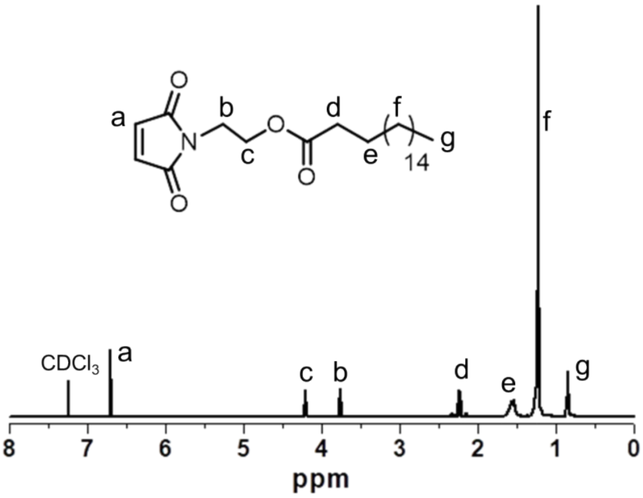


Fig. S4 ^{1}H NMR spectrum of *N*-substituted maleimide attached stearic acid (**MS**).

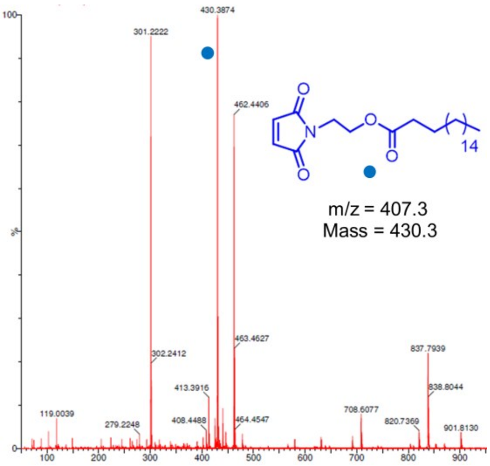


Fig. S5 ESI-MS spectrum of **MS**; observed *m*/*z* for [**MS** + Na]$^+$ = 430.38, calculated *m*/*z* for [**MS** + Na]$^+$ = 430.30.

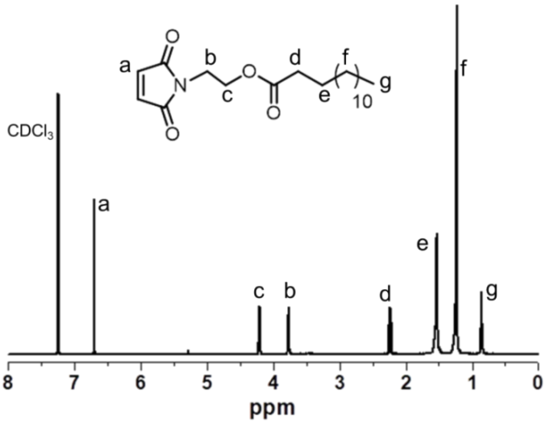


Fig. S6 ^{1}H NMR spectrum of *N*-substituted maleimide attached myristic acid (**MM**).

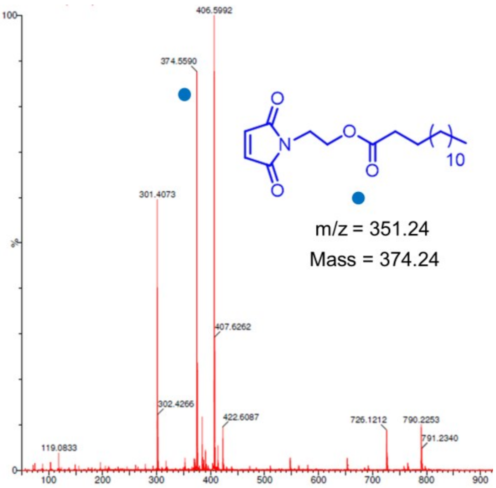


Fig. S7 ESI-MS spectrum of **MM**; observed *m*/*z* for [**MM** + Na]$^+$ = 374.55, calculated *m*/*z* for [**MM** + Na]$^+$ = 374.24.

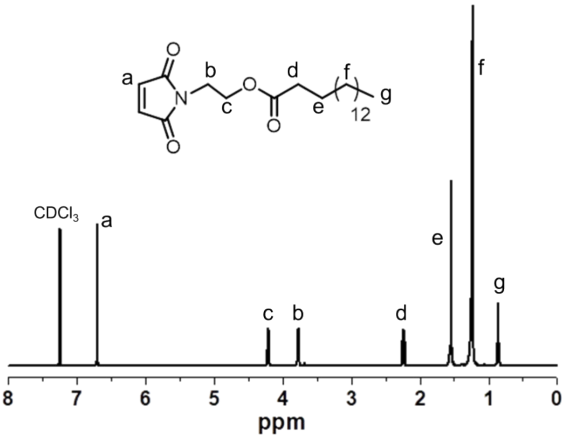


Fig. S8 ^{1}H NMR spectrum of *N*-substituted maleimide attached palmitic acid (**MP**).

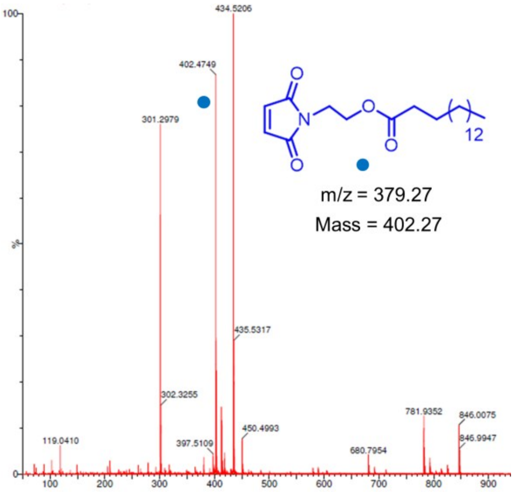
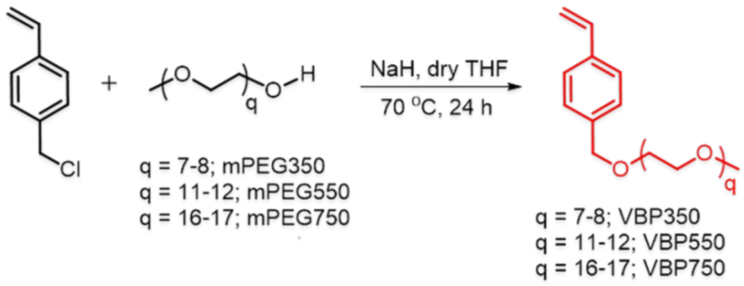


Fig. S9 ESI-MS spectrum of **MP**; observed *m*/*z* for [**MP** + Na]$^+$ = 402.47, calculated *m*/*z* for [**MP** + Na]$^+$ = 402.27.



Scheme S1. Synthesis of mPEG functionalised styrenic monomers.

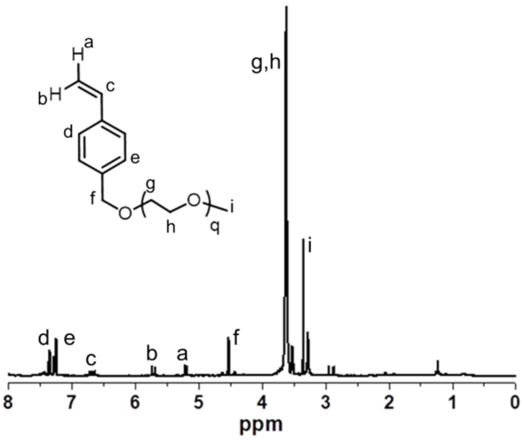


Fig. S10 ^{1}H NMR spectrum of mPEG750 appended styrene (**VBP750**).

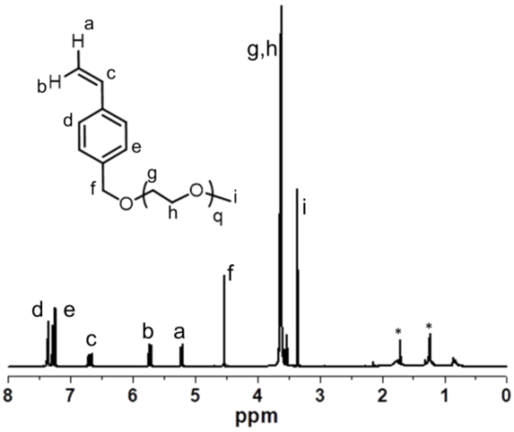


Fig. S11 ^{1}H NMR spectrum of mPEG550 appended styrene (**VBP550**).

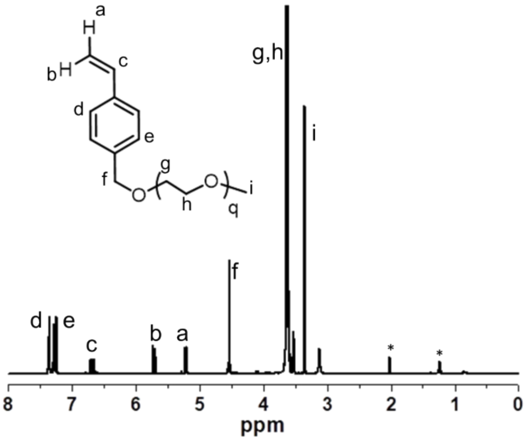


Fig. S12 ^{1}H NMR spectrum of mPEG350 appended styrene (**VBP350**).

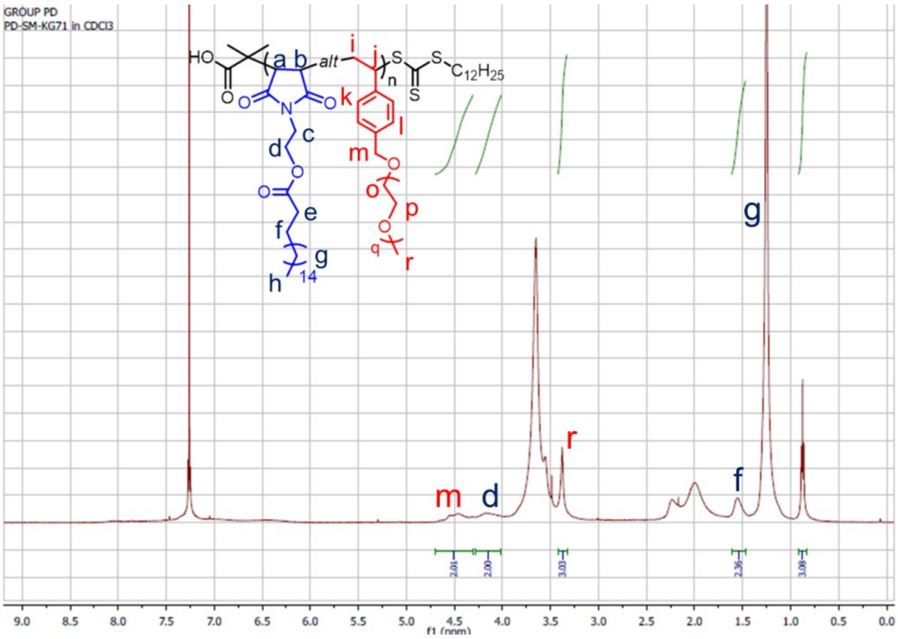


Fig. S13 The ^{1}H NMR of P(MS-*alt*-VBP350) at lower (20%) conversion.

Table S1. Characterization data for various P(MS-*alt*-VBP550) polymers.

Polymer	[**MS**]/[**VBP550**]/[DMP][a]	Conv.[b] (%)	$M_{n,SEC}$[c] (g/mol)	Đ[c]	$M_{n,theo}$[d] (g/mol)
P(MS-*alt*-VBP550)	10/10/1	53	3600	1.30	11750
P(MS-*alt*-VBP550)$_{20}$	20/20/1	54	4500	1.36	23500
P(MS-*alt*-VBP550)$_{35}$	35/35/1	48	6700	1.29	36400
P(MS-*alt*-VBP550)$_{50}$	50/50/1	47	12000	1.48	50800

[a] [DMP]/[AIBN] = 1:0.5 for all the polymerization reactions. Time = 24 h. [b] Determined gravimetrically. [c] Measured by SEC analysis in THF. [d] $M_{n,theo}$= [([**MS**+**VBP550**]/[DMP] × (molecular weight of (*MW*) of **MS** + *MW* of **VBP550**) × conversion) + *MW* of DMP].

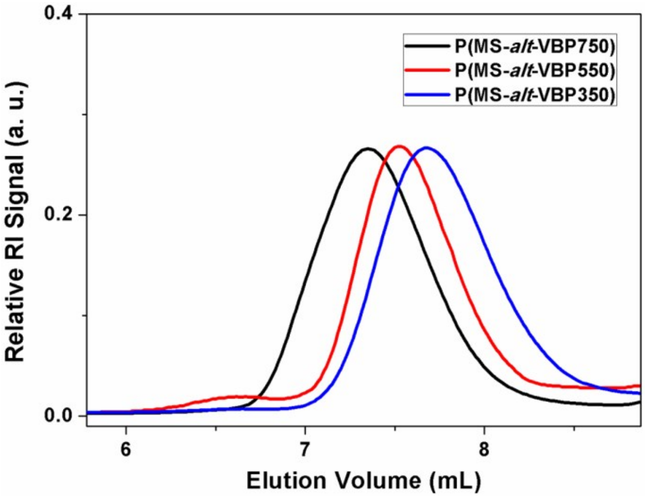


Fig. S14 The SEC RI traces of P(MS-*alt*-VBP) copolymers. Polystyrene standards with M_n = 801 (Đ =1.1), 2620 (Đ =1.06), 6240 (Đ =1.04), 9590 (Đ =1.07) and 41400 (Đ =1.02) g/mol were used to determine the molecular weights of the polymers.

Determination of molecular weight by UV-vis spectroscopy. The molecular weight of the polymers ($M_{n,\text{UV-vis}}$) was determined from UV-vis spectroscopy. The detailed process is as follows: At first the average molar absorptivity (ε) was determined by measuring the absorbance of DMP solution of known concentration in THF at room temperature. 3 mg of DMP (molecular weight (MW) = 364.63 g/mol) was dissolved in 3 mL of THF and from this solution 50 µL was taken out and was added in 3 mL of THF. UV-vis spectrophotometer (path length = 1 cm) was used to determine absorbance at 308 nm, which was 0.5895. From this result, ε was calculated as 13112 M^{-1} cm^{-1}. This process was carried out for two more times: (1) 3.1 mg of DMP was dissolved in 3 mL of THF and from this solution 50 µL was taken out and was added in 3 mL of THF. Absorbance at 308 nm was determined as 0.5975. From this result, the ε value was calculated as 12877 M^{-1} cm^{-1}. (2) 3.2 mg of DMP was dissolved in 3 mL of THF and from this solution 50 µL was taken out and was added in 3 mL of THF. Absorbance at 308 nm was determined as 0.5996. From this result, the ε value was calculated as 12511 M^{-1} cm^{-1}. The average ε value = 12833 M^{-1} cm^{-1} was used for further calculations.

Next, the absorbance value of the polymer solutions were determined at 308 nm and using ε value = 12833 M^{-1} cm^{-1}, the molecular weight ($M_{n,UV\text{-}vis}$) of the copolymers were evaluated with the help of Beer-Lambert law.[1,2] For example, a solution of 1.0 mg (W) of P(MP-*alt*-VBP750) in 2.5 mL (V) THF shows an absorbance (A) of 0.2752 at 308 nm. Then the $M_{n,UV\text{-}vis}$ of the polymer was calculated to be 18650 g/mol with the help of Beer-Lambert law ($A = \varepsilon Cl$ where $C = \frac{W}{M_{n,UV-vis}V}$).

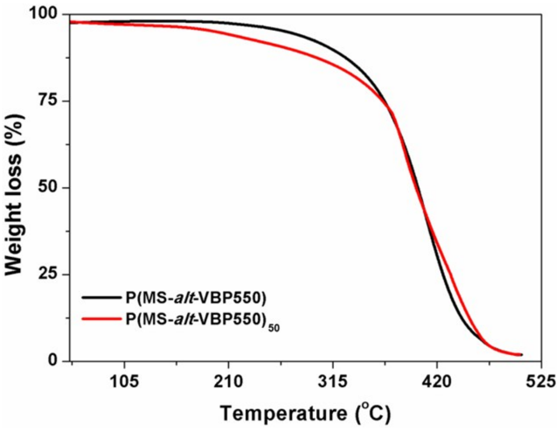


Fig. S15 TGA thermograms of P(MS-*alt*-VBP550) and P(MS-*alt*-VBP550)$_{50}$ at 10 °C/min heating rate.

Studies with homopolymers and random copolymers

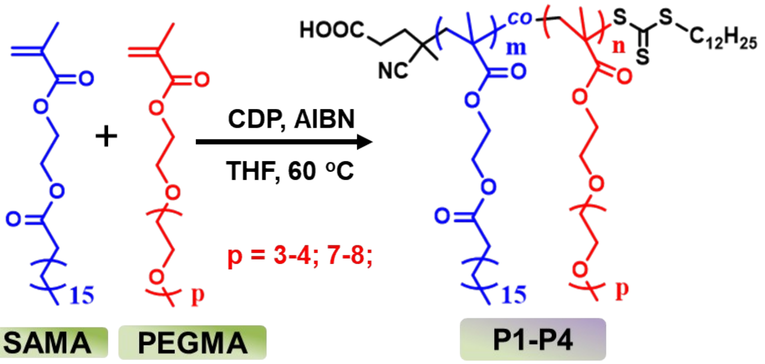
Materials. Poly(ethylene glycol) methyl ether methacrylate (PEGMA) (average molecular weights 300 (PEGMA300) and 475 g/mol (PEGMA475)) monomers were obtained from

Sigma-Aldrich and purified by passing through a basic alumina column. 4-Cyano (dodecylsulfanylthiocarbonyl)sulfanylpentanoic acid (CDP) was synthesized following earlier reports.[3] The methacrylate monomer with side-chain stearic acid (SAMA) was prepared as reported earlier.[4]

Synthesis of homopolymers P(VBP). P(VBP) homopolymers were synthesized *via* RAFT polymerization technique. Typically, the homopolymer P(VBP350) is synthesized as following: **VBP350** (100.0 mg, 0.214 mmol), CDP (5.76 mg, 0.014 mmol) and AIBN (0.46 mg, 0.0028 mmol, from stock solution in 1,4-dioxane) were dissolved in 1,4-dioxane (400 mg) in a 20 mL septa sealed polymerization vial followed by purging with dry N_2 for 10 min in ice-water bath. The vial was then placed in a preheated reaction block at 70 °C for 24 h under stirring, after which the vial was cooled in an ice-water bath and exposed to air to quench the polymerization reaction. After evaporating the solvent, excess amount of hexane was added to the vial during which the polymer got precipitated. The polymer was dissolved in minimum amount of acetone and again precipitated from excess hexane. After repeating this precipitation process for five to six times, the resulting precipitate was dried under vacuum for 7 h at 45 ^{o}C to collect the polymer P(VBP350) with a conversion of 60%, as determined gravimetrically. Similarly, P(VBP550) and P(VBP750) were also prepared.

Synthesis of homopolymers P(MF). P(MF) homopolymers were synthesized *via* free radical polymerization technique. Typically, the homopolymer P(MS) is synthesized as following: **MS** (200.0 mg, 0.491 mmol) and AIBN (2.02 mg, 0.0123 mmol, from stock solution in 1,4-dioxane) were dissolved in 1,4-dioxane (800 mg) in a 20 mL septa sealed polymerization vial followed by purging with dry N_2 for 10 min in ice-water bath. After heating the mixture at 70 °C for 24 h, the reaction was quenched *via* placing the vial in ice water bath followed by exposing to air. The solvent was then reduced under vacuum following which excess methanol was added to the vial to precipitate the polymer. After purifying for six to seven times from hexane/methanol mixtures, the polymer was dried under vacuum for 10 h at 45 ^{o}C to obtain P(MS) as a white solid. Similarly, P(MP) and P(MM) were also synthesized.

Synthesis of random copolymers P1-P4. The copolymers **P1** and **P2** were synthesized from SAMA and PEGMA300 monomers whereas **P3** and **P4** were prepared from SAMA and PEGMA475 through RAFT polymerization technique (Scheme S2, Table S2). A typical procedure for the synthesis of random copolymer **P1** is as follows: a mixture of SAMA (114 mg, 0.287 mmol), PEGMA300 (86 mg, 0.287 mmol), AIBN (0.75 mg, 0.0046 mmol, from stock solution in THF), CDP (9.23 mg, 0.0229 mmol) and THF (800 mg) was taken in a 20 mL reaction which was purged with dry N_2 for 10 min and placed in a preheated reaction block at 60 °C for 7 h. After that the vial was cooled in an ice-water bath and exposed to air to quench the polymerization reaction. Finally, the solution was taken into a dialysis bag with cut-off molecular weight of 1.0 kDa and dialysed against fresh methanol for two days during which the methanol was changed for 6-8 times in every 2-8 h. The resulting polymer **(P1)** was then collected by evaporating the solvent and dried under vacuum for 10 h at 45 ^{o}C. The feed ratios of SAMA and PEGMA were varied to get copolymers (**P1-P4**) of different compositions, as summarized in Table S2. The ^{1}H NMR spectrum of **P1** is assigned in Fig. S16A, where the integration areas of peak 'e' and 'm' are compared to determine the compositions of the copolymers. Furthermore, the integration area of chain end protons at 2.4-2.5 ppm is compared to that of peak 'e' and 'm' to calculate the number average degrees of polymerization of SAMA and PEGMA units in the copolymer which enables the evaluation of number average molecular weight ($M_{\mathrm{n,NMR}}$), provided in Table S2 . Moreover, the number-average molecular weight ($M_{\mathrm{n,GPC}}$) of the copolymers were also determined from GPC measurements. Fig. S16B shows symmetric and unimodal traces for **P1**-**P4** copolymers which signifies the absence of any bimolecular termination mechanisms as well as the well-controlled nature of the polymerization reaction.



Scheme S2. Synthetic scheme of RAFT-made random copolymers (**P1-P4**).

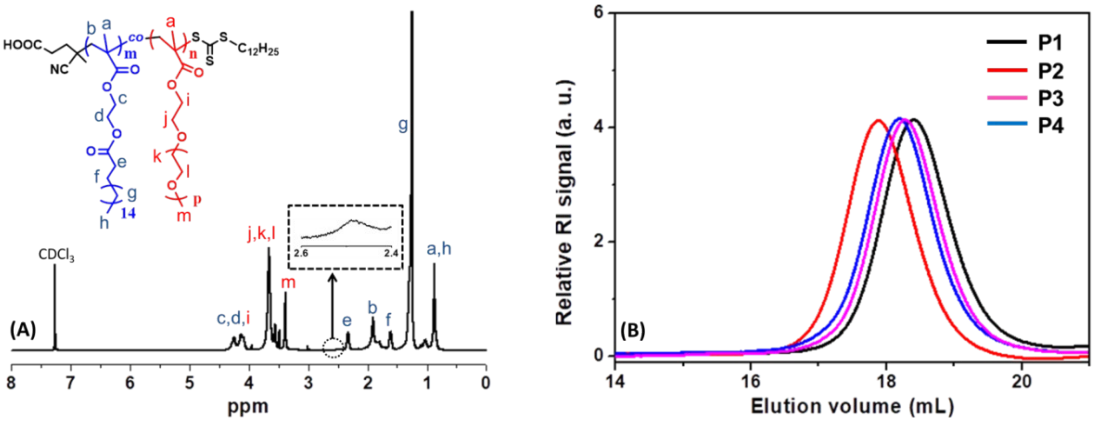


Fig. S16 (A) ^{1}H NMR spectrum of **P1** in $CDCl_3$ and (B) SEC RI traces of **P1**-**P4** copolymers.

Table S2. Synthesis and characterization of PEGMA/SAMA random copolymers.

Polymer[a]	SAMA content in feed	Conv.[b] (%)	SAMA content in Copolymer[c]	$M_{n,theo}$[d] (g/mol)	$M_{n,GPC}$[e] (g/mol)	$Đ$[e]	$M_{n,NMR}$[f] (g/mol)	T_m[g] (°C)
P1	50	78	50	7200	9200	1.16	8760	31.3
P2	55	83	56	7730	13860	1.16	10650	32.3
P3	50	76	52	8700	10440	1.15	9500	31.2
P4	55	79	57	8950	11200	1.15	11600	32.4

[a]Conditions: [SAMA]:[PEGMA300] = 50:50 (**P1**), 55:45 (**P2**); [SAMA]:[PEGMA475] = 50:50 (**P3**), 55:45 (**P4**); Time = 420 min, Target degree of polymerization = 25. [b]Determined gravimetrically. [c]Determined from ^{1}H NMR analysis. [d]$M_{n,theo}$ = (([monomer]/[CDP] × average molecular weight (MW) of monomer × conversion) + (MW of CDP)). [e]Measured by GPC in DMF. [f]Calculated by ^{1}H NMR from the integration ratio of the repeating unit protons to that of the polymer chain end protons. [g]Obtained from DSC study.

Thermal properties of homopolymers and random copolymers. Fig. S17 reveals the T_m values of P(VBP), P(MF) homopolymers and **P1-P4** copolymers as obtained from DSC study under a N_2 atmosphere at 10 °C/min heating rate. Note that **P1** and **P3** copolymers which have similar SAMA content show an almost identical value of T_m (31.31 and 31.26 °C, respectively, Fig. S17C, Table S2) which signifies that the increase of molecular weight of PEGMA units (from 300 to 475 g/mol) has negligible effect on the crystallization behaviour. A similar result was also obtained for **P2** (T_m = 32.30 °C) and **P4** (T_m =3 2.46 °C) copolymers as revealed from Fig. S17C. Thus, the above outcome suggests that the modification of T_m

values was not attainable through the variation of PEGMA chain lengths in case of random copolymers.

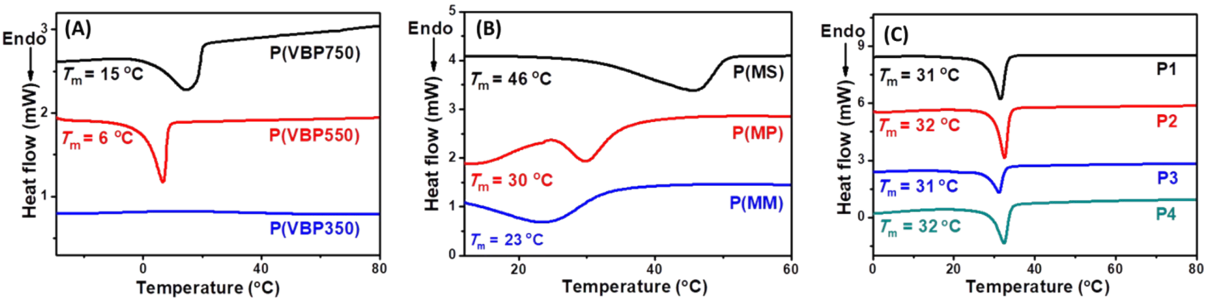


Fig. S17 DSC thermograms of (A) P(VBP) series, (B) P(MF) series, and (C) **P1-P4** copolymers.

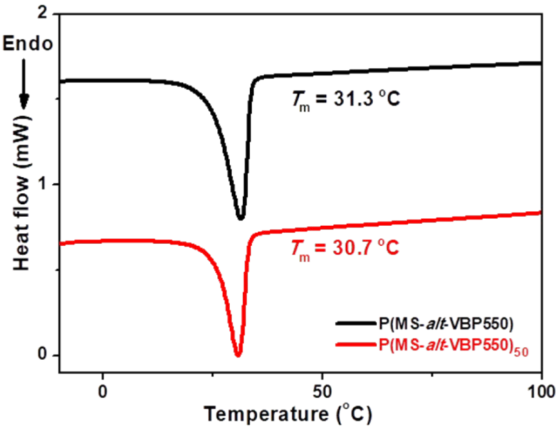


Fig. S18 DSC thermograms of P(MS-*alt*-VBP550) and P(MS-*alt*-VBP550)$_{50}$.

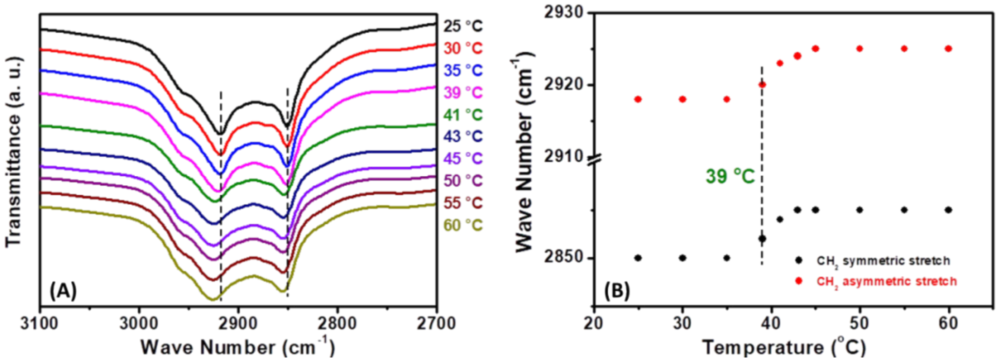


Fig. S19 (A) Variable temperature FT-IR spectra of the C-H stretching region of P(MS-*alt*-VBP750) copolymer, (B) The variation of -CH_2 symmetric and -CH_2 asymmetric stretching frequencies as a function of temperature. It is reported that during the melting of crystalline *n*-alkanes comprising of all-*trans* alkyl chains, there occurs a shifting of the signals corresponding to the symmetric (v_{sym}) and asymmetric (v_{asym}) C-H stretching vibrations from 2850 to 2856 cm^{-1} and from 2920 to 2928 cm^{-1}, respectively.[5] As shown in Fig. S19, with the gradual increase of temperature, the net shift in v_{sym} is from 2850 to 2855 cm^{-1}, whereas the v_{asym} signal shifts from 2918 to 2925 cm^{-1}. The onset of the peak shifting (at ~39 °C) matches well with the DSC endotherm (at ~ 40°C) suggesting a phase transition for the respective copolymer.

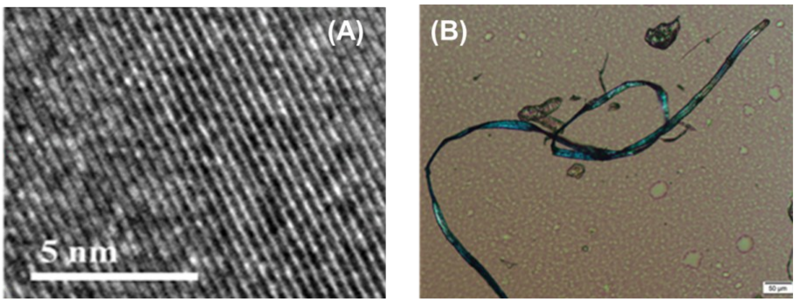


Fig. S20 (A) TEM image of P(MS-*alt*-VBP350) and (B) polarizing optical micrographs of P(MS-*alt*-VBP550) at 25 °C, scale length = 50 µm.

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