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ARTICLE

Alternating Copolymers of Functionalized α -methyl Styrene Monomers and Maleic Anhydride

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Alkyl and tertiary amine functionalized α -methyl styrene (AMS) monomers have been synthesized via reactive coupling of 3-isopropenyl- α,α -dimethylbenzyl isocyanate (TMI) with primary amines. Primary amines utilized include hexylamine, octadecylamine and *N,N*-dimethylethylenediamine to synthesize monomers, 3-hexyl-1-[1-(*m*-isopropenylphenyl)-1-methylethyl]urea (AMSC₆), 3-Octadecyl-1-[1-(*m*-isopropenylphenyl)-1-methylethyl]urea (AMSC₁₈) and 3-(2-(dimethylamino)ethyl)-1-[1-(*m*-isopropenylphenyl)-1-methylethyl]urea (AMSDMA), respectively. The structures of these functionalized AMS monomers have been confirmed by ¹H-NMR, ¹³C-NMR and FT-IR. AMS, AMSC₆ or AMSC₁₈ were then successfully copolymerized with maleic anhydride (MaA) via free radical polymerization initiated by azobisisobutyronitrile to synthesize alternating copolymers. Free radical homopolymerizations of AMS, AMSC₆, AMSC₁₈ and MaA were performed to reveal no monomer conversion by gas chromatography and no formation of polymer chains by gel permeation chromatography (GPC). Alternating copolymers were characterized by GPC, ¹H-NMR, FT-IR and MALDI-TOF MS. Finally, post-polymerization modification of P[(AMSC₁₈)-*a*-(MaA)] by imidization of the MaA repeat unit with a primary amine was performed. This leads to the synthesis of alternating dual functionalized copolymers in an efficient and simple way.

Introduction

Styrene-maleic anhydride copolymers (P(SMaA)) are a versatile and well utilized class of copolymer as they have many desirable properties such as; high temperature resistance, reactivity of the anhydride moiety and transparency. Owing to these desirable characteristics P(SMaA) copolymers have been applied in many applications from; polymer-protein conjugates as drug delivery vehicles, emulsifiers for the formation of microcapsules and dispersant viscosity modifiers within the engine oil industry.¹⁻⁵

Copolymerization of styrene (S) and maleic anhydride (MaA) is a well-known and accepted method of synthesizing alternating copolymers.⁶ Although there remains debate over the exact mechanism of how this alternating behavior occurs, it is expected to be a result of MaA monomer's inability to homopolymerize, as MaA is a strongly electron accepting monomer and when copolymerized with a strongly electron

donating monomer this will lead towards greater tendency to cross propagate.^{6,7} However, homopolymerization of S is still possible and this will lead to a small number of mis-insertions in the copolymer alternating structure. S mis-insertions are more likely to occur when copolymerisation is performed at higher temperatures or when S is in excess to MaA. Therefore, Charleux and co-workers were able to demonstrate near perfect alternation by performing S-MaA copolymerisation at 60 °C in the presence of a dithiobenzoate RAFT agent.¹³ Another possible method of reducing S mis-insertions is to utilize α -methyl styrene (AMS) as comonomer in place of styrene. AMS has a very low ceiling temperature (61 °C), therefore polymerization at or above this temperature results in a rate of depolymerization that is greater than the rate of homopolymerization. This distinct behavior further reduces the possibility of AMS homopolymerization and any mis-insertions in the final alternating copolymer structure.⁸ Although, AMS-MaA copolymerization will provide control over the final copolymer substructure, well defined polymer molecular weight and polymer dispersity at present is not possible to obtain as controlled radical polymerization techniques, such as ATRP and RAFT, are ineffective for these monomers.^{6,9} This is opposed to S-MaA copolymerizations, which have adapted to living radical techniques, namely NMP and RAFT, to synthesize well defined alternating and block copolymers.⁹⁻¹⁵

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Furthermore, CCTP has been utilized to copolymerize mixtures of S/AMS and MalA, providing control over which monomer is present as the copolymer end group.¹⁶

Given that AMS-MalA copolymerizations will yield alternating copolymers, functional derivatives of these monomers may also exhibit the same cross propagation behavior and thus preparation of functionalized alternating copolymers. Considering this, 3-isopropenyl- α,α -dimethylbenzyl isocyanate (TMI) has been an ideal commercially available monomer to utilize. TMI features an α -unsaturation as well as a reactive isocyanate functionality. Via the α -unsaturation TMI has been radically copolymerized with a variety of monomers, such as styrene, methyl methacrylate, *n*-butyl acrylate, ethyl acrylate and chlorotrifluoroethylene.¹⁷⁻²³ TMI has also been shown to capable of being homopolymerized and copolymerized cationically.²⁴⁻²⁷ Finally, TMI's pendant isocyanate moiety has been reacted with primary amines and hydroxyls to synthesize monomers with new pendant functionality,²⁸ functionalize polymer end groups,²⁹ and undergo post-polymerization modification to add further functionality.^{22,23,25-27,30}

In the present article, we exploit the free radical copolymerization behavior of functionalized TMI monomers with MalA to synthesize alternating copolymers that bear a desired moiety on every AMS repeat unit. Furthermore, the MalA repeat unit is modified post-polymerization with a primary amine to add further versatility to the alternating copolymer. We believe these copolymers represent a new class of copolymers that exhibit alternating functionality that could have many conceivable derivatives and could potentially cater for a number of applications that already utilize P(SMalA) copolymers.

Experimental

Materials

Maleic anhydride (Aldrich, 99%), 2,2'-Azobis(2-methylpropionitrile) (Aldrich, 98%), 3-Isopropenyl- α,α -dimethylbenzyl isocyanate (Aldrich, 95%), hexylamine (Aldrich, 99%), octadecylamine (Aldrich, 97%), α -methylstyrene dimer (Aldrich, 97%), *N,N*-dimethylethylenediamine (Aldrich, \geq 98%), 4-(aminomethyl)pyridine (Aldrich, 99%) were all used as received.

α -Methylstyrene (Aldrich, 99%) was destabilised before use by passing through a short column of basic aluminium oxide.

Butanone, and toluene were all HPLC grade and used as received. Caromax 20 was provided by Innospec LTD and used as received. All other solvents were of general lab quality and used as received.

Synthetic Procedures

Free radical copolymerization of AMS and MalA. In a typical copolymerization; AMS (1 mL, 7.7 mmol), MalA (0.75 g, 7.7 mmol), AIBN (mmol as in Table 1) and MEK (2 mL) were charged into Schlenk tube and degassed by gentle

bubbling of N₂ gas for 20 minutes. Schlenk tube was submerged into an oil bath at 80 °C and removed after 4 hours. Product was precipitated into a large volume of methanol, filtered and placed into a vacuum oven overnight to remove all solvent. ¹H-NMR (400 MHz, (CD₃)₂CO): δ / ppm 0.31 – 1.97 (m, -CH₂- and -(CH₃), P(AMS) repeat unit), 2.12 – 3.55 (m, -CH-, P(MalA) repeat unit), 6.80 – 7.90 (m, -(C₆H₅), P(AMS) repeat unit). FT-IR (neat): (cm⁻¹) 2981 (w), 2361 (w), 2341 (w), 1856 (m), 1772 (s), 1498 (w), 1479 (w), 1446 (w), 1393 (w), 1252 (w), 1058 (m), 1001 (w), 909 (s), 757 (m), 700 (s), 611 (m).

Synthesis of AMSC₆. Hexylamine (4 mL, 30.3 mmol, 1.2 eq.) was added drop wise to a solution of TMI (5 mL, 25.3 mmol, 1 eq.) in toluene (20 mL) and left stirring at room temperature for 3 hours. Product precipitated out of solution. Reaction mixture cooled to 0 °C, product collected by vacuum filtration and dried overnight under vacuum. ¹H-NMR (400 MHz, CDCl₃): δ / ppm 0.84 (t, 3 H), 0.99 – 1.28 (m, 8 H), 1.63 (s, 6 H), 2.15 (s, 3 H), 3.02 (q, 2H), 4.14 (t, 1 H), 4.92 (s, 1 H), 5.10 (t, 1 H), 5.36 (s, 1 H), 7.27 – 7.39 (m, 3 H), 7.57 (t, 1 H). ¹³C-NMR (400 MHz, CDCl₃): δ / ppm 13.96 (s), 21.83 (s), 22.46 (s), 26.29 (s), 29.87 (s), 30.35 (s), 31.41 (s), 54.76 (s), 112.75 (s), 122.44 (s), 124.34 (s), 128.58 (s), 141.71 (s), 143.19 (s), 146.43 (s), 157.60 (s). FT-IR (neat): (cm⁻¹) 3364 (m), 3299 (m), 2966 (m), 2931 (m), 2856 (m), 2361 (w), 1632 (s), 1560 (s), 1485 (m), 1457 (m), 1439 (w), 1378 (w), 1359 (w), 1270 (s), 1240 (w), 1218 (w), 1149 (m), 887 (m), 800 (m), 723 (w), 655 (m), 530 (m).

Free radical copolymerization of AMSC₆ and MalA. In a typical copolymerization; AMSC₆ (0.25 g, 0.83 mmol) MalA (0.08 g, 0.84 mmol), AIBN (mmol as in Table 1) and MEK (3 mL) were charged into Schlenk tube and degassed by gentle bubbling of N₂ gas for 20 minutes. Schlenk tube was submerged into an oil bath at 80 °C and removed after 4 hours. Product was precipitated into a large volume of methanol, filtered and placed into a vacuum oven overnight to remove all solvent. ¹H-NMR (400 MHz, (CD₃)₂CO): δ / ppm 0.56 – 1.03 (m, -CH₂(CH₂)₄CH₃, P(AMSC₆) repeat unit), 1.04 – 1.93 (m, -CH₂-, -(CH₃), -CH₂(CH₂)₄CH₃, -NH-C(CH₃)₂-, P(AMSC₆) repeat unit), 2.18 – 2.65 (m, -CH₂(CH₂)₄CH₃, P(AMSC₆) repeat unit), 2.65 – 3.56 (m, -CH-, P(MalA) repeat unit), 5.41 – 6.52 (m, -NHCONH-, P(AMSC₆) repeat unit), 6.52 – 7.82 (m, -(C₆H₄)-, P(AMSC₆) repeat unit). FT-IR (neat): (cm⁻¹) 3380 (br, w), 2928 (w), 2857 (w), 2361 (m), 2341 (m), 1857 (w), 1775 (s), 1641 (w), 1560 (m), 1487 (m), 1381 (w), 1361 (w), 1265 (m), 1167 (w), 1088 (m), 912 (s), 796 (w), 768 (m), 651 (w), 500 (w).

Synthesis of AMSC₁₈. Octadecylamine. (4.2 g, 15.6 mmol, 1.2 eq.) was dissolved in a mixture of chloroform (5 mL) and toluene (15 mL) and added drop wise to a solution of TMI (2.5 mL, 12.6 mmol, 1 eq.) in toluene (5 mL) and chloroform (1.5 mL) and left stirring at room temperature for 3 hours. Product precipitated out of solution. Reaction mixture cooled to 0 °C, product collected by vacuum filtration and dried overnight under vacuum. ¹H-NMR (400 MHz, CDCl₃): δ / ppm 0.88 (t, 3 H), 1.00 (m, 2 H), 1.09 – 1.32 (m, 3 H), 1.63 (s, 6 H), 2.15 (s, 3 H), 3.03 (q, 2 H), 3.98 (t, 1 H), 4.78 (s, 1 H), 5.10 (t, 1 H), 5.36

(s, 1 H), 7.30 – 7.40 (m, 3 H), 7.58 (t, 1 H). ^{13}C -NMR (400 MHz, CDCl_3): δ / ppm 14.10 (s), 21.87 (s), 22.67 (s), 26.62 (s), 29.26 (s), 29.34 (s), 29.68 (m), 29.88 (s), 30.39 (s), 31.91 (s), 40.09 (s), 54.74 (s), 112.86 (s), 122.52 (s), 124.46 (s), 128.67 (s), 141.83 (s), 143.16 (s), 146.23 (s), 157.53 (s). FT-IR (neat): (cm^{-1}) 3364 (w), 3301 (w), 2967 (m), 2919 (m), 2851 (m), 2361 (w), 1631 (s), 1560 (s), 1485 (m), 1379 (w), 1270 (m), 1147 (m), 887 (m), 801 (m), 723 (m), 653 (m), 505 (m).

Free radical copolymerization of AMSC₁₈ and MalA. In a typical copolymerization; AMSC₁₈ (0.25 g, 0.53 mmol), MalA (0.052 g, 0.53 mmol), and MEK (2.5 mL) were charged into Schlenk tube and heated to 35 °C to fully homogenize the mixture. Degassed by gentle bubbling of N_2 gas for 10 minutes. Schlenk tube was submerged into an oil bath at 80 °C before the addition of a degassed solution of AIBN (mmol as in Table 1) in MEK (0.5 mL). Schlenk tube was removed from the oil bath after 4 hours. Mixture was allowed to cool before diluting with *n*-hexane. Organic phase was extracted with distilled water twice to remove the unconverted MalA. All remaining solvent was evaporated and product was placed into a vacuum oven overnight to remove all remaining solvent. ^1H -NMR (400 MHz, CDCl_3): δ / ppm 0.83 – 0.95 (m, $-\text{CH}_2(\text{CH}_2)_{16}\text{CH}_3$, P(AMSC₁₈) repeat unit), 0.96 – 1.85 (m, $-\text{CH}_2$ -, $-(\text{CH}_3)$ -, $-\text{CH}_2(\text{CH}_2)_{16}\text{CH}_3$ -, $-\text{NH}-\text{C}(\text{CH}_3)_2$ -, P(AMSC₁₈) repeat unit), 2.80 – 3.26 (m, $-\text{CH}$ -, P(MalA) repeat unit), 6.35 – 7.45 (m, $-\text{NHCONH}$ -, $-(\text{C}_6\text{H}_4)$ -, P(AMSC₁₈) repeat unit). FT-IR (neat): (cm^{-1}) 3371 (w), 2922 (s), 2852 (m), 2361 (m), 2341 (m), 1857 (w), 1776 (s), 1639 (w), 1562 (m), 1464 (w), 1381 (w), 1361 (w), 1261 (m), 1167 (w), 1060 (m), 914 (s), 797 (w), 709 (m), 506 (m).

Free radical copolymerization of AMSC₁₈ and MalA using AMSD as a CTA. In a typical copolymerization; AMSC₁₈, (0.25 g, 0.53 mmol), MalA (0.052 g, 0.53 mmol), and MEK (2.5 mL) were charged into Schlenk tube and heated to 35 °C to fully homogenize the mixture. Degassed by gentle bubbling of N_2 gas for 10 minutes. Schlenk tube was submerged into an oil bath at 80 °C before the addition of a degassed solution of AIBN (3.5 mg, 0.021 mmol) and AMSD (mmol as in Table 1) in MEK (0.5 mL). Schlenk tube was removed from the oil bath after 4 hours. Mixture was allowed to cool before diluting with *n*-hexane. Organic phase was extracted with distilled water twice to remove the unconverted MalA. All remaining solvent was evaporated and product was placed into a vacuum oven overnight to remove all remaining solvent. ^1H -NMR (400 MHz, CDCl_3): δ / ppm 0.83 – 0.95 (m, $-\text{CH}_2(\text{CH}_2)_{16}\text{CH}_3$, P(AMSC₁₈) repeat unit), 0.96 – 1.88 (m, $-\text{CH}_2$ -, $-(\text{CH}_3)$ -, $-\text{CH}_2(\text{CH}_2)_{16}\text{CH}_3$ -, $-\text{NH}-\text{C}(\text{CH}_3)_2$ -, P(AMSC₁₈) repeat unit), 2.65 – 3.38 (m, $-\text{CH}$ -, P(MalA) repeat unit), 4.80 (m, $-\text{C}(\text{C}_6\text{H}_4)=\text{CH}_{\text{trans}}\text{H}_{\text{cis}}$, end group), 5.14 (m, $-\text{C}(\text{C}_6\text{H}_4)=\text{CH}_{\text{trans}}\text{H}_{\text{cis}}$, end group), 6.35 – 7.97 (m, $-\text{NHCONH}$ -, $-(\text{C}_6\text{H}_4)$ -, P(AMSC₁₈) repeat unit). FT-IR (neat): (cm^{-1}) 3350 (w), 2922 (s), 2852 (s), 1858 (w), 1777 (s), 1639 (s), 1558 (s), 1465 (w), 1381 (w), 1361 (w), 1257 (m), 1168 (w), 1061 (m), 913 (s), 797 (w), 707 (s), 509 (s).

Synthesis of AMSDMA. *N,N*-dimethylethylenediamine (4.15 mL, 38.0 mmol, 1.5 eq.) was added drop wise to a solution of TMI (5 mL, 25.3 mmol, 1 eq.) in toluene (40 mL) and left stirring at room temperature for 3 hours. Product precipitated

out of solution. Reaction mixture cooled to 0 °C, product collected by filtration, washed with cold toluene and dried overnight under vacuum. ^1H -NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ / ppm 1.62 (s, 6 H), 2.14 (s, 9 H), 2.26 (t, 2 H), 3.11 (q, 2 H), 5.06 (m, 1 H), 5.37 (m, 1 H), 5.42 (m, 1 H), 6.14 (s, 1 H), 7.21–7.37 (m, 3 H), 7.59 (t, 1 H). ^{13}C -NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ / ppm 22.14 (s), 30.72 (s), 38.39 (s), 45.62 (s), 55.39 (s), 60.15 (s), 112.42 (m), 123.16 (s), 123.89 (s), 125.32 (s), 128.72 (s), 141.56 (s), 144.76 (s), 150.11 (s), 158.19.

Imidization of P[(AMSC₁₈)-a-(MalA)]. P[(AMSC₁₈)-a-(MalA)] (P3e, 0.10 g, 1 eq.) was dissolved in Caromax 20 (2 mL) at 60 °C. 4-(aminomethyl)pyridine (36 μL , 0.352 mmol, 2 eq.) was added drop wise to the reaction mixture before equipping the round bottom flask with Dean-Stark condenser and increasing the temperature to 160 °C. After 4 hours the reaction was cooled to room temperature and the polymer was precipitated into *n*-hexane twice from chloroform and dried overnight under vacuum. ^1H -NMR (400 MHz, CDCl_3): δ / ppm 0.71 – 0.96 (m, $-\text{CH}_2(\text{CH}_2)_{16}\text{CH}_3$, P(AMSC₁₈) repeat unit), 0.96 – 1.95 (m, $-\text{CH}_2$ -, $-(\text{CH}_3)$ -, $-\text{CH}_2(\text{CH}_2)_{16}\text{CH}_3$ -, $-\text{NH}-\text{C}(\text{CH}_3)_2$ -, P(AMSC₁₈) repeat unit), 1.99 – 3.05 (m, $-\text{CH}$ -, P(MalA) repeat unit), 4.00 – 5.03 (m, $-\text{CH}_2(\text{C}_5\text{H}_4\text{N})$, P(PyMI) repeat unit), 6.16 – 7.93 (m, $-\text{NHCONH}$ -, $-(\text{C}_6\text{H}_4)$ -, P(AMSC₁₈) repeat unit, $-\text{CH}_2(\text{C}_5\text{H}_4\text{N})$, P(PyMI) repeat unit), 8.04 – 8.96 (m, $-\text{CH}_2(\text{C}_5\text{H}_4\text{N})$, P(PyMI) repeat unit). FT-IR (neat): (cm^{-1}) 3399 (br, w), 2954 (w), 2919 (m), 2849 (m), 1771 (w), 1698 (s), 1613 (w), 1592 (m), 1571 (m), 1469 (m), 1435 (w), 1395 (w), 1336 (w), 1287 (m), 1252 (s), 1170 (s), 1048 (w), 995 (w), 914 (m), 795 (m), 751 (s), 708 (s), 511(m). GPC (DMF, 5 mM NH_4BF_4): M_n 14300 $\text{g}\cdot\text{mol}^{-1}$, M_w 27500 $\text{g}\cdot\text{mol}^{-1}$ D 1.92.

Characterisation techniques

Gel Permeation Chromatography. GPC was utilized to calculate molecular weight averages and polymer dispersity. GPC measurements were performed on two different systems. System 1 was an Agilent 390-LC system equipped with a PL-AS RT autosampler, 2 PLgel 5 μm mixed-C columns (300 \times 7.5 mm), a PLgel 5 mm guard column (50 \times 7.5 mm), and a differential refractive index (DRI). The system was eluted with THF at a flow rate of 1 $\text{mL}\cdot\text{min}^{-1}$ and the DRI was calibrated with linear narrow polystyrene standards. System 2 was an Agilent 1260 infinity system equipped with 2 \times PLgel 5 μm mixed-D columns (300 \times 7.5 mm), a PLgel 5 mm guard column (50 \times 7.5 mm), a differential refractive index (DRI), and variable wavelength detector (VWD). The system was eluted with DMF containing 5 mM ammonium tetrafluoroborate at a flow rate of 1 $\text{mL}\cdot\text{min}^{-1}$ and the DRI detector was calibrated with linear narrow poly(methyl methacrylate) standards.

Nuclear magnetic resonance spectroscopy. ^1H -NMR and ^{13}C -NMR spectra were measured using a Bruker AV-400 at 298 K. Chemical shifts are reported in parts per million (ppm) and all spectra are referenced against the residual solvent peak found in the deuterated NMR solvent. Abbreviations used for peak multiplicity are as follows; s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet.

Gas chromatography – flame ionisation detection. GC-FID was used to measure monomer conversions for homopolymerisation of DMA. GC-FID analysis was performed using an Agilent Technologies 7820A. An Agilent J&W HP-5 capillary column of 30 m × 0.320 mm, film thickness 0.25 μm was used. The oven temperature was programmed as follows: 40 °C (hold for 1 minute) increase at 30 °C·min⁻¹ to 300 °C (hold for 2.5 minutes). The injector was operated at 250 °C and the FID was operated at 320 °C. Nitrogen was used as carrier gas at flow rate of 6.5 mL·min⁻¹ and a split ratio of 1:1 was applied. Chromatographic data was processed using OpenLab CDS ChemStation Edition, version C.01.05.

Fourier transform infrared Spectroscopy. FT-IR spectra were recorded on a Bruker Vector-22 spectrometer using a Golden Gate diamond attenuated total reflection cell. All FT-IR spectra are plotted transmittance against wavenumbers (cm⁻¹).

Matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry. MALDI-TOF MS was performed using a Bruker Daltonics Autoflex MALDI-TOF mass spectrometer, equipped with a nitrogen laser at 337 nm with positive ion ToF detection. Solutions in THF of trans-2-[3-(4-tertbutylphenyl)-2-methyl-2-propylidene]malonitrile (DCTB) as matrix (30 mg·mL⁻¹), potassium trifluoroacetate as cationisation agent (10 mg·mL⁻¹) and sample (10 mg·mL⁻¹) were mixed together in a 1 : 3 : 1 volume ratio for a total volume of 75 μL. 1 μL of the mixture was applied to the target plate. Spectra were recorded in reflectron mode and the mass spectrometer was calibrated with a peptide mixture up to 6000 Da.

Results and Discussion

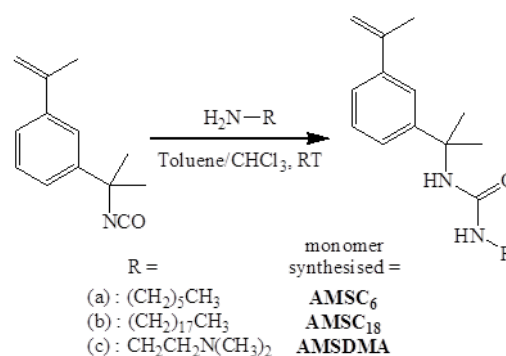
Synthesis of dual functionalized AMS-MaA copolymers could be achieved via one of two synthetic pathways. Functionalized TMI can be copolymerized with MaA to synthesize an alternating copolymer. The alternating copolymer's MaA repeat unit can then be imidized to a cyclic imide and thus furnish a dual functionalized copolymer. Alternatively, maleimides could be copolymerized with TMI before functionalization of the pendant isocyanate. It was decided to pursue the first route as this would avoid requiring stringent and very pure polymerization conditions, which are often required for polymerizing monomers that contain isocyanate groups.

Functionalised α -methyl styrene monomers synthesis

As discussed earlier, TMI was selected as a monomer to be functionalized due to its commercial availability and the reactivity of the isocyanate towards hydroxyls and primary amines. Reacting a primary amine with an isocyanate results in the formation of a urea linkage. Therefore, utilizing the isocyanate on TMI will result in functionalized AMS monomers that contain a urea linkage. This may prove problematic for future copolymerization with MaA as MaA can be potentially ring opened by primary and secondary amines as well as decarboxylated or homopolymerized by tertiary amines.³¹ Therefore, it is essential to determine if the nitrogen present in the urea linkage will exhibit any of these

negative effects on MaA during copolymerization. To test this, an AMS monomer was synthesized with a small alkyl chain to act as a mimic for a functional monomer, which will contain larger alkyl functionalities.

This was achieved by reacting hexylamine with TMI to synthesize 3-hexyl-1-[1-(*m*-isopropenylphenyl)-1-methylethyl]urea (AMSC₆), Scheme 1. AMSC₆ will be subsequently copolymerized with MaA to ensure the urea linkage does not interfere with the copolymerization. AMSC₆ was synthesized successfully. After 3 hours of stirring at room temperature the product precipitated from toluene and was simply filtered before drying under vacuum to obtain the product (yield = 86%) and expected structure was confirmed by ¹H-NMR (Figure 1) and ¹³C-NMR spectroscopy (Figure S1-S3). Furthermore, FT-IR showed no peak at 2259 cm⁻¹, which corresponds to the isocyanate group on TMI, thereby confirming all of the isocyanate had been consumed.



Scheme 1 Synthesis of AMSC₆, AMSC₁₈, and AMSDMA monomers.

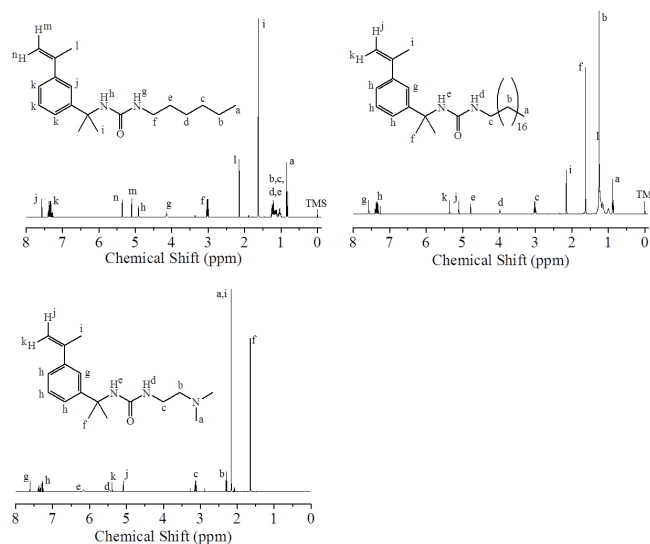


Figure 1 ¹H-NMR spectra of AMSC₆ (top left), AMSC₁₈ (top right) and AMSDMA (bottom left).

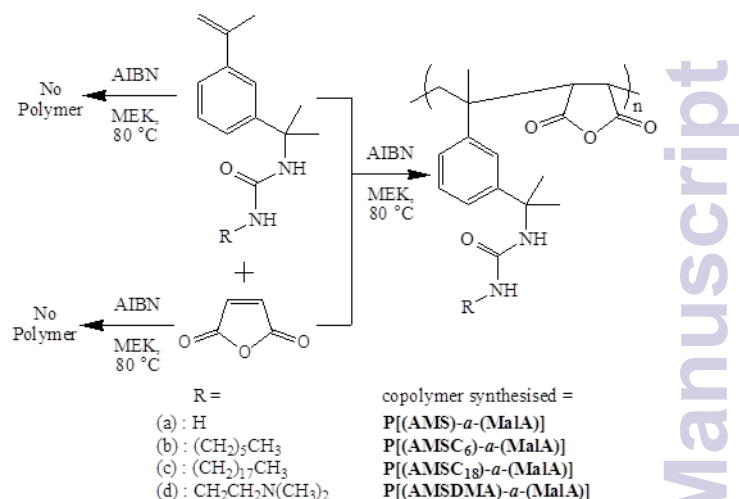
AMSC₆ synthesis proved to be a highly efficient reaction with minimal work up required to obtain high yields of pure product, furthermore AMSC₆ contains the required urea linkage to test if it may have any negative or positive implications throughout copolymerization with MalA, this will be examined in the next section. This synthesis was extended to synthesizing another AMS monomer that contains a larger alkyl group, from hexyl to octadecyl, which will add more hydrophobic character to the final copolymer. Octadecylamine was reacted with TMI to synthesize 3-Octadecyl-1-[1-(*m*-isopropenylphenyl)-1-methylethyl]urea (AMSC₁₈), Scheme 1. AMSC₁₈ synthesis was also successful and the reaction proceeded very similarly to that of AMSC₆, except addition of CHCl₃ was required to initially dissolve octadecylamine. After 3 hours of stirring at room temperature the desired product precipitated out of solution and was again purified by filtration and drying under vacuum. Expected structure was confirmed by ¹H-NMR (Figure 1) and ¹³C-NMR, see supplementary information. FT-IR again showed no presence of residual isocyanate.

The syntheses of previous two monomers were designed to functionalize an AMS monomer with a hydrophobic alkyl chain, which will then be copolymerized with MalA before further modification. A third monomer was synthesized to bear a tertiary amine that would examine if copolymerizations with MalA can tolerate the presence of such tertiary amines. *N,N*-dimethylethylenediamine was coupled with TMI to synthesize, 3-(2-(dimethylamino)ethyl)-1-[1-(*m*-isopropenylphenyl)-1-methylethyl]urea (AMSDMA), Scheme 1.

Synthesis of AMSDMA was performed using the same reaction conditions as those for AMSC₆ and the reaction proceeded in a similar fashion. After 3 hours of reacting at room temperature the monomer precipitated out of solution, purified by gravity filtration, and washed with acetone before drying under vacuum. The expected monomer structure was confirmed by ¹H-NMR (Figure 1) and ¹³C-NMR spectroscopy, see supplementary information.

Copolymerization of functional AMS monomers and maleic anhydride

AMS and MalA were copolymerized by free radical polymerization initiated by AIBN, Scheme 2. Free radical polymerization was chosen, as other controlled radical techniques are ineffective at controlling AMS-MalA copolymerization. MalA is suspected to interact with the transition metal complexes that are used to mediate ATRP. RAFT copolymerization of AMS and MalA have also provided poor control with little evidence of the RAFT agent mediating the copolymerization, potentially caused by a low chain transfer constant to the RAFT agent.^{6,9} Copolymerization of AMS and MalA is expected to give an alternating monomer sequence, as both monomers are incapable of homopolymerization under selected conditions. However, it is essential to confirm this before copolymerizing the two monomers. Therefore, a short series of control homopolymerizations are summarized in Table 1 for AMS, MalA, AMSC₆ and AMSC₁₈, which are coded as samples C1 – C4, respectively.



Scheme 2 Schematic representation for the synthesis of P[(AMS)-*a*-(MalA)], P[(AMSC₆)-*a*-(MalA)], P[(AMSC₁₈)-*a*-(MalA)], and P[(AMSDMA)-*a*-(MalA)].

Monomer conversions for each of these control homopolymerizations were found to be 0% by GC-FID. Furthermore, GPC was utilized to identify if any higher molecular weight species had formed even at negligible monomer conversions. MalA control (C2) showed no higher molecular weight species. AMS control (C1) did show a very low molecular weight species, M_n 330 g·mol⁻¹, which potentially could be the formation of dimer/trimer species, Figure S4. Finally, the GPC measurement of AMSC₆ control (C3) does show a higher molecular weight species with an M_n of 450 g·mol⁻¹ and dispersity of 1.02. However, this species is only 2.7% of the total integration area when integrated with the AMSC₆ distribution; M_n 220 g·mol⁻¹ and dispersity of 1.01. Therefore, this specie is expected to be either a dimer of AMSC₆ or potentially an AMSC₆ that has been initiated by a cyanoisopropyl radical and unable to propagate further. AMSC₁₈ control (C4) showed similar results to that of AMSC₆, a low molecular weight species has formed, M_n 1200 g·mol⁻¹ with a dispersity of 1.02, however this species is only 3% of the total integration when the AMSC₁₈ distribution is also measured; M_n 570 g·mol⁻¹ and dispersity of 1.01.

Based on these control polymerizations, we are confident that none of these monomers significantly homopolymerize under free radical polymerization conditions. Moreover, AMS and MalA were copolymerized at a variety of monomer to initiator ratios. This would determine if initiator concentration has an effect on final molecular weight and monomer conversions.

As expected, increasing the ratio of monomer to initiator also increased the M_n of P[(AMS)-*a*-(MalA)] copolymers, had no significant effect on the dispersity obtained (1.80-1.83), and the monomer conversions remained consistently above 70%, Table 1 (P1a, P1b, and P1c).

Table 1 Characterization for the free radical copolymerizations of functionalized AMS monomers and MalA.

Sample	M ¹	[M ¹]:[MalA]:[AMSD]:[AIBN]	[AIBN] (mmol)	M ¹ Conversion (%) ^a	MalA Conversion (%) ^a	M _{n, GPC} (g·mol ⁻¹) ^β	Đ ^β
C1	AMS	25:0:0:1	0.31	0	-	330	1.15
C2	-	0:25:0:1	0.31	-	0	-	-
C3	AMSC ₆	25:0:0:1	0.033	0	-	450	1.02
C4	AMSC ₁₈	25:0:0:1	0.021	0	-	1200	1.02
P1a	AMS	10:10:0:1	0.767	74	86	6500	1.81
P1b	AMS	25:25:0:1	0.311	76	83	10700	1.83
P1c	AMS	50:50:0:1	0.152	78	84	14500	1.80
P2a	AMSC ₆	10:10:0:1	0.083	95	91	8700	1.81
P2b	AMSC ₆	25:25:0:1	0.033	92	93	10400	1.90
P2c	AMSC ₆	50:50:0:1	0.016	81	85	17200	1.89
P3a	AMSC ₁₈	5:5:0:1	0.10	72	74	4000	1.70
P3b	AMSC ₁₈	15:15:0:1	0.035	74	76	6000	1.84
P3c	AMSC ₁₈	25:25:0:1	0.021	72	77	7500	1.91
P3d	AMSC ₁₈	25:25:1:1	0.021	72	76	7000	3.30
P3e	AMSC ₁₈	25:25:5:1	0.021	72	73	3300	2.00
P4	AMSDMA	25:25:0:1	0.056	0	0	-	-

^a Calculated using GC-FID. ^β THF eluent, PS calibration

GPC chromatograms of these three copolymers depict slightly asymmetrical peaks, Figure 2. This may be due to the nature of free radical polymerization, which is known to undergo high rates of termination and yield polymers with high dispersity. However, it is also possible that the MalA repeat unit interacts with the GPC column packing material (styrene-divinylbenzene) by adsorbing to the surface of said packing material, which causes a delay in the polymer elution and as a result reduces the calculated M_n. This behavior may also be the reason of the tailing observed on the GPC traces.³² Furthermore, MalA repeat units are easily hydrolyzed to the corresponding dicarboxylic acid, maleic acid (MalAc), which is known to interact even more strongly with the GPC column material.³² Therefore, all precipitated polymer samples were well dried before measuring to ensure as much of the copolymer as possible has the desired ring closed structure.

As stated earlier, AMSC₆ was primarily synthesized to determine if the resulting urea linkage formed after reacting TMI with hexylamine would result in any negative complications, namely the decarboxylation or homopolymerization of MalA, during the copolymerization with MalA. Free radical copolymerization of AMSC₆ and MalA was performed under the same conditions shown earlier to be effective for AMS and MalA, Scheme 2. Once again the monomer to initiator was varied to determine if this would have any implications on the final polymer molecular weight as well as monomer conversions. Copolymerization of AMSC₆ and MalA was found to be possible. Similar trends were observed to what was obtained for the AMS and MalA copolymerization. Increasing the monomer to initiator ratio leads to a higher M_n whereas polymer dispersity remains consistently around 1.81 to 1.90, Table 1 (P2a, P2b, and P2c). However, increasing the

concentration of initiator in this system lead to a higher overall monomer conversion compared to AMS and MalA where conversions which were largely unaffected by the [M]/[I] ratios attempted. This might potentially become an issue if higher molecular weight copolymers were desired. GPC chromatograms show that different molecular weight copolymers are synthesizable and the traces are reasonably symmetrical with some low molecular weight tailing, Figure 2.

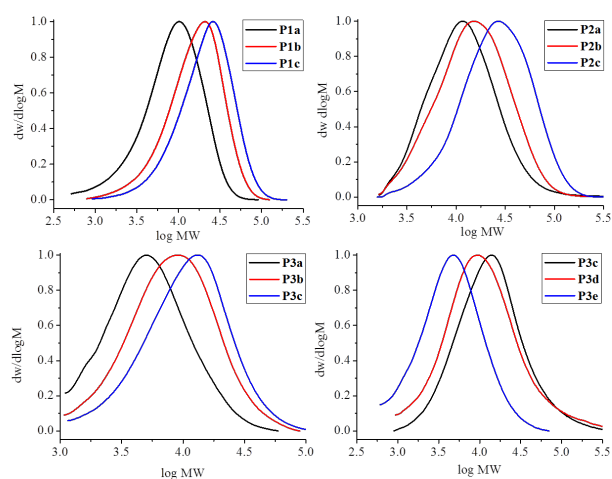


Figure 2 GPC traces of P[(AMS)-*a*-(MalA)] (top left), P[(AMSC₆)-*a*-(MalA)] (top right), P[(AMSC₁₈)-*a*-(MalA)] (bottom left), and P[(AMSC₁₈)-*a*-(MalA)] prepared in the presence of AMSD (bottom right).

Furthermore, MALDI-TOF MS has been utilized to confirm the alternating nature of P[(AMSC₆)-*a*-(MaLA)] copolymers as it provides much more in depth analysis on the micro structure of polymers.³³⁻³⁴ As these copolymers are alternating the MALDI-TOF spectrum is expected to show a single distribution, which has peaks separated by the combined mass of AMSC₆ and MaLA (400.3 Da). The repeat unit masses are combined as there should never be homopolymerization of either monomer and therefore a difference of 302.2 or 98.0 Da, for AMSC₆ and MaLA, respectively, should not be observed. This expectation is observed on the MALDI-TOF spectrum, Figure 3. However, two significant distributions are observed, these two distributions are caused by different mechanisms of termination throughout the free radical copolymerization. The most intense distribution has expected masses that corresponded to copolymers that are both initiated and terminated by cyanoisopropyl radicals generated from AIBN decomposition. The second most intense distribution is also initiated by cyanoisopropyl radicals but has expected masses that correspond to copolymers terminated by disproportionation. Furthermore, on examining the masses of these distributions in conjunction with theoretical masses, only copolymers where AMSC₆ is both the first and last monomer in the copolymer chain exist. Furthermore, MALDI-TOF MS also reveals the presence of copolymers, which contain one ring opened MaLA repeat unit to a MalAc repeat unit, + 18.0 Da. As well as a MaLA repeat unit opened by methanol to the corresponding half ester (MalMe), + 32.0 Da, this presumably occurred during purification as the copolymer was precipitated into methanol. These side reactions could be suppressed by increasing the time spent drying the copolymer as well as precipitating into isopropanol instead of methanol.⁶ Furthermore, upon close inspection of the MALDI-TOF spectrum there is evidence of one distribution, which is still separated by 302.2 Da, (Figure 3 peaks (1) and (6)) that can only occur after homopolymerisation of AMSC₆. This distribution contains 2 fewer MaLA repeat units than AMSC₆ and therefore AMSC₆ has likely homopolymerised once to create this distribution. There is one final side product which shows a separation of 56.2 Da from the main distributions. This side product has not been formally identified yet but is not caused by mis-insertions of monomer units so the alternating structure is unaffected. This is good evidence that the urea linkage found on AMSC₆ is having no detrimental effects on the MaLA throughout copolymerization, as such it is expected a urea linkage on future AMS monomers will also have no negative effects on MaLA during free radical copolymerization.

Following the successful copolymerization of AMSC₆ and MaLA, copolymerization of AMSC₁₈ and MaLA was attempted to synthesize an alternating copolymer bearing longer alkyl grafts than previously synthesized. Reaction conditions utilized were the same as those found to be effective for the free radical copolymerization of AMS/AMSC₆ and MaLA, Scheme 2. Free radical copolymerization of AMSC₁₈ with MaLA was successful and continued to show the same trends observed for AMS and MaLA copolymerization. Lowering the monomer to initiator

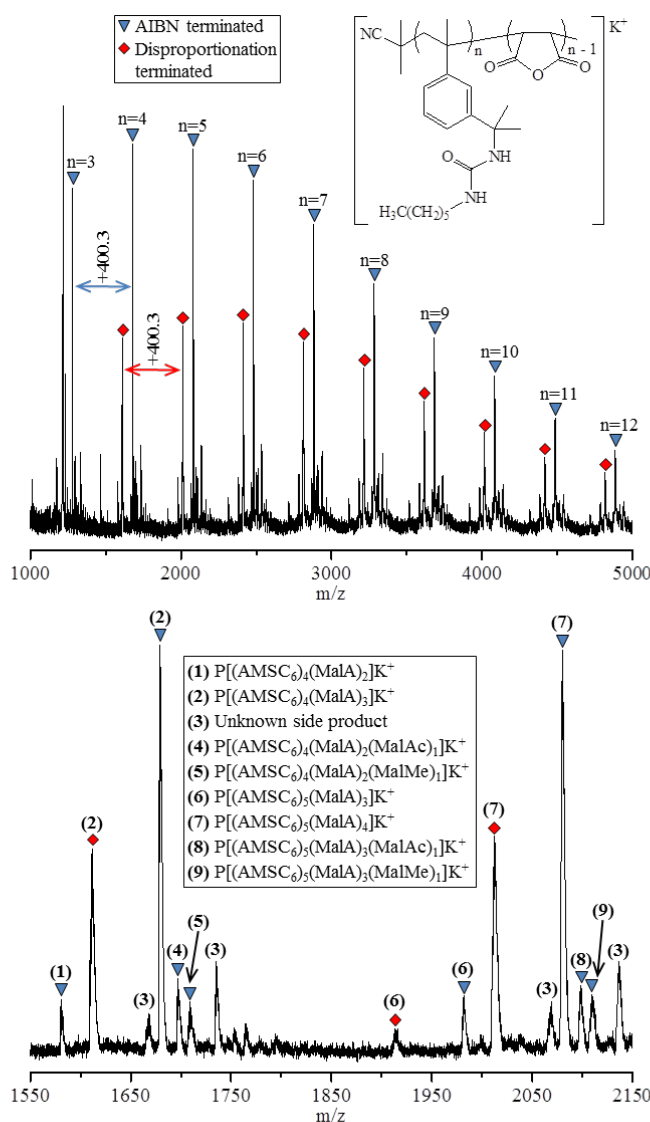


Figure 3 MALDI-TOF spectrum of P[(AMSC₆)-*a*-(MaLA)] (sample **P2a**) (top) and zoomed in region between 1550 and 2150 Da (bottom).

ratio led to a decrease in M_n and monomer conversions remained consistent for all three initiator concentrations tested, ~75 %, Table 1 (**P3a**, **P3b**, and **P3c**). Polymer dispersity values slightly decrease as the initiator concentration is increased. However, this is an issue by determining the molecular weight averages by GPC as the monomer (AMSC₁₈) and the copolymer (P[(AMSC₁₈)-*a*-(MaLA)]) begin to coelute when the copolymer is of sufficiently low molecular weight. As such this issue is most apparent for **P3a** and can be seen on the GPC chromatograms by the trace not returning to the base line at 3.0 log MW, Figure 2. Furthermore, removal of AMSC₁₈ from the final copolymer proved to be very challenging and could not be

achieved by precipitation without removing a significant portion of the lower molecular weight P[(AMSC₁₈)-*a*-(MalA)]. Therefore, only MalA was successfully removed from P[(AMSC₁₈)-*a*-(MalA)] samples.

MALDI-TOF MS was utilized to confirm the alternating nature of the synthesized P[(AMSC₁₈)-*a*-(MalA)] copolymers. Similar characteristics to the P[(AMSC₆)-*a*-(MalA)] copolymers are observed. Alternating behavior is again confirmed by the distributions showing a mass difference between repeat units that is the combined mass of AMSC₁₈ and MalA, 568.5 Da. Therefore, confirming no homopolymerization of AMSC₁₈ or MalA occurred throughout the copolymerization. There is again two dominant distributions; the more intense distribution corresponding to copolymers initiated and terminated by cyanoisopropyl radicals and the other distribution corresponding to copolymers terminated by disproportionation, Figure 4. There is again an evidence of some MalA repeat units being ring opened to MalAc repeat units by water. There is also evidence of AMSC₁₈ homopolymerisation. One distribution which is still separated by 568.5 Da (Figure 4 peaks (1) and (6)) can only occur after homopolymerisation of AMSC₁₈. This distribution contains 2 fewer MalA repeat units than AMSC₁₈ and therefore AMSC₁₈ has likely homopolymerised once to create this distribution. Furthermore, the unknown side product that appears + 56.2 Da from the main distributions is also present in this sample. This clearly indicates that the unknown side product results from end group rather than monomer structure. Comparing theoretical masses with the measured masses shows that all observable copolymer chains start and terminate with an AMSC₁₈ monomer unit.

Monomer to initiator concentration was capable of influencing the final molecular weight of P[(AMSC₁₈)-*a*-(MalA)] synthesized. However, large quantities of AIBN, 5.3 wt%, were required to achieve the lowest molecular weight copolymer synthesized (**P3a**). Large quantities of AIBN may be undesirable if P[(AMSC₁₈)-*a*-(MalA)] synthesis is scaled up. This is because free radical initiators such as AIBN are explosive compounds and heating large quantities during polymerization can lead to excessive nitrogen gas generation and thermal runaway. Therefore, chain transfer was considered as a means of decreasing the molecular weight by adding a chain transfer agent (CTA) rather than using higher concentrations of initiator. Various thiols and halogens were considered as possible CTAs, however the final compound selected was α -methyl styrene dimer (AMSD) as this has been previously utilized as a CTA for AMS/MalA copolymerisations.³⁵ AMSD has been shown to be a powerful CTA with a mechanism of chain transfer based on a reversible addition fragmentation chain transfer, which has been capable of displaying living polymerisations.^{36,37} Therefore, AMSD was added as a CTA to the free radical copolymerization of AMSC₁₈ and MalA to investigate if any reduction in molecular weight could be achieved.

AMSD was capable of reducing the M_n of final P[(AMSC₁₈)-*a*-(MalA)] copolymer obtained, Table 1 (**P3c**, **P3d**, and **P3e**).

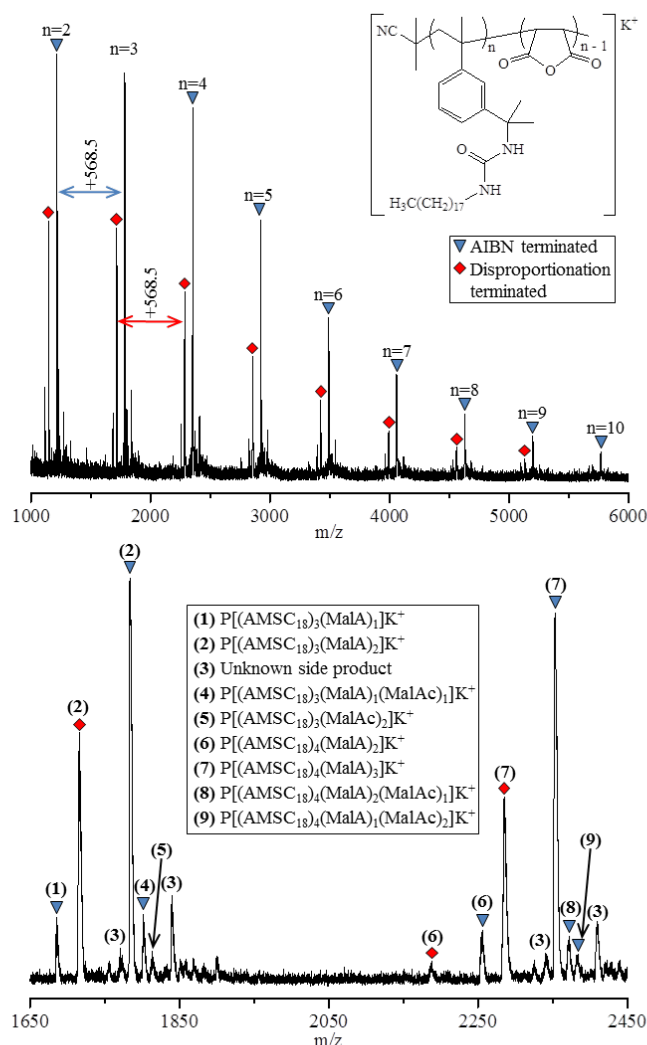


Figure 4 MALDI-TOF spectrum of P[(AMSC₁₈)-*a*-(MalA)] (**P3a**) (top) and zoomed in region between 1650 and 2450 Da (bottom).

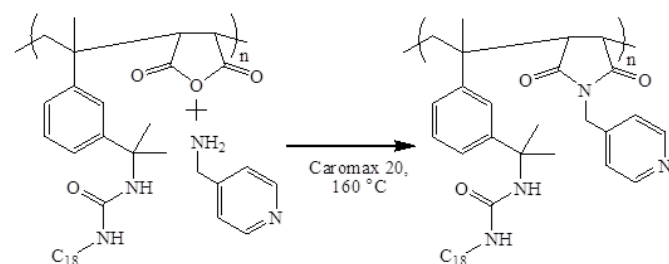
Five equivalents of AMSD relative to initiator reduced the molecular weight by over half whilst maintaining monomer conversions above 70%. As a result lower molecular weight P[(AMSC₁₈)-*a*-(MalA)] can now be synthesized by addition of AMSD rather than larger quantities of AIBN, reducing the wt % required from 5.3% to 1.5%, an attractive quality for scaling up the copolymerization.

The final copolymerization attempted was between AMSDMA and MalA to synthesize an alternating copolymer with a pendant tertiary amine on the AMS repeat unit. However, despite utilizing conditions found to be effective for the three previous AMS monomers, AMSDMA-MalA copolymerization was unsuccessful. The reaction mixture quickly turned brown after heating to 80 °C and after four hours at this temperature the mixture was completely opaque with much black precipitate

that was insoluble in all solvents tested. It is expected that the tertiary amine on AMSDMA both decarboxylated and homopolymerized MalA. This demonstrates a potential drawback of this synthetic methodology as tertiary amine species may not be introduced before copolymerization with MalA.

Post polymerization modification of alternating copolymers

Post-polymerization modification techniques have an important role in the synthesis of functional polymers where the direct polymerization of the functional monomer is not straightforward.³⁸⁻⁴² Following the successful synthesis of P[(AMSC₁₈)-*a*-(MalA)], an alternating copolymer of linear alkyl grafts and reactive anhydride moieties, which can be synthesized at variable molecular weights utilizing AMSD as a CTA. The final stage of the synthesis is to functionalize the maleic anhydride repeat units with a primary amine at high temperature to form cyclic imides bearing a chosen functionality. In this case a primary amine bearing a pyridine was selected, 4-(aminomethyl)pyridine, which after coupling with MalA repeat units gives the new repeat unit, *N*-(4-methylpyridine)maleimide (PyMI), Scheme 3.



Scheme 3 Imidization of P[(AMSC₁₈)-*a*-(MalA)] with 4-(aminomethyl)pyridine to synthesize P[(AMSC₁₈)-*a*-(PyMI)].

Imidization of cyclic anhydrides to cyclic imides is a two-step reaction. Firstly the primary amine ring opens the cyclic anhydride to form a new amide bond and a carboxylic acid. Given sufficiently high temperature, long enough reaction times and continual removal of water, the carboxylic acid and amide bond will cyclize with loss of water to form a cyclic imide retaining the functionality present on the original primary amine. Imidization of P[(AMSC₁₈)-*a*-(MalA)] was shown to be successful by FT-IR as there was loss of cyclic anhydride peaks at 1858 cm⁻¹ and 1777 cm⁻¹, which were replaced by new peaks at 1771 cm⁻¹ and 1698 cm⁻¹, Figure 5. ¹H-NMR also confirms imidization as there are now two broad signals centered at 7.55 ppm and 8.43 ppm corresponding to the new pyridine functionality. Furthermore, tertiary amines have been shown to degrade P(SMaLA) copolymers, therefore GPC was used to that P[(AMSC₁₈)-*a*-(MalA)] was not degraded throughout the reaction.

Following the functionalization of P[(AMSC₁₈)-*a*-(MalA)] the resulting product was rendered insoluble in THF and as such

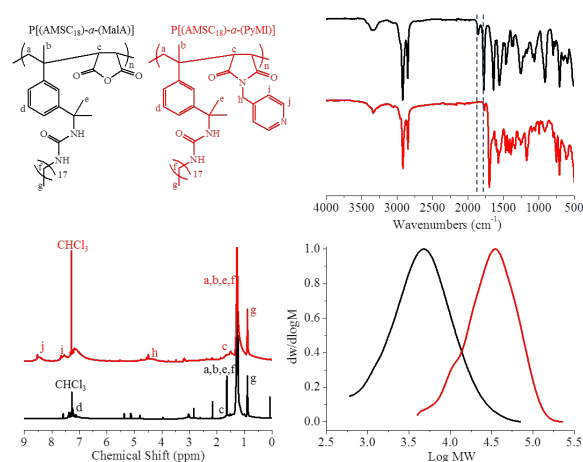


Figure 5 Chemical structures (top left), FT-IR spectra (top right) ¹H-NMR spectra (bottom left) and GPC traces (bottom right) of P[(AMSC₁₈)-*a*-(MalA)] (black) and P[(AMSC₁₈)-*a*-(PyMI)] (red).

had to be measured by GPC eluted with DMF containing 5 mM ammonium tetrafluoroborate. A very significant increase in M_n was measured from 3300 g·mol⁻¹ to 14300 g·mol⁻¹ following imidization. An increase in molecular weight was expected as mass was added to every maleic anhydride repeat unit, however this alone may not explain the large mass increase. It was discussed earlier that P(SMaLA) copolymers are known to adsorb to GPC columns when neat THF is used as an eluent; this increases the copolymer retention time and thus causes underestimation in the molecular weight. Therefore, it is now possible that the functionalized copolymer P[(AMSC₁₈)-*a*-(PyMI)] will not adsorb to the GPC column as strongly thus, lowering the copolymer retention time and increasing the calculated molecular weight.

Conclusions

Coupling TMI and primary amines has been shown to be a simple and efficient method for synthesizing AMS monomers functionalized with linear alkyl chains, hexyl and octadecyl, as well as a dimethylamino. The alkyl group functionalized monomers were than successfully copolymerized with MalA by free radical copolymerization to synthesize alternating copolymers. Alternating structure of the copolymers was supported by control reactions of the individual monomers (AMS, MalA, AMSC₆ and AMSC₁₈), which do not homopolymerize. Furthermore, MALDI-TOF MS characterization also demonstrates how the distributions repeat units are separated by mass that corresponds to the combined mass of AMS monomers and MalA, indicating a highly-ordered alternating structure. Moreover, MALDI-TOF demonstrates that all copolymer chains begin and terminate with AMS monomers. Alternating copolymer molecular weight could be

influenced by the initiator concentration. Higher concentrations of initiator provided lower molecular weight copolymers, whilst retaining high monomer conversions > 70% and dispersity remained consistent around 1.80 to 2.00. Furthermore, no adverse effects were observed by the presence of a urea linkage on the MalA throughout copolymerization, namely homopolymerization or decarboxylation of the MalA.

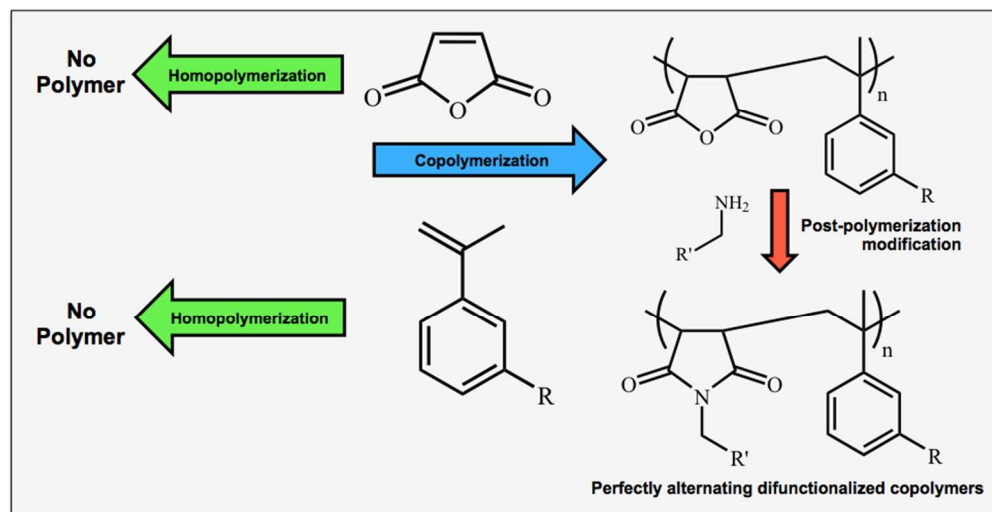
Finally, synthesized alternating copolymers were functionalized by imidization of the MalA repeat unit by reacting at 160 °C with 4-(aminomethyl)pyridine to synthesize P[(AMSC₁₈)-*a*-(PyMI)]. Synthesizing a copolymer that bears alternating linear alkyl grafts and pyridine moieties. This reaction allows the incorporation of a desired functionality by simply changing the primary amine utilized. Therefore, this work demonstrates a new class of alternating copolymers that are capable of being functionalized on both the AMS and MalA repeat unit that allows for great versatility.

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