

Supporting Information:

Synthesis of Polymers

Section 1: Synthesis for all Polymers Excluding MAC Et and MAST

Introduction

Since the crystalline nature of n-alkanes dominates the behavior or wax crystallization in crude oils,^{1, 2} polymers were chosen that provide various types of crystalline domains. This was accomplished by choice of polymer architecture and by choice of the size (or average size) of the crystalline domains. The poly(ethylene butene) and ethylene-vinyl acetate co-polymers (designated PEB and EVA, respectively) were random co-polymers that introduced crystalline domains along the backbone (see Figure 1). The frequency of branches along the backbone indicate the average degree of crystallinity. The maleic anhydride co-polymers (MAC) introduced crystallinity *via* alkyl side chains appended to the backbone. The degree of crystallinity was characterized by the length of the alkyl appendage. **Figure 2** through **Figure 5** show all structure for the remaining polymers.

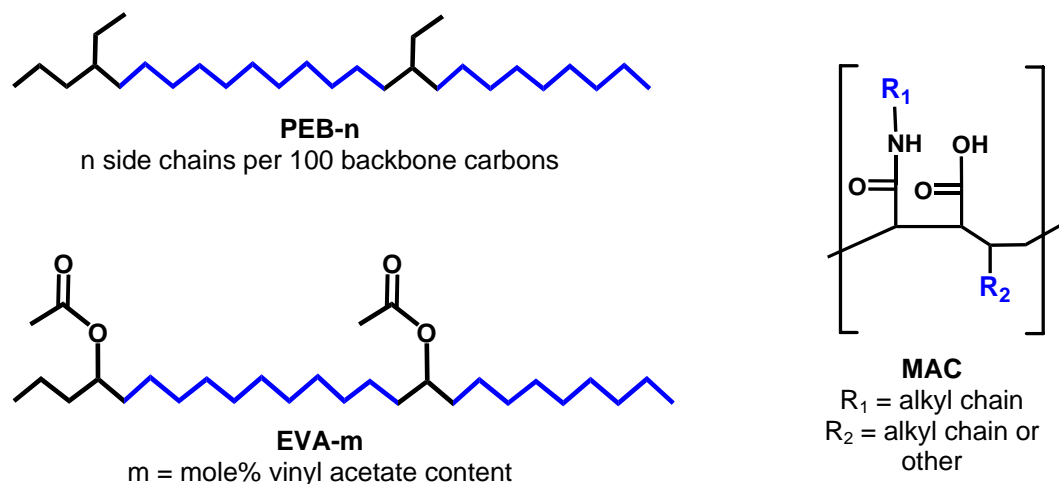


Figure 1 Example molecules showing the structural features of poly(ethylene butene) (PEB), an ethylene vinyl acetate co-polymer (EVA) and a maleic anhydride co-polymer (MAC). Entire molecule and repeating units not shown. Sufficiently long ethylene segments can be incorporated to provide crystallinity (blue portions).

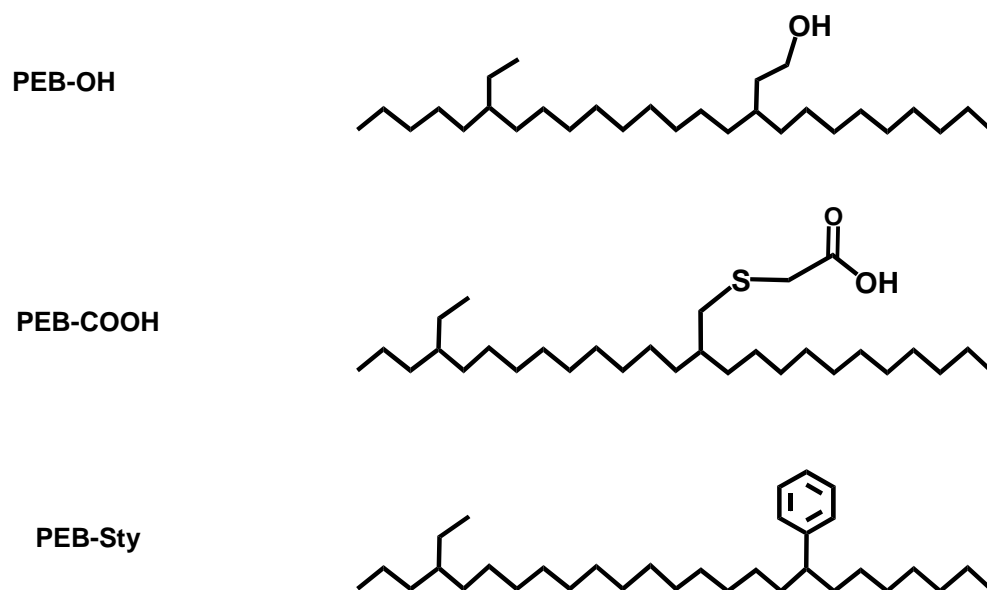


Figure 2 PEB polymers with incorporated hydroxyl (PEB-OH), carboxylic acid (PEB-COOH) and styrene (PEB-Sty).

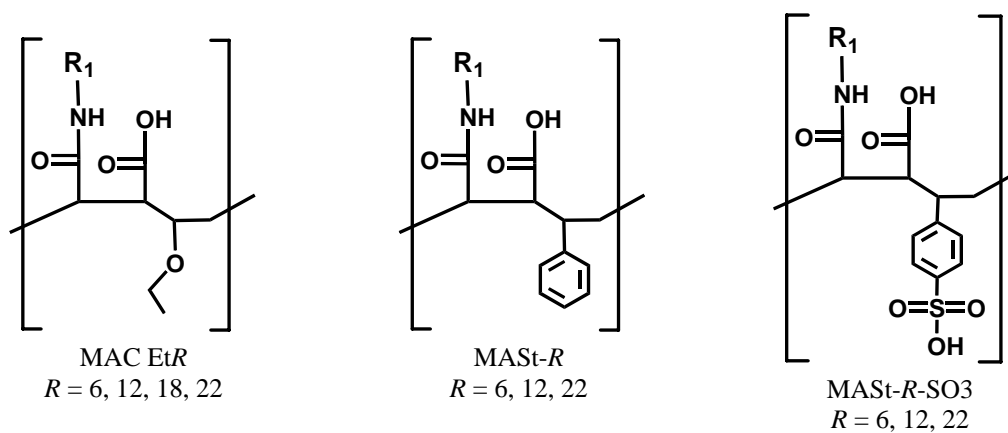


Figure 3 Structure of maleic anhydride co-polymers with co-monomers of vinyl ethyl ether (MAC Et), styrene (MASt) and styrene which was subsequently modified with sulfonic acid. (MASt-R-SO₃). The length of attached alkyl chains is indicated by *R*.

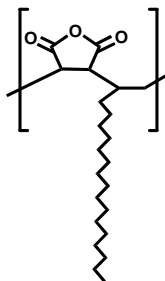


Figure 4 Co-polymer of maleic anhydride and octadecene used by Chang and Fogler to disperse asphaltenes.³

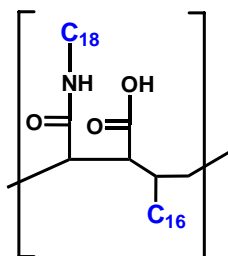


Figure 5 MAC16-18

Synthesis and Characterization Information

PEB polymers

Poly(ethylene butene) (PEB) was formed by anionic polymerization of butadiene by Dr. Douglas Adamson of the Princeton Institute for the Science and Technology of Materials (PRISM) at Princeton University. *Tert*-butyllithium was used as an initiator and triethylamine was used to control the ratio of 1,2 addition to 1,4 addition. Hydrogenation removed the double bonds, producing a polyethylene chain with ethyl side branches where 1,2 addition occurred. Hydrogenation was typically performed at 400psi H₂ at 80°C for at least 48 hours using homogeneous catalyst formed from the complexation of 1.02g Ni(II)ethylhexanoate with 10mL of 1 molar triethylaluminum in

heptane. In the case of PEB-7.2 a heterogeneous palladium catalyst was used instead: 5% reduced Pd on calcium carbonate powder (Alfa Aesar No.11723). Butylated hydroxytoluene (BHT or 2,6-Di-*tert*-butyl-4-methylphenol, Aldrich No. D4,740-4) was used with this catalyst at ratio 100:1 (polymer:catalyst) to prevent radical degradation.

The degree of side branching was characterized by ¹H-NMR of the unhydrogenated polymer, showing an averages of 7.2 side branches per 100 backbone carbons. The hydrogenated version of this polymer is thus labeled PEB-7.2. The molecular weight as determined by gel permeation chromatography (GPC) are listed in Table 1, which summarized key characteristics of all the PEB polymers.

Polymer	n, total ^a side chains per 100 backbone C	Functional side chains per 100 backbone C	Mn	Mw/Mn
PEB-7.2	7.2	-	5.32	1.07
PEB-OH ^{b,f}	8.0	2.7	21.7	1.13
PEB-COOH “1” ^{c,f}	7.2	0.05	6.70k	1.48
PEB-COOH “5” ^{c,f}	7.2	1.3	6.25	1.61
PEB-Sty ^{d,f}	8	4.5	12.4	1.08

Table 1 Characterization data for PEB polymers

NOTES: ^a Total side chains includes all other functional side-chains that disrupt crystallinity of the polymer backbone. ^b Before hydroxylation. ^c After reaction with thiol glycolic acid, before hydrogenation. ^d Before sulfonation. ^e This reported value is Mw, not Mn. ^f Mn for these polymers are relative to a polystyrene standard in GPC.

PEB-OH

The polybutadiene was synthesized via anionic polymerization to provide a controlled ratio of 1,2 and 1,4 addition, as described above. Hydroxyl groups were added according to the method of Chung *et al.*⁴ Side chain double bonds were reacted with 9-BBN in THF, using a molar ratio to react roughly half of side chains. Subsequent addition of NaOH and then H₂O₂ replaced the boron complex attached to the side chain with a hydroxyl group. The polymer was distilled in methanol to remove the boric acid, precipitated in water, redissolved in isopropanol and then washed in 1M KOH to neutralize any remaining boric acid. The isolated polymer was hydrogenated in toluene using the homogeneous nickel-aluminum complexation catalyst described above. GPC of the unhydroxylated polybutadiene showed a Mn = 21.7 and Mw/Mn = 1.13, relative to polystyrene standards. NMR analysis of the original polybutadiene showed the polymer to have an average of 8.0 side chains per 100 backbone carbons. NMR analysis of the final hydrogenated polymer showed that 2.7 of the 8.0 side chains were had hydroxyl groups. The polymer was found to be very insoluble in non-polar alkane solvents due to its high level of functionalization.

PEB-COOH

The polybutadiene used for the PEB-7.2 was used for synthesis of the PEB with carboxylic acid chains. Thiol glycolic acid was used to attach the sulfur to the side chain double bond according to the method of Justynaska and Schlaad⁵ with the goal of two functionalization levels of 1 and 5 COOH groups per chain. They were thus designated PEB-COOH 1 and PEB-COOH 5. Addition of thiol glycolic acid was performed by Devang Amin under the direction of Dr. Douglas Adamson. The modified polymer was hydrogenated in heptane using the same nickel-aluminum catalyst previously described.

^1H NMR of the unhydrogenated polymers showed an average of 0.20 COOH and 3.15 COOH per chain, corresponding to 0.05 and 1.3 COOH per 100 backbone carbons, respectively. Molecular weights and polydispersities as measured by GPC were increased relative to the parent polybutadiene used for PEB-7.2 (Table 1, above), indicating some cross-linking occurred during the thiol reaction. The presence of carboxylic acid groups was confirmed by Fourier transform infrared spectroscopy (FTIR) for both polymers. Though NMR for the PEB-COOH 1 suggest that only one in five chains has a carboxylic acid, the polarity of this polymer still appeared significant in that the polymer formed very stable water-heptane emulsions during the washing process subsequent to the hydrogenation process. ^1H NMR of the hydrogenated PEB-COOH 5 showed that roughly half the double bonds remained after hydrogenation. The polymer was tested without further hydrogenation.

PEB-Sty

PEB-Sty was synthesized by polymerization of butadiene with styrene. The synthesis of poly(butadiene-*r*-styrene) was performed by Dr. Douglas Adamson at Princeton University using standard high vacuum techniques.⁶ Potassium *tert*-butoxide was used as a promoter for the random incorporation of monomers in the growing chain. A typical procedure starts by adding approximately 0.24 moles of potassium *tert*-butoxide to a reaction vessel equipped with a magnetic stir bar and with reagents contained by break-seals. These reagents were *sec*-butyllithium, methanol, styrene and butadiene, which were all in ampules attached to the reactor. The reaction vessel was then evacuated on a vacuum manifold. To this was then added by vacuum distillation approximately 300 ml of cyclohexane containing 10% benzene dried over *sec*-butyllithium with diphenyl ethylene as an indicator. The reactor was then removed from the line and 8.0 mmoles of

sec-butyllithium added by way of a break-seal. Next was added by way of a break-seal 17.8 ml of styrene and 91.4 ml of butadiene. This was warmed to 40 °C and stirred for 5 days. It was then quenched with degassed methanol. The polymer was then filtered into a four liter beaker, 20 ml of acetone added. Filtration removed the Li salts that are formed by the quenching (as well as removing pieces of broken glass from the break-seals). The polymer passed through the filter. To this were added 3 liters of methanol to precipitate the polymer, followed by drying under vacuum. The polymer was hydrogenated with the homogenous nickel-aluminum catalyst described above to preserve the aromatic rings. Due to the general performance of polar modified PEBs, additional synthesis was not pursued. GPC of the unmodified polybutadiene showed a $M_n = 12.4$ and $M_w/M_n = 1.08$, relative to polystyrene standards. ^1H NMR of the unhydrogenated polymer showed that there were there were 3.5 ethyl side chains and 4.5 styrenes per 100 backbone carbons, on average.

EVA

EVA co-polymers were obtained from Infiniem, Ltd. Due to the polymerization process the vinyl acetate distribution should be random and the average length of the crystalline segments controlled by the vinyl acetate content of the co-polymer. The vinyl acetate contents of 9%, 12% and 15% (molar) were used and labeled EVA-9, EVA-12, EVA-15, respectively. Small angle neutron scattering on dilute solutions with these polymers showed that portions of these polymers aggregated over the temperature ranges of interest to our study (0-90°C).⁷ This was attributed to the presence of some very long crystallizable ethylene segments that resulted from the polymerization process. Further discussion is provided by Ashbaugh *et al.*⁷

MAC Et22, MAC Et18, MAC Et12

Two sets of maleic anhydride co-polymers were synthesized by Reversible Addition-Fragmentation Transfer polymerization (RAFT) of maleic anhydride with either ethyl vinyl ether or with styrene. Such polymerization provides a backbone with strictly alternating monomers to which were appended either C22 or C12 alkyl tails via amidation with either docosanyl amine or dodecyl amine, respectively. The synthesis was performed at Halliburton in Duncan, Oklahoma, by Dr. Robert Kriegel and Dr. Rajesh Saini. Details of the synthesis are provided in Section 2. Table 2 below lists the molecular weights, as determined by GPC relative to polystyrene standards, as well as the fraction of carboxylic acids from the maleic anhydride to which alkyl chains have been attached, as determined by ^1H NMR.

Polymer	Mw	Mw/Mn	Percent carboxylic acids with alkyl chain
MAC Et22	146k	1.26	45%
MAC Et18	6.26k	1.46	73%
MAC Et12	29.8k	1.87	51%
MAC Et6	31.6k	1.68	<i>nt</i>
MASt-22	34.9k	1.77	41%
MASt-12	390	2.69	57%
MASt-22-SO ₃	109k	2.42	41%
MASt-12-SO ₃	4.31k	1.53	57%

Table 2 Molecular Weight and Polydispersity for polymers, as determined by GPC relative to polystyrene standards. (*nt* = not tested)

Sulfonation of MAST

Styrene groups were added to MAST-22 and MAST-12 using acetyl sulfate in dichloromethane according the method of Carvalho and Curvelo.⁸ Molecular weights of the final polymers are provided in Table 2. The MAST-12-SO₃ and MAST-22-SO₃ contained 6.7% and 10% sulfonate with respect to styrene according to elemental analysis.

MAC16-18

Free radical polymerization was used to prepare a co-polymer of maleic anhydride and octadecene. Subsequent modification with an octadecyl amine opened the anhydride to form a C18 amide.⁹ Thus, the resulting polymer contained C16 and C18 alkyl appendages extending from the backbone. The molecular weight (M_w) was 12 300 with a polydispersity index of 1.4, as determined by GPC. ¹H NMR shows that 23% of the carboxylic acids from the maleic anhydride have C18 appendages. Synthesis was performed by Dr. Xuhong Guo while at Princeton University.

References

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Section 2: Synthesis and Subsequent Modification Maleic Anhydride Co-polymerized with Styrene (MASt) and with Vinyl Ethyl Ether (MAC Et) via RAFT Polymerization

Experimental Section

Materials

Carbon disulfide was obtained from Aldrich Chemical Company and distilled from MgSO₄ prior to use. Diethyl ether and THF were of anhydrous grade from Aldrich Chemical Company. Mg⁰ was obtained from Aldrich as thin shavings that were washed three times with 0.05M HCl, rinsed with water and then acetone and dried under vacuum. Maleic anhydride was obtained from Fisher Baxter Scientific and recrystallized from dry benzene and vacuum dried prior to use. Bromobenzene, ethylvinyl ether, AIBN and LiAlH₄ were obtained from Aldrich Chemical Company and used as received. Behenamide was obtained from TCI America and used without further purification.

Instrumentation

NMR analyses (¹H and ¹³C) were performed using a Bruker Avance 300 MHz NMR. Gel Permeation Chromatography was performed by Halliburton Energy Services Analytical Group using Waters GPC pumps, Polymer Laboratories columns and a Wyatt Technologies DAWN multiangle laser light scattering detector. The mobile phase for GPC analysis was THF at a flow rate of 1 mL/min. Infrared spectra were obtained using a Nicolet 6700 FTIR with an ATR attachment.

Dithiobenzoic acid, 9355-09

To a mixture of Mg⁰ (3.41 g, 0.142 mol) in diethyl ether (90 mL), bromobenzene (22.18 g, 0.1420 mol) was added dropwise over a period of several hours under inert atmosphere. After the addition was complete, the mixture was heated at reflux for 4 additional hours and then cooled to ambient temperature. Carbon disulfide (25 mL) was added dropwise over 2 hours and the resulting mixture stirred for an additional 8 hours. The reaction was then quenched by the addition of water (200 mL) and the organic layer

removed. The aqueous layer was washed twice with diethyl ether (100 mL) and the aqueous layer then acidified with HCl (conc.). Dithiobenzoic acid was extracted from the aqueous layer by two washings with diethyl ether (100 mL) and ether washings were combined. The dithiobenzoic acid was then extracted from the organic phase with 10% NaOH (aq.) (250 mL). The aqueous extract was acidified with HCl(aq., conc.) and the dithiobenzoic acid again extracted with diethylether (150 mL). The ether layer was removed under reduced pressure and the residue dried under vacuum over night to give dithiobenzoic acid as dark red liquid. Yield: 12.25 g (56%) ^1H NMR (300 MHz, CDCl_3): δ 8.21 (d, $J=7$ Hz, 2H), 7.3-7.6 (m, 4 H), plus small amounts of biphenyl and other minor impurities. ^{13}C NMR (75 MHz, CDCl_3): δ 225.43, 143.31, 133.23, 128.63, 126.76 (additional signals from biphenyl and other minor impurities)

1-Phenylethyl benzodithioate, 9355-13ⁱ

A solution of CCl_4 (25 mL), dithiobenzoic acid (9.01 g, 58.4 mmol) and styrene (16.36 g, 157.1 mmol) was heated to reflux for several hours until TLC showed the complete consumption of dithiobenzoic acid (alumina, Pet. Ether (20-40 °C)). The solvent was removed under reduced pressure and the residue dried under high vacuum at ambient temperature overnight. The remaining residue was then subjected to column chromatography (alumina, neutral, Pet. ether (20-40 °C)) to give 1-phenylethyl benzodithioate as a dark red liquid. Yield: 10.11 g (67%) ^1H NMR (300 MHz, CDCl_3): δ 8.03 (d, $J=6.6$ Hz, 2H), 7.29-7.47 (m, 8H), 5.31 (q, $J=7.1$ Hz, 1H), 1.86 (d, $J=7.1$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 226.60, 144.84, 141.15, 132.18, 128.55, 128.16, 127.72, 127.58, 126.82, 50.13, 20.67. IR (Neat): 3059.6, 3027.7, 2966.9, 2923.6, 2862.8, 1590.0, 1491.7, 1444.4, 1227.5, 1042.3, 876.5, 762.7, 699.0 cm^{-1} .

Docosanylamine, 9355-29ⁱⁱ

A mixture of behenamide (80.08 g, 0.236 mol) in THF (500 mL) was gently warmed to effect complete dissolution of the solid. The mixture was cooled to 30 °C and a suspension of LiAlH_4 (15.26 g, 0.402 mol) in THF (100 mL) was added dropwise over the course of 1 hour. The mixture was stirred at 30 °C for 1 hour and then heated under reflux conditions for an additional 50 hours. The mixture was cooled to 0 °C and water (200 mL) added slowly with vigorous stirring. The mixture was allowed to stand for 24

hours to solids removed by filtration. The solid was then recrystallized from dodecane and vacuum dried at 100 °C to give docosaniline as a tan solid. Yield: 50.54g (65.7%)
¹H NMR (CDCl₃, 300 MHz): δ 2.73 (t, *J*=7.2 Hz, 2H), 1.25-1.50 (br, . ¹³C NMR (CDCl₃, 75 MHz): δ 42.03, 33.41, 31.93, 29.66, 29.49, 29.35, 26.90, 22.67, 14.05. IR (Neat): 2915.9, 2848.4, 1577.5, 1463.7, 719.3 cm⁻¹.

Poly(styrene-*alt*-maleic anhydride), 9355-15³ⁱⁱⁱ

A solution of styrene (30.98 g, 297.4 mmol), maleic anhydride (29.17 g, 297.4 mmol), AIBN (698 mg, 4.26 mmol) and *S*-(2-phenethyl) dithiobenzoic acid (2.19 g, 8.49 mmol) in THF (114.3 g) was degassed with Ar for 30 minutes in a Schlenk flask. The flask was stoppered tightly with a head of Ar and placed in a 60 °C oil bath for 11.75 h with samples taken at 4.5 and 9 h. At the conclusion of the reaction, the flask was cooled to ambient temperature and opened to the air. The polymer was precipitated by slowly pouring the read solution into 2 volumes of cold diethyl ether. The polymer was fully dispersed and removed by filtration and vacuum dried to give poly(styrene-*alt*-maleic anhydride) as a light pink polymer, 49.1 g, 78.7 % yield (conversion). ¹H NMR (300 MHz, CDCl₃/DMSO-*d*₆): δ 6.0-7.6 (br, 5 H), 2.8-3.8 (br, 3H), 1.6-2.8 (br, 2 H). ¹³C NMR (75 MHz, CDCl₃/DMSO-*d*₆): δ 170-174 (br, C=O), 126-128 (br, aromatic C), 48-52 (br), 30-35 (br).

Poly(ethyl vinyl ether-*alt*-maleic anhydride), 9355-19

A solution of ethylvinyl ether (25.46 g, 0.3531 mol), maleic anhydride (31.96 g, 0.3261 mol), AIBN (0.754 g, 4.54 mmol) and 1-phenylethyl benzodithioate (2.250 g, 8.71 mmol) in THF (115.8 g) was degassed with Ar for 30 minutes in a Schlenk flask. The flask was stoppered tightly with a head of Ar and placed in a 60 °C oil bath for 20 h with samples taken at 3 and 6 h. At the conclusion of the reaction, the flask was cooled to ambient temperature and opened to the air. The polymer was precipitated by slowly pouring the read solution into 2 volumes of cold diethyl ether. The polymer was fully dispersed and removed by filtration and vacuum dried to give poly(ethylvinyl ether-*alt*-maleic anhydride) as a light pink polymer, 47.71 g, 83 % yield (conversion).

Hexylamine modified 9355-15, 9355-16

A solution of **9355-15** (13.330 g) and hexylamine (6.683 g) in THF (130 mL) was heated at reflux for 28 h. The solution was cooled to ambient temperature and the solvent removed under reduced pressure and further vacuum dried over night. Yield 19.427 g (97%)

Dodecylamine Modified 9355-15, **9355-17**

A solution of **9355-15** (10.46 g) and dodecylamine (9.566 g) in THF (90 mL) was heated at reflux for 29 h. The solution was cooled to ambient temperature and the solvent removed under reduced pressure and further vacuum dried over night. Yield 19.624 g (98%)

Docosanylamine Modified 9355-15, **9355-34**

A solution of **9355-15** (9.71 g) and **9355-29** (15.65 g) in THF (100 mL) was heated at reflux for 22 h. The solution was cooled to ambient temperature and the solvent removed under reduced pressure and the solid further vacuum dried over night at 220 °F and 1.5 torr. Yield 18.22 g (72%)

Hexylamine modified 9355-19, **9355-20**

A solution of **9355-19** (12.52 g) and hexylamine (7.46 g) in THF (90 mL) was heated at reflux for 17 h. The solution was cooled to ambient temperature and the solvent removed under reduced pressure and further vacuum dried over night. Yield 19.14 g (96%)

Dodecylamine Modified **9355-19**, **9355-21**

A solution of **9355-19** (9.61 g) and dodecylamine (10.46 g) in THF (100 mL) was heated at reflux for 17 h. The solution was cooled to ambient temperature and the solvent removed under reduced pressure and further vacuum dried over night. Yield 18.57 g (93%)

Docosanylamine Modified 9355-19, **9355-35**

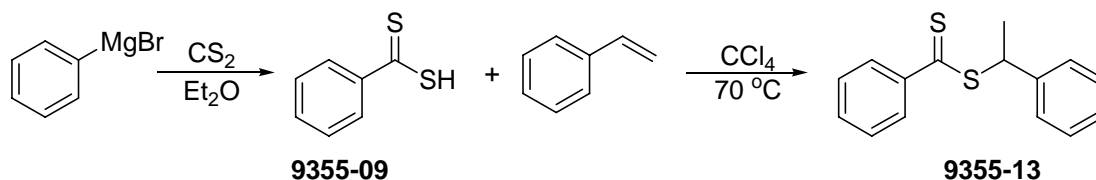
A solution of **9355-19** (8.77 g) and **9355-29** (17.27 g) in THF (100 mL) was heated at reflux for 21 h. The solution was cooled to ambient temperature and the solvent removed under reduced pressure and the solid further vacuum dried over night at 220 °F and 1.5 torr. Yield 20.19 g (77%)

Results and Discussion

Synthesis of RAFT agent, 9355-13.

The RAFT agent needed for this was obtained in two steps by treatment of the Grignard of bromobenzene with carbon disulfide to give the phenyldithiobenzoic acid. This was then treated with excess styrene in carbon tetrachloride to give the desired 1-phenylethyl benzodithioate (**9355-13**), Scheme 1.ⁱ

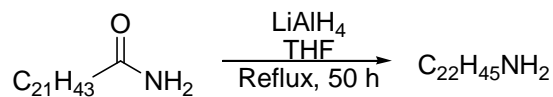
Scheme 1. Synthesis of Raft Agent, **9355-13**



Synthesis of Docosanylamine, 9355-29.

Due to the lack of commercial sources of pure docosanylamine ($C_{22}H_{45}NH_2$), the compound was prepared in the lab by the reduction of commercially available behenamide ($C_{21}H_{43}CONH_2$) by reduction with $LiAlH_4$ in THF. The separation of the amide from the amine was predicted to be difficult so the reaction was carried for 50 hours to ensure the complete reduction of the amide, Scheme 2. Characterization of the **9355-29** shows no indication of the presence of a carbonyl group by IR spectroscopy or ^{13}C NMR spectrometry.

Scheme2. Synthesis of Docosanylamine, **9355-29**.

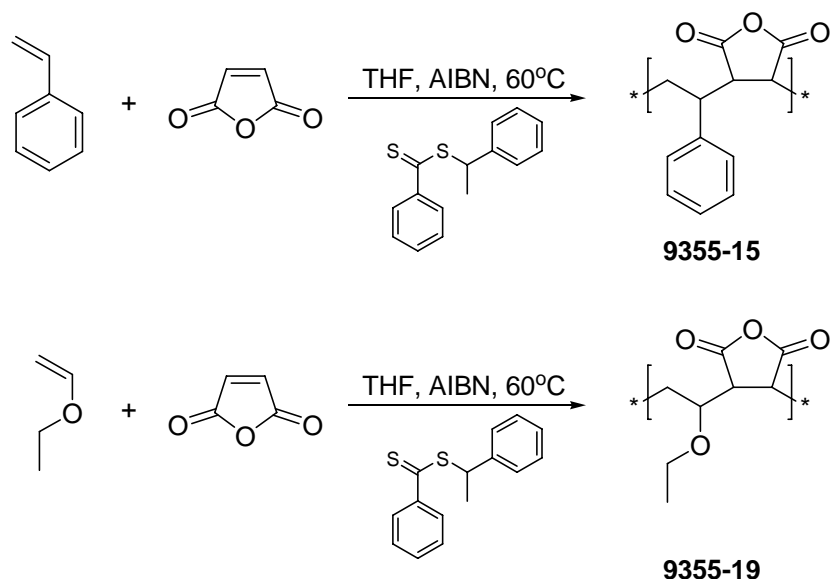


Synthesis of Alternating Copolymers, 9355-15 and 9355-19.

Copolymers of maleic anhydride and styrene (**9355-15**) and maleic anhydride and ethylvinyl ether (**9355-19**) were obtained by the RAFT copolymerization of either styrene

or ethylvinyl ether with maleic anhydride in THF with **9355-13** as the chain length control agent, Scheme 3. Previous experience demonstrated that in the absence of a control agent, the polymerization at 60 °C was complete after four hours. With the RAFT agent present, the rate of polymerization was significantly retarded, which is consistent with the mechanism of RAFT using the agent employed. The conditions employed used an initiator to RAFT agent ratio of 1:2 and a RAFT agent to monomer ratio of 70:1. This ratio was chosen to give a polymer chain of approximately 7000 Daltons at 100% conversion. The measured conversions were 78 and 83% respectively for **9355-15** and **9355-19**, so the M_n should theoretically approximate 5000 Daltons.

Scheme 3. Synthesis of Alternating Copolymers, **9355-15** and **9355-19**.

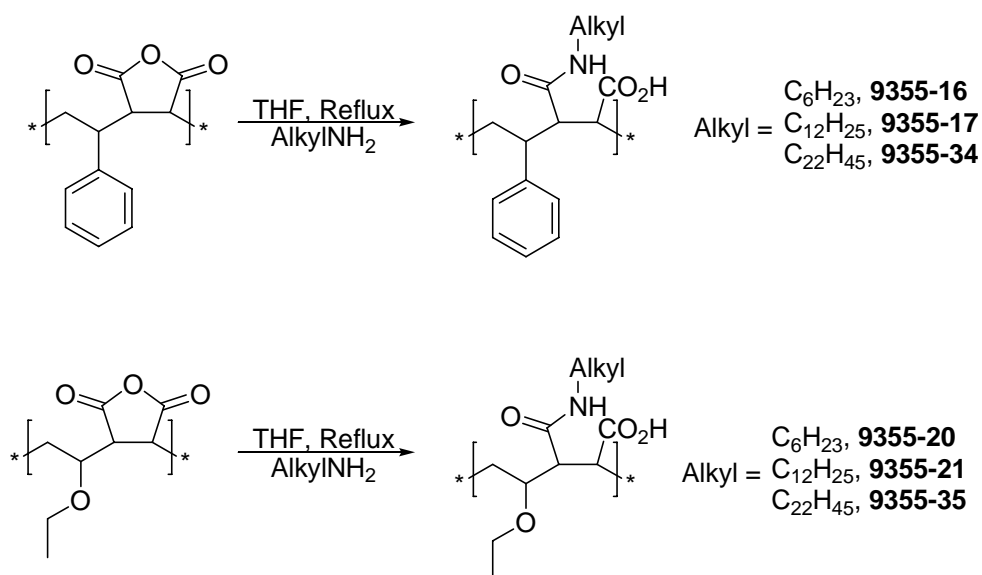


NMR spectra of the polymers show the expected broad peaks due to the polymeric nature of the materials, with the signals due to backbone protons and carbons being almost absent. More importantly, the IR spectra show signals due to the asymmetric and symmetric stretching of the anhydride rings at 1855 and 1776 cm^{-1} .

Modification of RAFT polymers with alkylamines (9355-16, 9355-17, 9355-34, 9355-20, 9355-21, 9355-35)ⁱⁱ

Addition of alkyl amines to carboxylic acid anhydrides results in the formation of an amide functional group and a free carboxylic acid, Scheme 4. Polymers **9355-15** and **9355-19** were dissolved into dry THF and the alkyl amine was slowly added followed by 18 to 24 hours of heating at reflux. The long reaction time and elevated temperature were employed to ensure complete reaction of the alkyl amine.

Scheme 4. Modification of alternating copolymers **9355-15** and **9355-19**



The polymers were vacuum dried at under high vacuum, however, only under extended heating could traces of residual THF be removed. All polymers were yellow orange solids with the exception of **9355-35**, which turned a dark purple color upon heating to 90 °C under vacuum. The IR and NMR spectra are consistent with the expected polymer structure and the material is soluble in organic solvents. There are several possible explanations for the change of color from chemical changes of the dithiocarboxylate to changes in the polymer backbone. However, with the characterization data obtained, it is impossible to comment in a confident manner as to the nature of the color change.

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