Supporting Information

Incorporation of Basic α-Hydroxy Acid Residues into Primitive Polyester Microdroplets for RNA Segregation

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Supplementary Methods

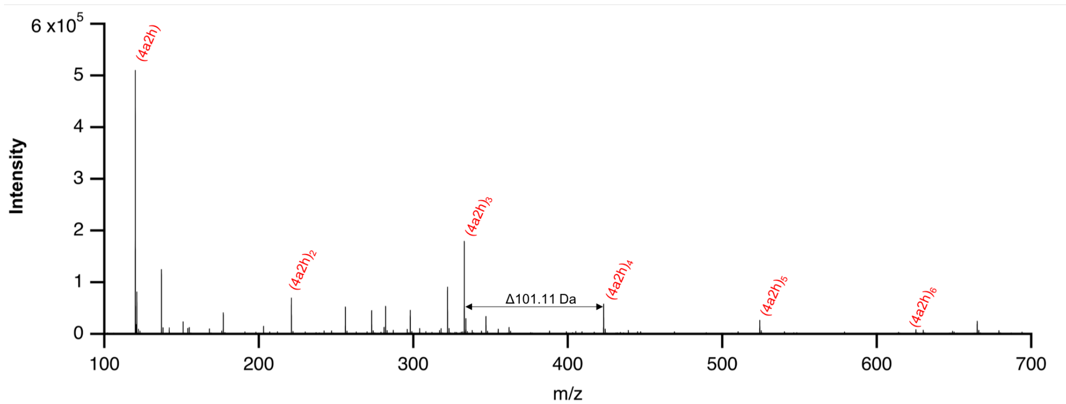
Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) peak identification. Monoisotopic peaks were identified by isolating the highest intensity peak in an isotope envelope that corresponded to a polymer product using a peak list generated from mMass[1–3] (Open Source Software, Prague, Czech Republic) after smoothing (Savitsky-Golay, window size = 0.3 m/z, 2 cycles), baselining (100 precision and 0 relative offset), and thresholding above an intensity of 5000, in that order. Major peaks were isolated by applying the following parameters: S/N > 10, absolute peak intensity > 5000, picking height at 100%, while applying baselining, smoothing, and deisotoping (maximum charge = 1, isotope mass tolerance = 0.1 m/z, isotope intensity tolerance = 50%, isotope mass shift = 0.0, remove isotopes, remove unknown, label envelope tool = 1st selected, envelope intensity = envelope maximum). Analytical settings, matrix, and thresholding parameters were identical for each experiment. Although other adducts were also observed, we list only the following adducts: M+H, M+H–H_2O (cyclic), M+Na–H_2O (cyclic), and M+Na+ethanolamine ("M+H/Na–H_2O (cyclic)": possibility of both dehydrated or cyclic species), which were the major adducts observed, and also ones that most clearly showed mass ladders. Mass accuracy in ppm was calculated by comparing the observed mass with the calculated mass for major peaks corresponding to polymerization products. Detailed peak lists are presented in **Tables S1–S12**.

Electrospray Ionization (ESI)-MS. Polymerized 4a2h homopolymer and 1:1 4a2h:αHA (α-hydroxy acid) samples (of GA, LA, PA, SA, and MA) were first rehydrated in 500 µL water. Then, a 1 mL sample of each polyester diluted 1000-fold (in HPLC-grade water) was subjected to positive-ion mode ESI-MS acquisition, on a Xevo TQ-S quadrupole time-of-flight mass spectrometer (Waters, Milford, Massachusetts, USA) with direct infusion. The following acquisition parameters: sample infusion flow rate of 10 µL min^{-1}, an ion source temperature of 100°C, a desolvation gas temperature of 250°C, a desolvation gas flow rate of 500 L h^{-1}, a cone voltage of 10 V, a cone gas flow rate of 100 L h^{-1}, and a capillary voltage of 3.0 kV. A water blank was injected between all samples. Peaks were identified using the information from the MALDI-TOF-MS peaklists (**Tables S1–S12**). Analytical settings, matrix, and thresholding parameters were identical among different runs of experiments. Although we also observed other adducts, including some of those listed in **Tables S1–S12**, we list only the M+H–H_2O (cyclic or dehydrated) adducts for ease of visualization.

Fluorescence Microscopy Analysis. For **Figs. 8**, **S16–S25**, and **S28**, fluorescence acquisition (excitation illumination strength and exposure time) and image processing parameters (brightness/contrast) were constant down each column. This was important to ensure the ability to directly compare fluorescence intensity values between the relevant images within each figure. Kymographs were acquired with Fiji across the same line, which was consistent down each row for each relevant figure. For Fig. **S41**, the powdery poly(4a2h) synthesis product was deposited directly onto a glass slide and observed by microscope.

Hammerhead Ribozyme Reaction. The hammerhead ribozyme reaction was performed by preparing a 5 µL sample containing 4 µM HH1 (5′-FAM-CGCGCCGAAACACCGUGUCUCGAGC-3′; FAM = 6-carboxyfluorescein), 6 µM HH2 (5′-GGCUCGACUGAUGAGGCGCG-3′), 200 mM MES pH 5.7, and 100 mM $MgCl_2$ in the presence or absence of polyester components. This was done by first mixing 3 µL of the appropriate stock polyester sample (after rehydration with 500 µL 4:1 water:acetonitrile; in this particular study, all samples were dissolved in 4:1 water:acetonitrile even if they did not require acetonitrile for rehydration, resulting in a 12% aqueous acetonitrile solvent) with 1.5 µL of the other components not including magnesium (0.2 µL HH1 (100 µM stock), 0.3 µL HH2 (100 µM stock), and 1µL MES pH 5.7 (1 M stock)). Otherwise in the absence of polyester samples, the reaction occurred in pure water. Then, 0.5 µL of a 1 M $MgCl_2$ stock solution (final $MgCl_2$ concentration of 100 mM) was added to initiate the reaction. All buffers used in this section were either made with RNAse-free water and subsequently filtered, or were purchased as RNAse free (except the sample loading buffer purchased from Thermo-Fisher). The reactions were stopped after 24 hours by adding 200 µL of 4:1 ethanol:RNAse-free water, 50 µg/mL glycogen, and 125 mM ammonium acetate solution, followed by 15 minutes incubation at –20°C for precipitation. After incubation, samples were subjected to centrifugation at 21,500 g for 15 minutes (4°C) in a himac CT 15RE benchtop centrifuge (Hitachi, Chiyoda-ku, Tokyo, Japan), followed by supernatant removal by pipet. The remaining pellet was allowed to air dry for several minutes, followed by dissolution in 5 µL of 2X Novex TBE-Urea Sample Buffer (Thermo-Fisher Scientific) by pipetting. 2.5 µL of each sample was loaded onto a pre-cast 12-well 6% Novex TBE-Urea gel, followed by electrophoresis (150 V, 35 minutes) in a Novex gel running box (Thermo-Fisher Scientific). The gel was then imaged (Blue channel (460 nm) on automatic mode) on an Amersham Imager 600 (GE Life Sciences, Shinjuku-ku, Tokyo, Japan) after separation from the plastic casing. Finally, the total gel band intensities were measured by FIJI, and the fraction of accumulated product was calculated by dividing the total intensity of the product fraction by the total intensity of both the product and remaining reactant fractions. Means and standard errors to the mean were calculated accordingly ($n = 4$).

Figure S1

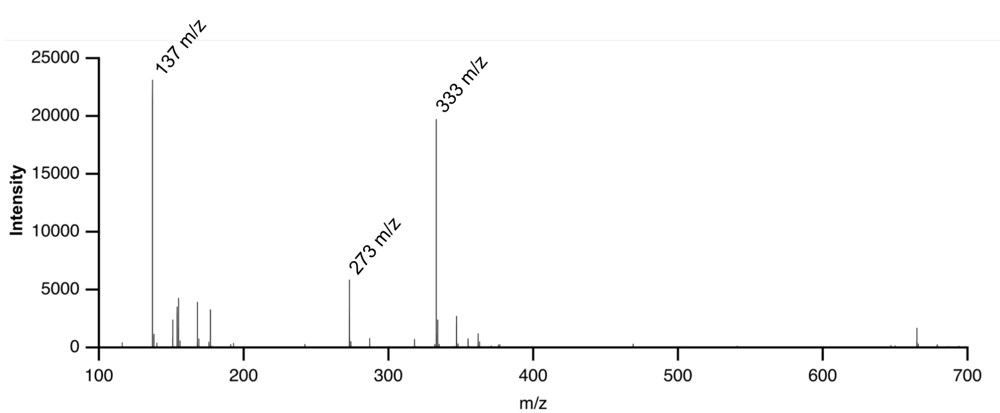


Positive ion-mode MALDI-TOF mass spectrum of the polymerization product (Δ101.11 Da) of complete drying of a 4a2h solution at 80°C for one week. Indicated peaks are proton adducts. MALDI-TOF-MS was chosen rather than ESI-MS due to the required dissolution (and possible hydrolysis) of the sample upon dilution in the aqueous sample running solvent. The peak list is shown in **Tables S1** and **S2**.

Figure S2

Photograph of white, powdery product resulting from drying 4a2h solution at 80°C for one week.

Figure S3

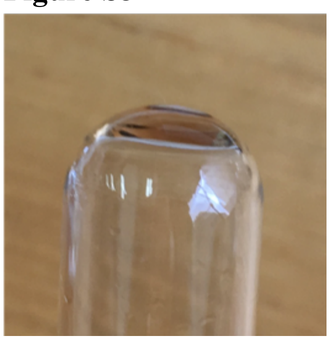


Positive ion mode MALDI-TOF mass spectrum of the SDHB matrix (9:1 (w/w) mixture of 2,5-Dihydroxybenzoic (DHB) and 2-hydroxy-5-methoxybenzoic acid).

Figure S4

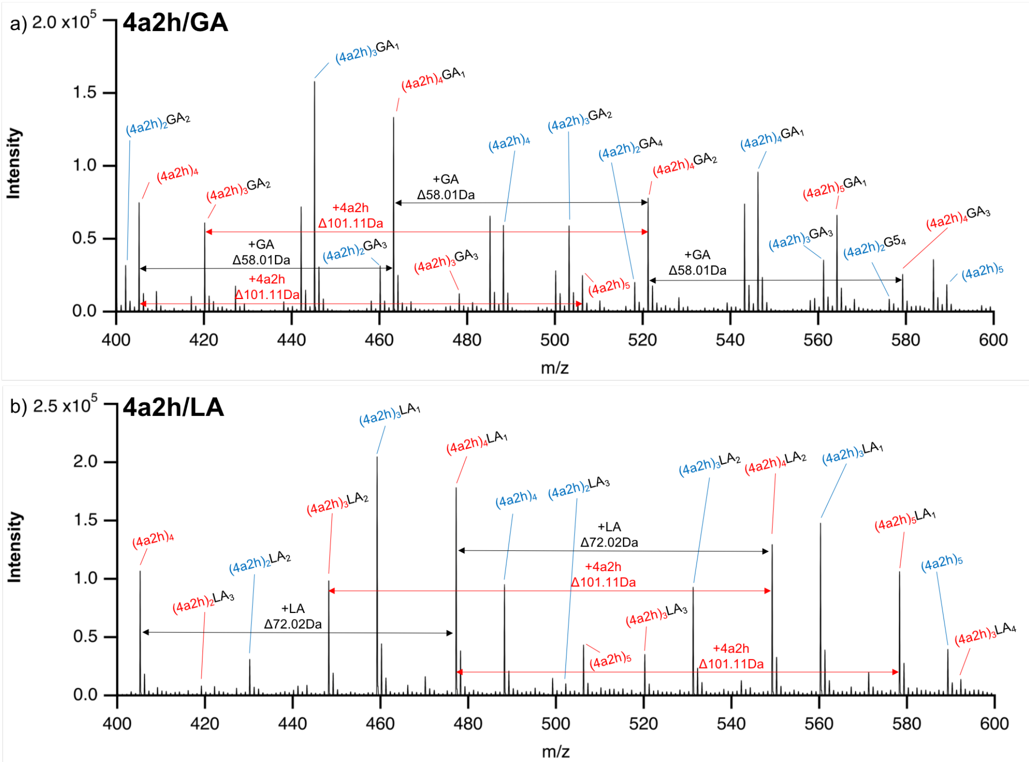
Photographs of the polymerization products of drying of 1:1 4a2h:uncharged αHA solutions and a solution of an equimolar combination of all six αHAs at 80°C for one week (**Fig. 1**). All samples contained 500 mM total monomer before polymerization. The brown color could be the result of products formed through degradation of the starting materials followed by melanoidin formation akin to Maillard-type reaction products or intermediates[4].

Figure S5



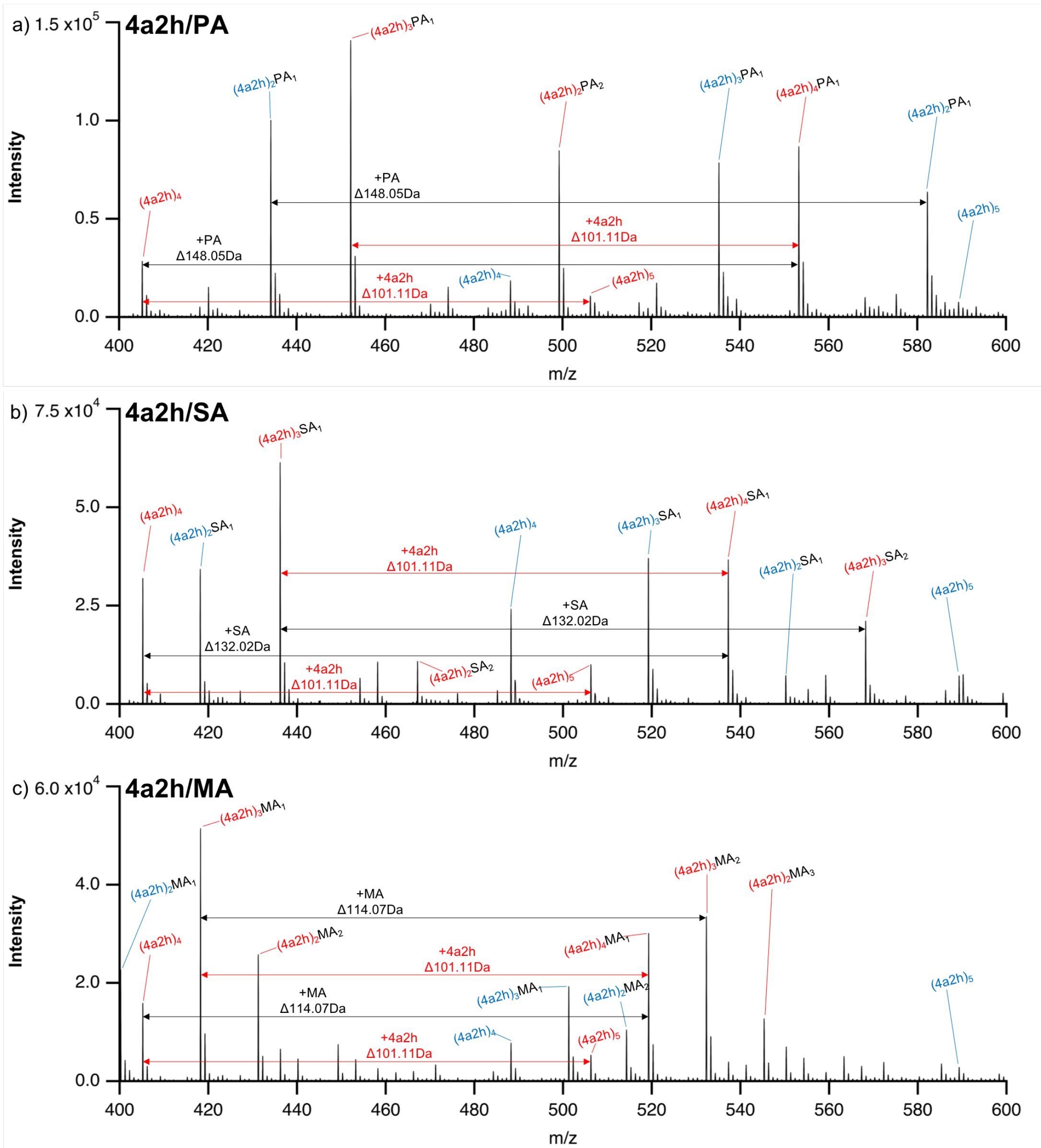
Photograph of the polymerization product of drying a solution of an equimolar combination of all six αHAs (500 mM total monomer before polymerization) at 80°C for one week.

Figure S6



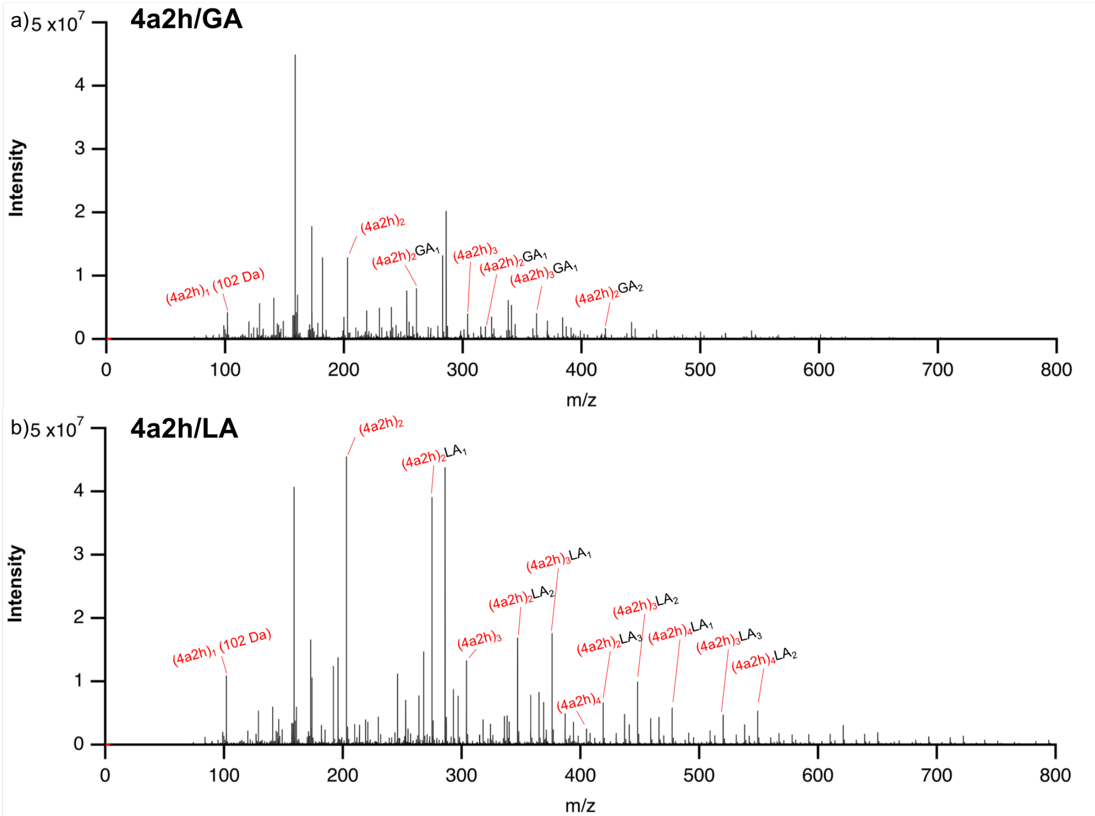
Zoomed-in positive ion mode MALDI-TOF mass spectra (400–600 m/z) of polymerization products resulting from drying of 1:1 (a) 4a2h:GA and (b) 4a2h:LA solutions (500 mM total monomer concentration) (**Fig. 2**). For ease of visualization, indicated peaks are only those which may be cyclic or dehydrated protonated species (red and black) and sodiated ethanolamine (**Fig. S10**) conjugated adducts (blue and black). Red double-sided arrows show mass difference indicative of addition of 4a2h (Δ101.11 Da); black arrows show mass difference indicative of addition of GA (Δ58.01 Da) or LA (Δ72.02 Da). Peak lists: **Tables S3–S4** (4a2h/GA) and **Tables S5–S6** (4a2h/LA). For ease of interpretation, we have included a set of tables sorted by mass (**Tables S3** and **S5**), as well as a set of tables sorted first by adduct and then by mass (**Tables S4** and **S6**). The only homopolymers observed were pure 4a2h homopolymers; no non-4a2h-containing homopolymers were observed. This could be potentially due to a preference of incorporation of 4a2h into the polymer products, or the increased stability of poly(4a2h) products. While it could be theoretically possible that the 4a2h oligomers are not polyesters, but rather linear or branched polymers assembled from the formation of an amide bond between the 4a2h side chain amino group and the α-hydroxy group, other similar studies did not observe such a phenomenon with 4a2h (although they observed such amide bond formation from similar polymerization of 6-amino-4-hydroxybutyric acid monomers)[5]. Thus, we believe that the homopolymer structures formed are likely to be polyesters, although it cannot be ruled out that poly(4a2h) peptides, depsipeptides, or even branched/hyperbranched structures were also present due to formation of amide bonds; a future study utilizing FTIR and/or NMR is planned.

Figure S7



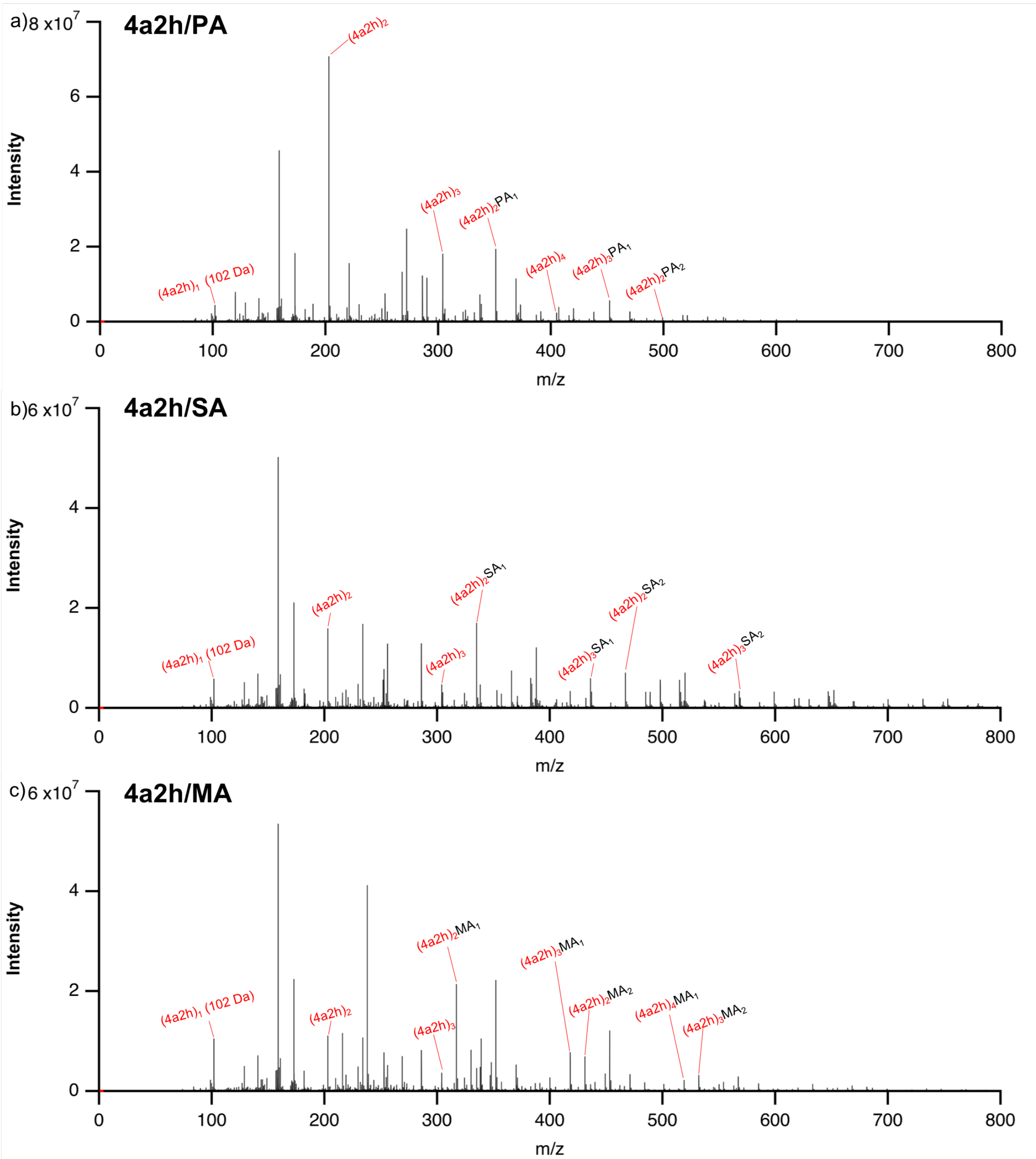
Zoomed-in positive ion mode MALDI-TOF mass spectra (400–600 m/z) of the polymerization products of complete drying of 1:1 (a) 4a2h:PA, (b) 4a2h:SA, and (c) 4a2h:MA solutions at 80°C for one week (500 mM total monomer concentration) (**Fig. 3**). For ease of visualization, indicated peaks are only those which may be cyclic or dehydrated protonated species (red and black) and sodiated ethanolamine (**Fig. S10**) conjugated adducts (blue and black). Red double-sided arrows indicate a mass difference indicative of addition of 4a2h (Δ101.11 Da), while black arrows indicate a mass difference indicative of addition of PA (Δ148.05 Da), SA (Δ132.02 Da), or MA (Δ114.07 Da). Peak lists: **Tables S7–S8** (4a2h/PA), **S9–S10** (4a2h/SA), and **S11–S12** (4a2h/MA).

Figure S8



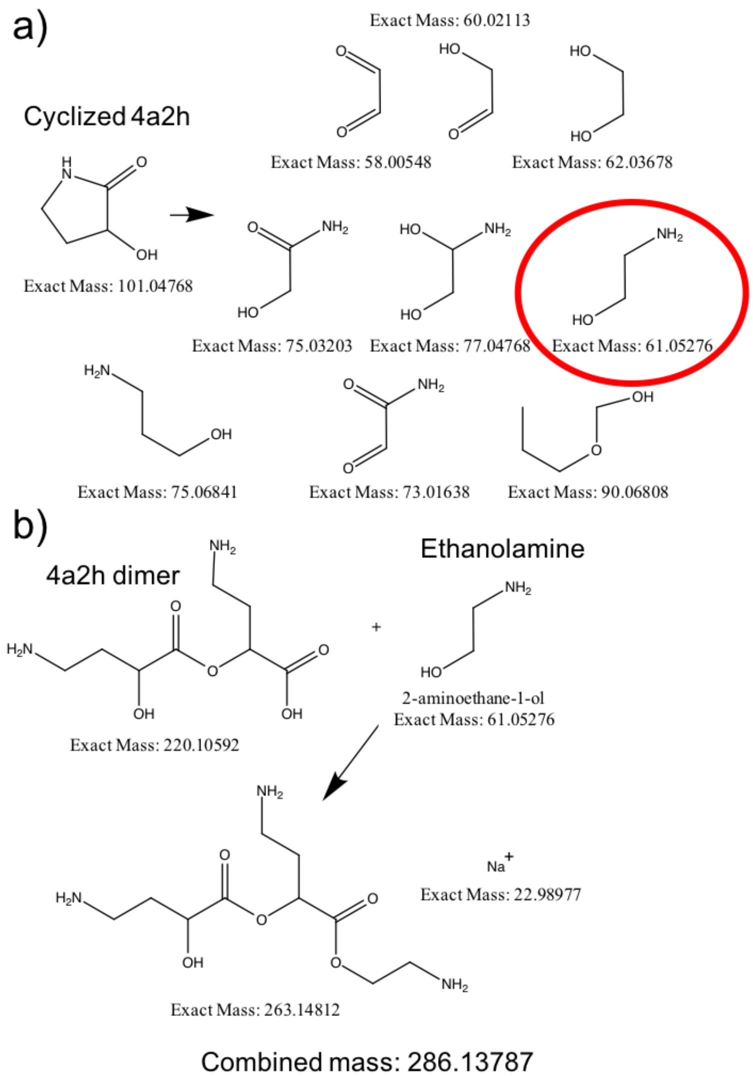
Positive ion of ESI mass spectra of polymerization products resulting from drying of (a) 1:1 4a2h:GA and (b) 4a2h:LA solutions at 500 mM total monomer concentration. Only product masses consistent with cyclic or dehydrated protonated adducts are annotated here for ease of visualization.

Figure S9



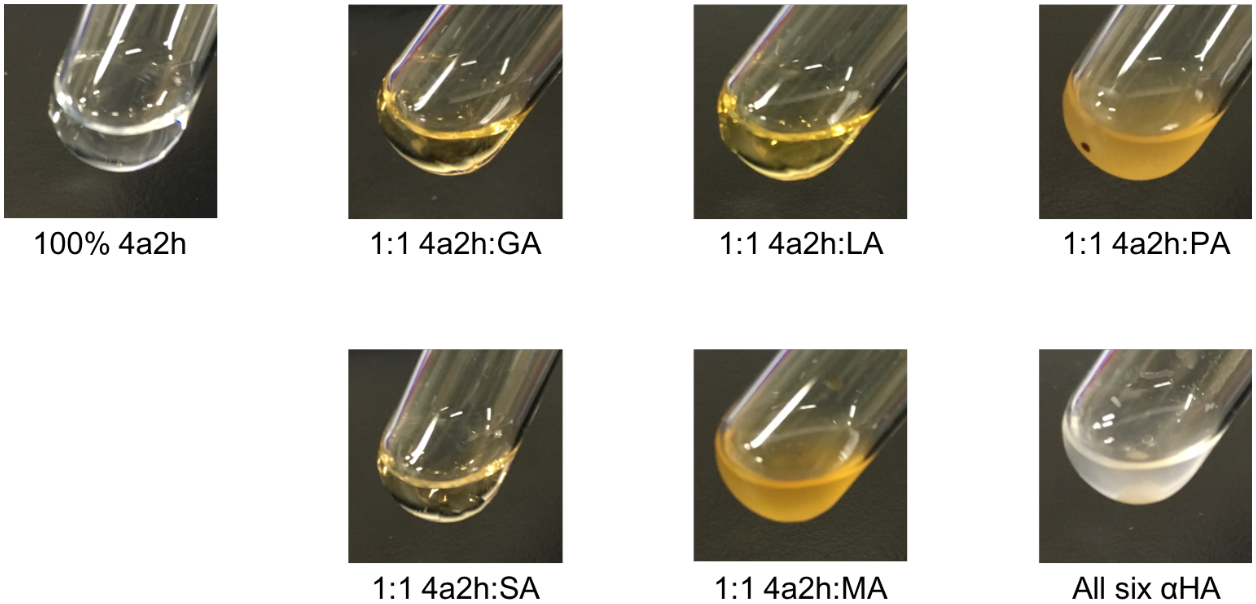
Positive ion of ESI mass spectra of polymerization products resulting from drying of (a) 1:1 4a2h:PA, (b) 4a2h:SA, and (c) 4a2h:MA solutions at 500 mM total monomer concentration. For ease of visualization, indicated peaks are only those which may be cyclic or dehydrated protonated species.

Figure S10



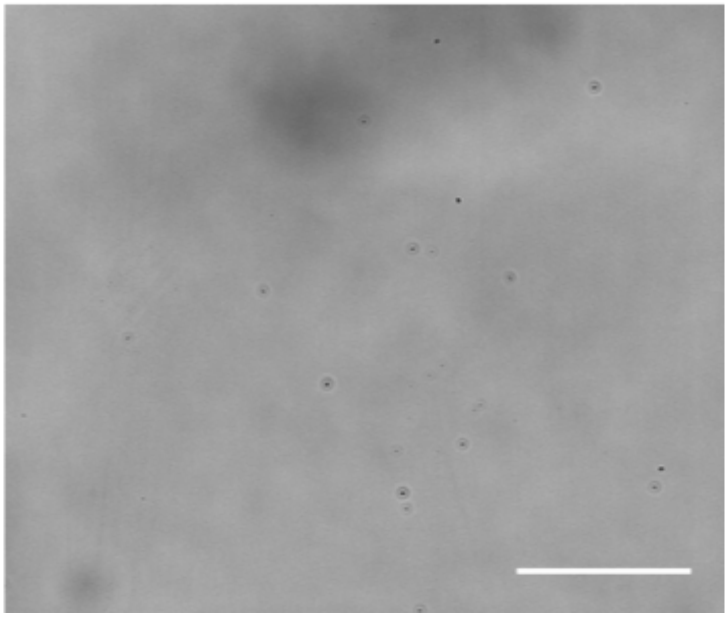
One of the peak series detected in all of the mixed samples initially reduced to monomeric additions (of 4a2h and the appropriate αHA) to a ~286 Da species. We speculate this compound to be a sodiated 4a2h oligoester dimer containing an ethanolamine conjugated to the free carboxyl group. a) Degradation of a cyclized 4a2h monomer lactam (3-hydroxypyrrolidin-2-one) (~101 Da detected previously in similar conditions[5]) into ethanolamine (and other various degradation products); this product could also have contributed to the brown coloration of the mixed sample products). b) The ethanolamine then could form an ester with the carboxyl group of a linear 4a2h ester dimer, resulting in a mass of ~286 Da after sodiation that matches that detected in all of the mixed sample product MALDI-TOF spectra. Co-existence of a peptide, *via* nucleophilic addition of the amine moiety of ethanolamine to the C-terminus of 4a2h dimer, with the identical mass is possible. All exact masses in the figure are represented in Da.

Figure S11



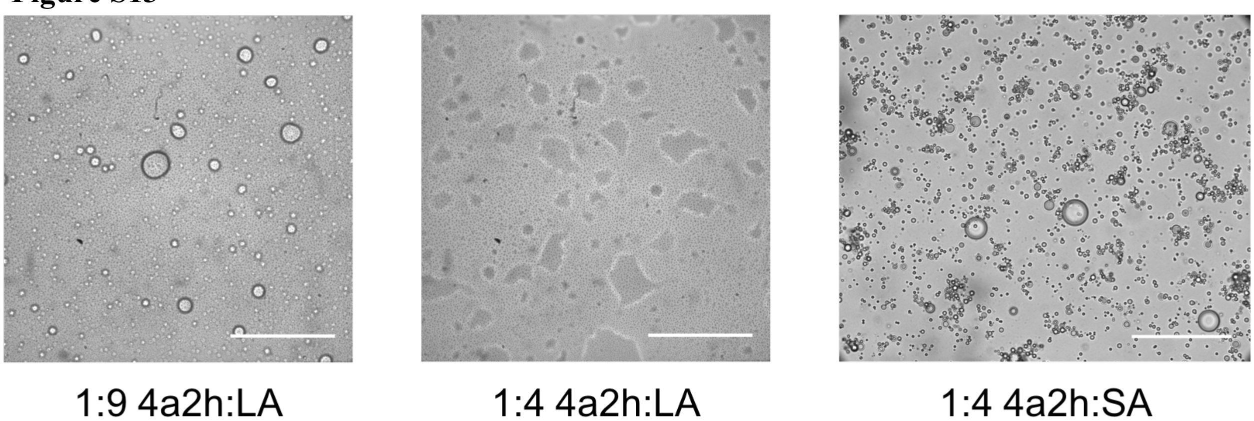
Rehydration of the dried polyester products (total of 500 mM monomer before polymerization, depicted in **Figs. S2**, **S3**, and **S5**) in 500 µL water resulted in a range of phase separation properties, including full solubility for some samples (100% 4a2h, 1:1 4a2h:GA, 1:1 4a2h:LA, and 1:1 4a2h:SA), and formation of microdroplets for other samples (1:1 4a2h:PA, 1:1 4a2h:MA, and All six monomers).

Figure S12



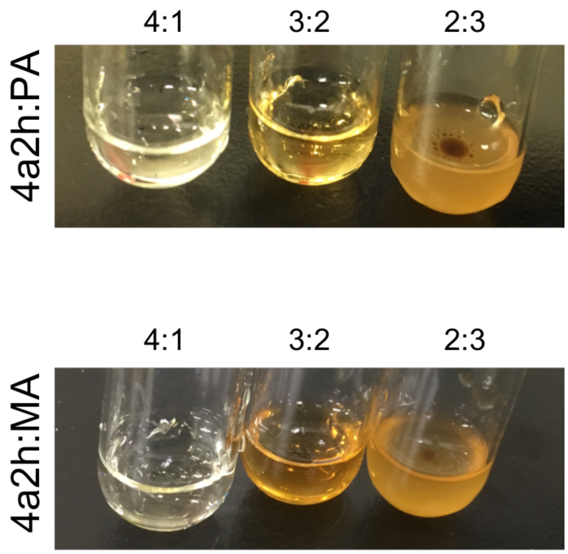
Representative optical microscopy image of a poly(4a2h) sample synthesized by drying of 500 mM 4a2h followed by rehydration. No droplets are observed (the small dots are likely impurities on the sample slide glass or objective). Scale bar is 100 µm.

Figure S13



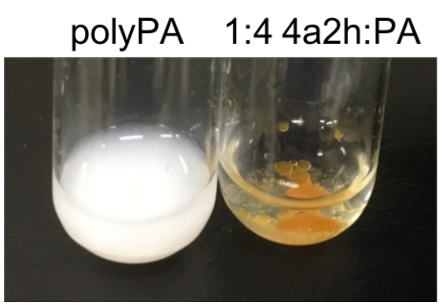
Representative optical microscopy images of samples containing 1:9 4a2h:LA, 1:4 4a2h:LA, and 1:4 4a2h:SA (500 mM total monomer concentration), followed by drying. Rehydration (in 4:1 water:acetonitrile) of 1:9 4a2h:LA and 1:4 4a2h:SA samples resulted in droplet assembly, suggesting that decreasing the ratio of 4a2h monomers in the starting mixture, followed by synthesis, can decrease the solubility of the polyester products, resulting in droplet assembly. Acetonitrile was also required to be added to the rehydration solvent, further suggesting the insolubility of the gel phase in pure water. Scale bars are 100 µm.

Figure S14



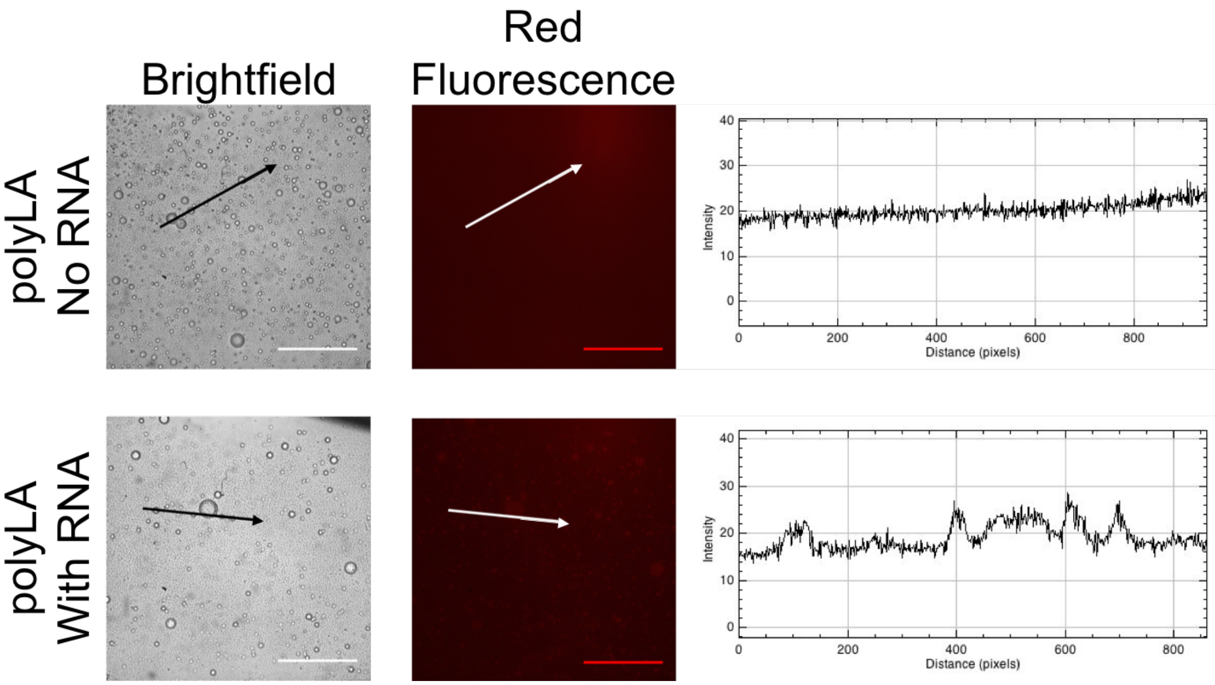
Rehydration of dried polyester products composed of varying ratios of 4a2h to PA and MA total of 500 mM monomer before polymerization) in 500 µL water (except for 2:3 4a2h:PA and 2:3 4a2h:MA samples, which were rehydrated in 4:1 water:acetonitrile) resulted in non-turbid solutions. This suggests that higher amounts of 4a2h incorporation, even to originally fairly apolar and insoluble polyesters, result in greater solubility of polyester products (although a some smaller droplets still form at higher 4a2h ratios). Turbid solutions formed at lower 4a2h proportions (and droplets as observed through microscopy in **Fig. 5**) suggest that droplet formation occurs readily at lower 4a2h ratios due to a decrease in solubility.

Figure S15



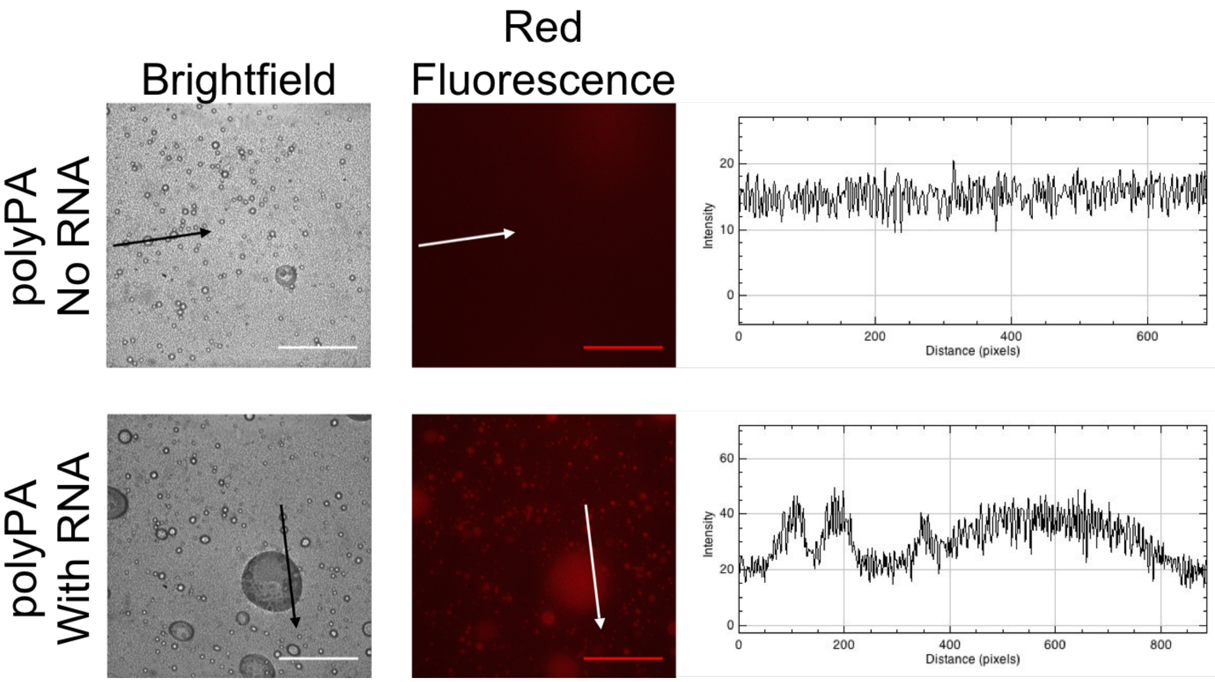
A photograph depicting rehydrated samples of polyPA and 1:4 4a2h:PA (500 mM total starting monomer concentration) after 24 hours. Droplets which contain 4a2h appear to coalesce much more quickly than those which do not contain 4a2h, as indicated by the observation of macroscopic phase separation. The brown color could be the result of products or intermediates formed through degradation of the starting materials followed by melanoidin formation akin to Maillard-type reaction products or intermediates[4].

Figure S16



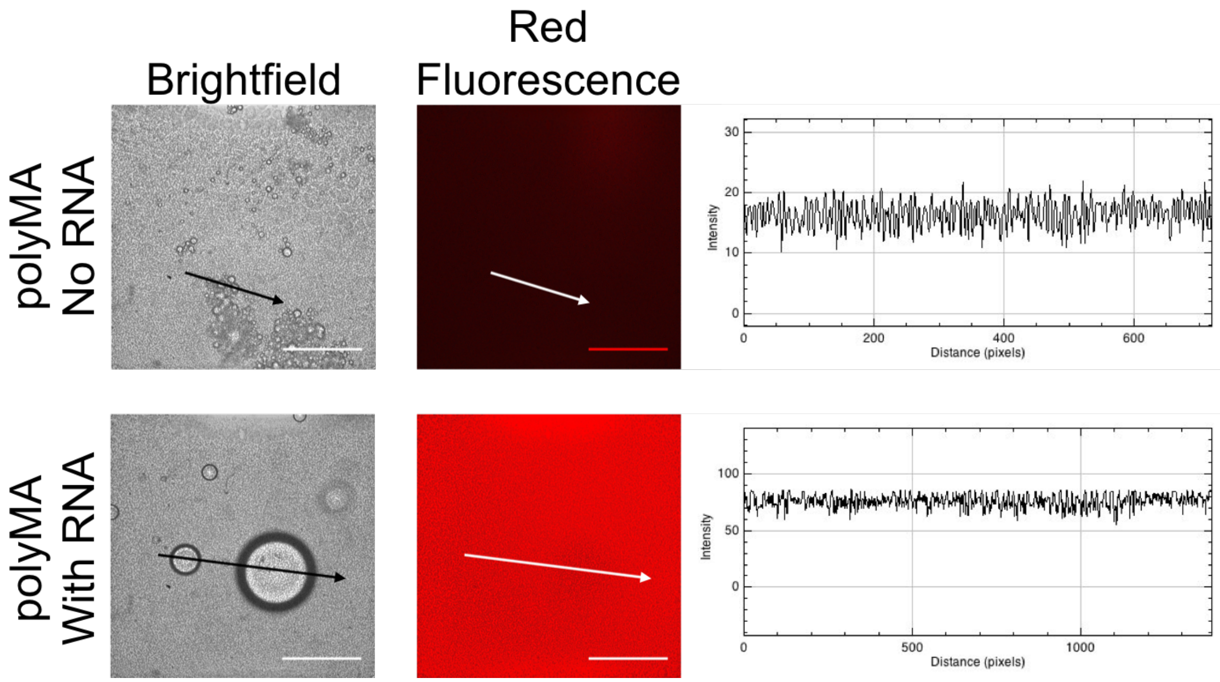
Representative brightfield (left) and fluorescence (middle) microscopy images of polyLA droplets (500 mM total monomer concentration before synthesis) with or without fluorescent RNA (5′-GCGUAGACUGACUGG-Cy3-3′) in the red emission channel (585 nm emission). Kymographs depict the same region of analysis and direction for each row (in black for brightfield image and in white for fluorescence images; arrows indicate direction of analysis). PolyLA is not intrinsically fluorescent in the red channel, while the fluorescent RNA appears to segregate somewhat weakly into the polyLA droplets based on kymograph analysis (in our previous study, a fluorescein-labeled RNA 25-mer was not observed to segregate into polyLA droplets[6]; however, the different chemical structure of the Cy3 fluorescent tag as well as the shorter length may assist in weak segregation of fluorescent RNA into polyLA droplets in this study). Scale bars are 100 µm (615.38 pixels). Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (brightness, contrast) parameters were constant between the rows.

Figure S17



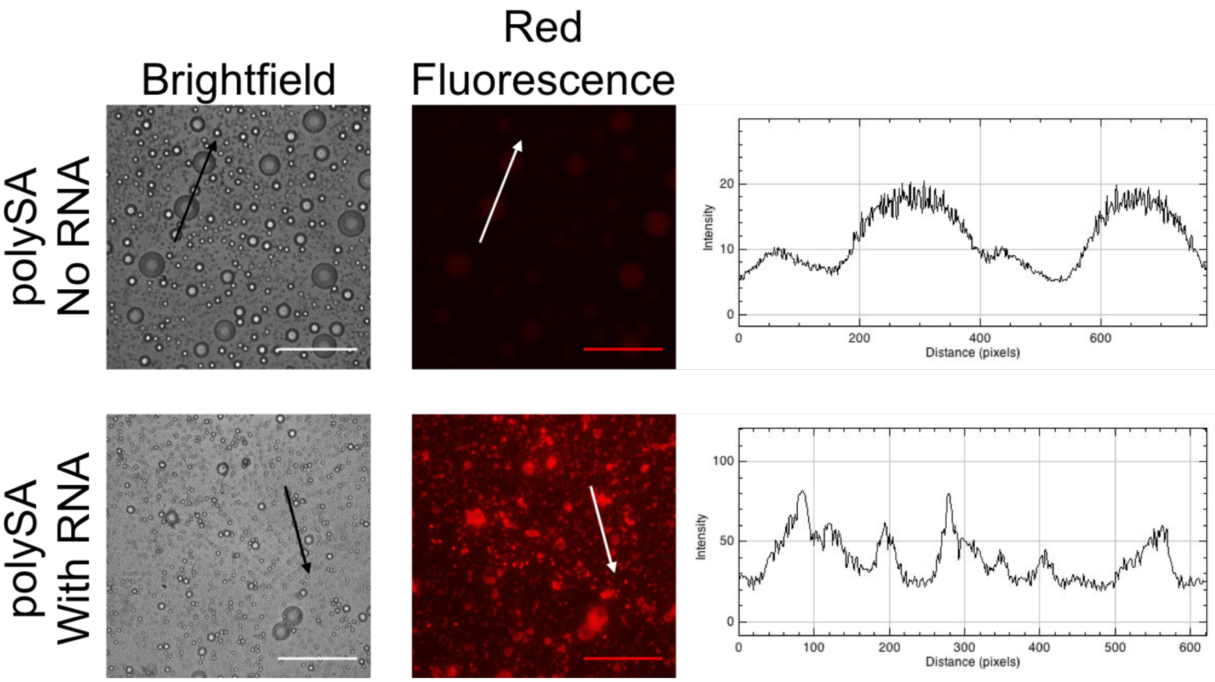
Representative brightfield (left) and fluorescence (middle) microscopy images of polyPA droplets (500 mM total monomer concentration before synthesis) with or without fluorescent RNA (5′-GCGUAGACUGACUGG-Cy3-3′) in the red emission channel (585 nm emission). Kymographs depict the same region of analysis and direction for each row (in black for brightfield image and in white for fluorescence images; arrows indicate direction of analysis). PolyPA is not intrinsically fluorescent in the red channel, while kymograph analysis shows that that fluorescent RNA segregates into the polyPA droplets[6]. Scale bars are 100 µm (615.38 pixels). Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (brightness, contrast) parameters were constant between the rows.

Figure S18



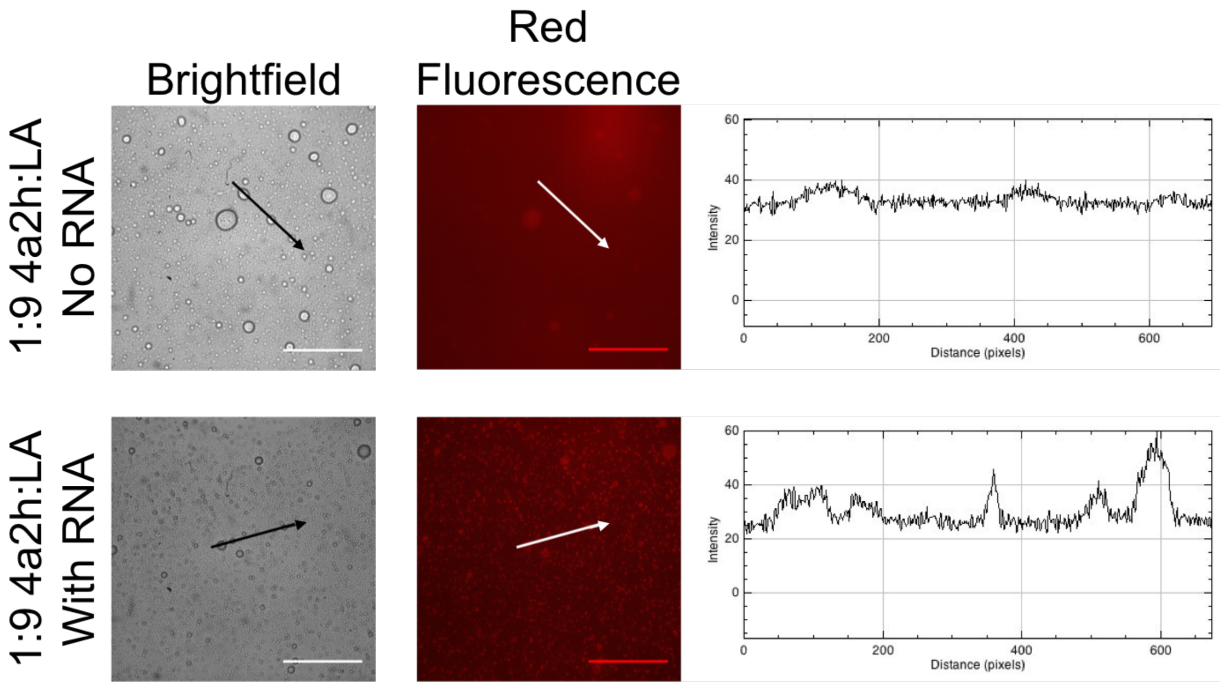
Representative brightfield (left) and fluorescence (middle) microscopy images of polyMA droplets (500 mM total monomer concentration before synthesis) with or without fluorescent RNA (5′-GCGUAGACUGACUGG-Cy3-3′) in the red emission channel (585 nm emission). Kymographs depict the same region of analysis and direction for each row (in black for brightfield image and in white for fluorescence images; arrows indicate direction of analysis). PolyMA is not intrinsically fluorescent in the red channel, while kymograph analysis also shows that the fluorescent RNA does not appear to segregate into the polyMA droplets[6]. Scale bars are 100 µm (615.38 pixels). Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (brightness, contrast) parameters were constant between the rows.

Figure S19



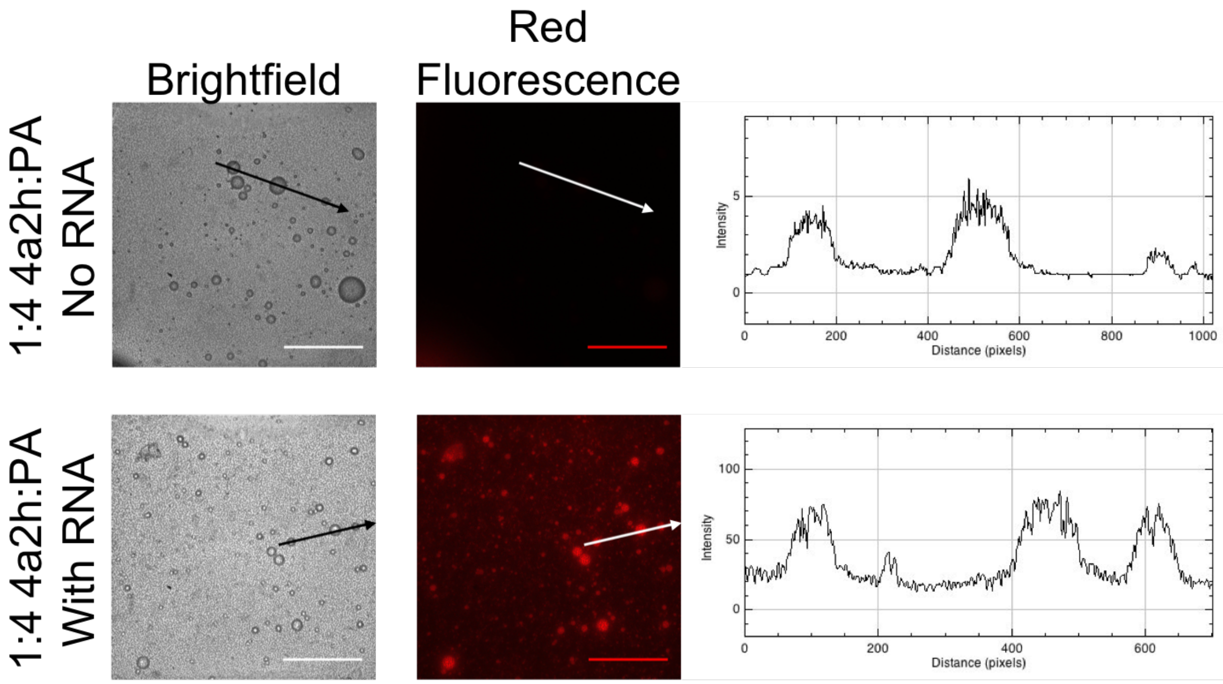
Representative brightfield (left) and fluorescence (middle) microscopy images of polySA droplets (500 mM total monomer concentration before synthesis) with or without fluorescent RNA (5′-GCGUAGACUGACUGG-Cy3-3′) in the red emission channel (585 nm emission). Kymographs depict the same region of analysis and direction for each row (in black for brightfield image and in white for fluorescence images; arrows indicate direction of analysis). PolySA appears to be fluorescent in the red channel, while the images and kymograph indicate that fluorescent RNA likely segregates into the polySA droplets based on the high fluorescence intensities localized to the droplets (in our previous study, a fluorescein-labeled RNA 25-mer was not observed to segregate into polyLA droplets[6]; however, the different chemical structure of the Cy3 fluorescent tag as well as the shorter length may assist in weak segregation of fluorescent RNA into polySA droplets in this study). However, the intrinsic fluorescent character of polySA may contribute to some of the increase in localized droplet fluorescence intensity even in the presence of fluorescent RNA; further quantitative analyses using confocal microscopy are planned. Scale bars are 100 µm (615.38 pixels). Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (brightness, contrast) parameters were constant between the rows.

Figure S20



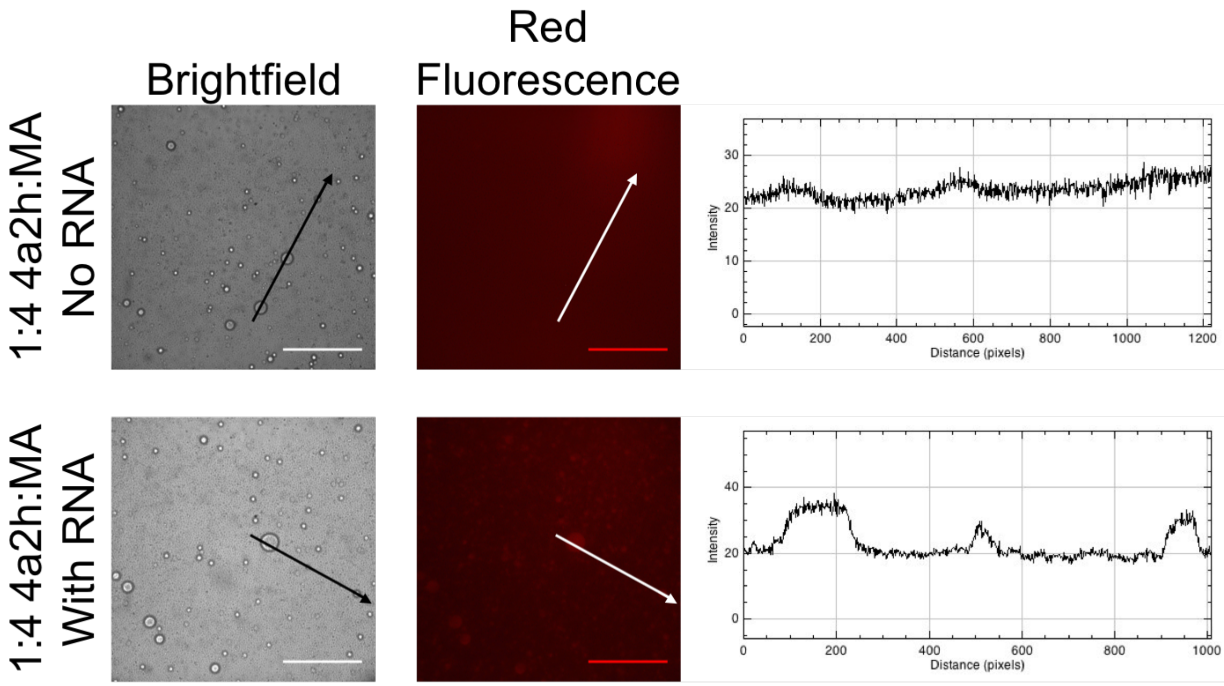
Representative brightfield (left) and fluorescence (middle) microscopy images of poly(4a2h-LA) droplets (1:9 4a2h:LA; 500 mM total monomer concentration before synthesis) with or without fluorescent RNA (5′-GCGUAGACUGACUGG-Cy3-3′) in the red emission channel (585 nm emission). Kymographs depict the same region of analysis and direction for each row (in black for brightfield image and in white for fluorescence images; arrows indicate direction of analysis). poly(4a2h-LA) droplets appear slightly fluorescent in the red channel. Although the fluorescence intensities localized to some droplets in the presence of RNA are higher than some droplets in the absence of RNA (which may show the ability of these droplets to segregate RNA), the current images and analyses are inconclusive on whether fluorescent RNA can definitively segregate into the droplets. The fluorescent character of poly(4a2h-LA) may contribute to some of the increase in localized droplet fluorescence intensity even in the presence of fluorescent RNA; further quantitative analyses using confocal microscopy are required to confirm whether these droplets can segregate RNA. Due to the fact that polyLA droplets showed the ability to segregate RNA, and no appearance of significant amounts of background fluorescence (due to significant amounts of RNA in solution and not segregated within droplets), it is likely that poly(4a2h-LA) droplets can segregate fluorescent RNA. Scale bars are 100 µm (615.38 pixels). Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (brightness, contrast) parameters were constant between the rows.

Figure S21



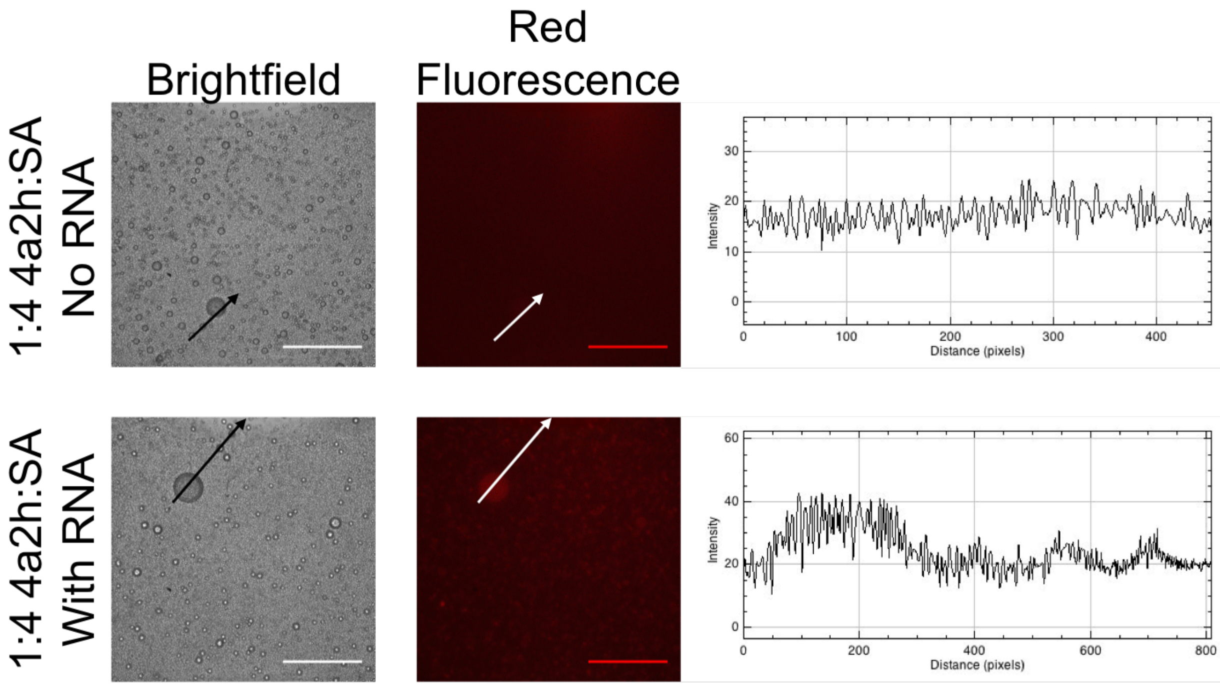
Representative brightfield (left) and fluorescence (middle) microscopy images of poly(4a2h-PA) droplets (1:4 4a2h:PA; 500 mM total monomer concentration before synthesis) with or without fluorescent RNA (5′-GCGUAGACUGACUGG-Cy3-3′) in the red emission channel (585 nm emission). Kymographs depict the same region of analysis and direction for each row (in black for brightfield image and in white for fluorescence images; arrows indicate direction of analysis). poly(4a2h-PA) appears slightly fluorescent in the red channel, however the significant increase in localized fluorescence intensity to the droplets in the presence of RNA suggests that fluorescent RNA segregates strongly into the poly(4a2h-PA) droplets based on kymograph analysis. The fluorescent character of poly(4a2h-PA) may contribute to some of the increase in localized droplet fluorescence intensity even in the presence of fluorescent RNA; further quantitative analyses using confocal microscopy are planned. Scale bars are 100 µm (615.38 pixels). Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (brightness, contrast) parameters were constant between the rows.

Figure S22



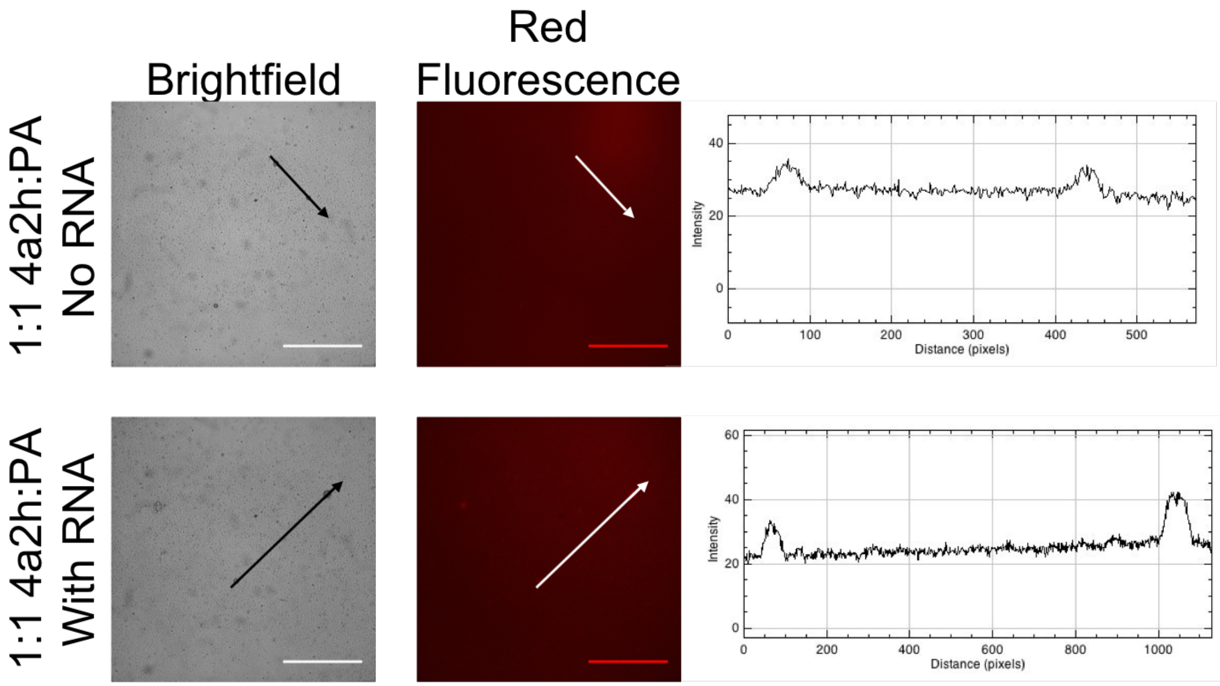
Representative brightfield (left) and fluorescence (middle) microscopy images of poly(4a2h-MA) droplets (1:4 4a2h:MA; 500 mM total monomer concentration before synthesis) with or without fluorescent RNA (5′-GCGUAGACUGACUGG-Cy3-3′) in the red emission channel (585 nm emission). Kymographs depict the same region of analysis and direction for each row (in black for brightfield image and in white for fluorescence images; arrows indicate direction of analysis). poly(4a2h-MA) appears intrinsically slightly fluorescent in the red channel. However, kymograph analysis suggests that fluorescent RNA does indeed segregate within the poly(4a2h-MA) droplets. The fluorescent intensity localized to droplets (and the fluorescence intensity increase compared to the background) is greater in the presence of RNA. Scale bars are 100 µm (615.38 pixels). Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (brightness, contrast) parameters were constant between the rows.

Figure S23



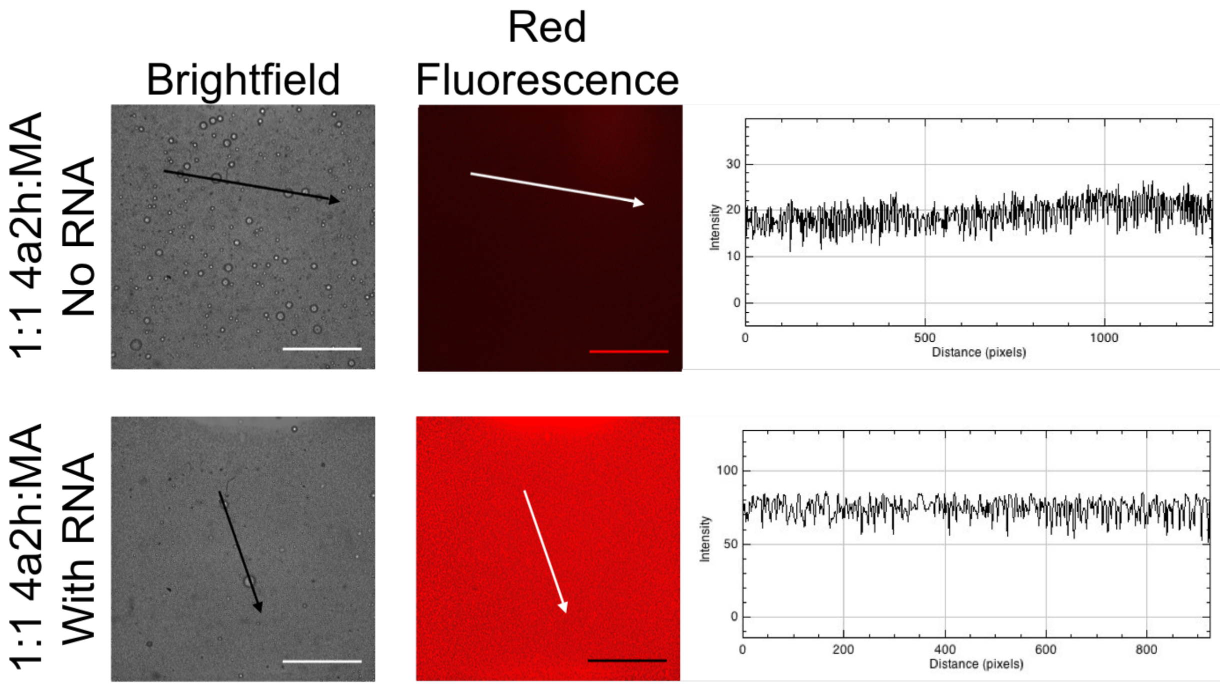
Representative brightfield (left) and fluorescence (middle) microscopy images of poly(4a2h-SA) droplets (1:4 4a2h:SA; 500 mM total monomer concentration before synthesis) with or without fluorescent RNA (5′-GCGUAGACUGACUGG-Cy3-3′) in the red emission channel (585 nm emission). Kymographs depict the same region of analysis and direction for each row (in black for brightfield image and in white for fluorescence images; arrows indicate direction of analysis). poly(4a2h-SA) may be intrinsically slightly fluorescent, but kymograph analysis suggests that fluorescent RNA clearly segregates to the poly(4a2h-SA) droplets. Scale bars are 100 µm (615.38 pixels). Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (brightness, contrast) parameters were constant between the rows.

Figure S24



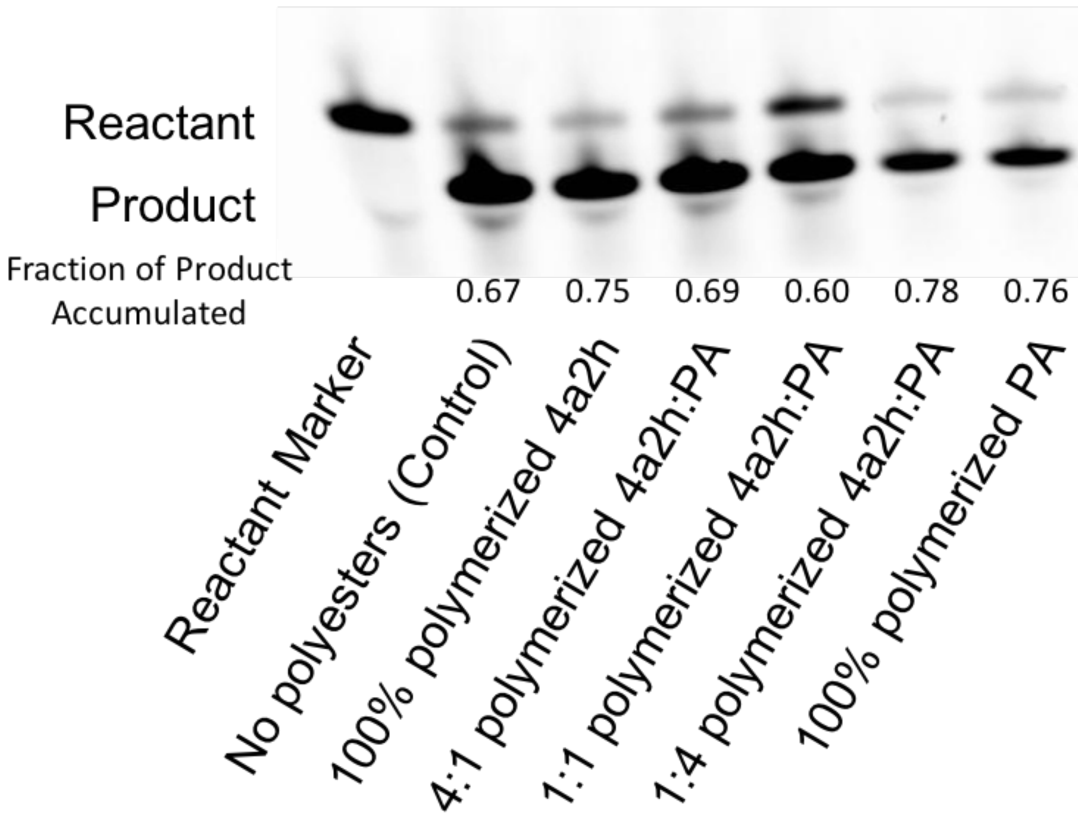
Representative brightfield (left) and fluorescence (middle) microscopy images of poly(4a2h-PA) droplets (1:1 4a2h:PA; 500 mM total monomer concentration before synthesis) with or without fluorescent RNA (5′-GCGUAGACUGACUGG-Cy3-3′) in the red emission channel (585 nm emission). Kymographs depict the same region of analysis and direction for each row (in black for brightfield image and in white for fluorescence images; arrows indicate direction of analysis). poly(4a2h-PA) droplets appear to be intrinsically slightly fluorescent in the red channel, and although there is some localized fluorescence intensity to the droplets in the presence of fluorescent, RNA, kymograph analysis is inconclusive as to whether these droplets retain the ability to segregate fluorescent RNA upon increasing the 4a2h:PA ratio to 1:1. In particular, the fluorescence intensity localized to the droplets is less compared to poly(4a2h-PA) droplets prepared with a 4a2h:PA ratio of 1:4. However, more quantitative studies, such as with confocal microscopy, are required to confirm whether these droplets can segregate RNA or not. Scale bars are 100 µm (615.38 pixels). Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (brightness, contrast) parameters were constant between the rows.

Figure S25



Representative brightfield (left) and fluorescence (middle) microscopy images of poly(4a2h-MA) droplets (1:1 4a2h:MA; 500 mM total monomer concentration before synthesis) with or without fluorescent RNA (5′-GCGUAGACUGACUGG-Cy3-3′) in the red emission channel (585 nm emission). Kymographs depict the same region of analysis and direction for each row (in black for brightfield image and in white for fluorescence images; arrows indicate direction of analysis). poly(4a2h-MA) droplets do not appear to be intrinsically fluorescent in the red channel. However, the fluorescence intensity in the presence of RNA is not localized to any droplets, suggesting that the ability to segregate fluorescent RNA may have been lost upon increasing the 4a2h:MA ratio to 1:1. Scale bars are 100 µm (615.38 pixels). Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (brightness, contrast) parameters were constant between the rows.

Figure S26



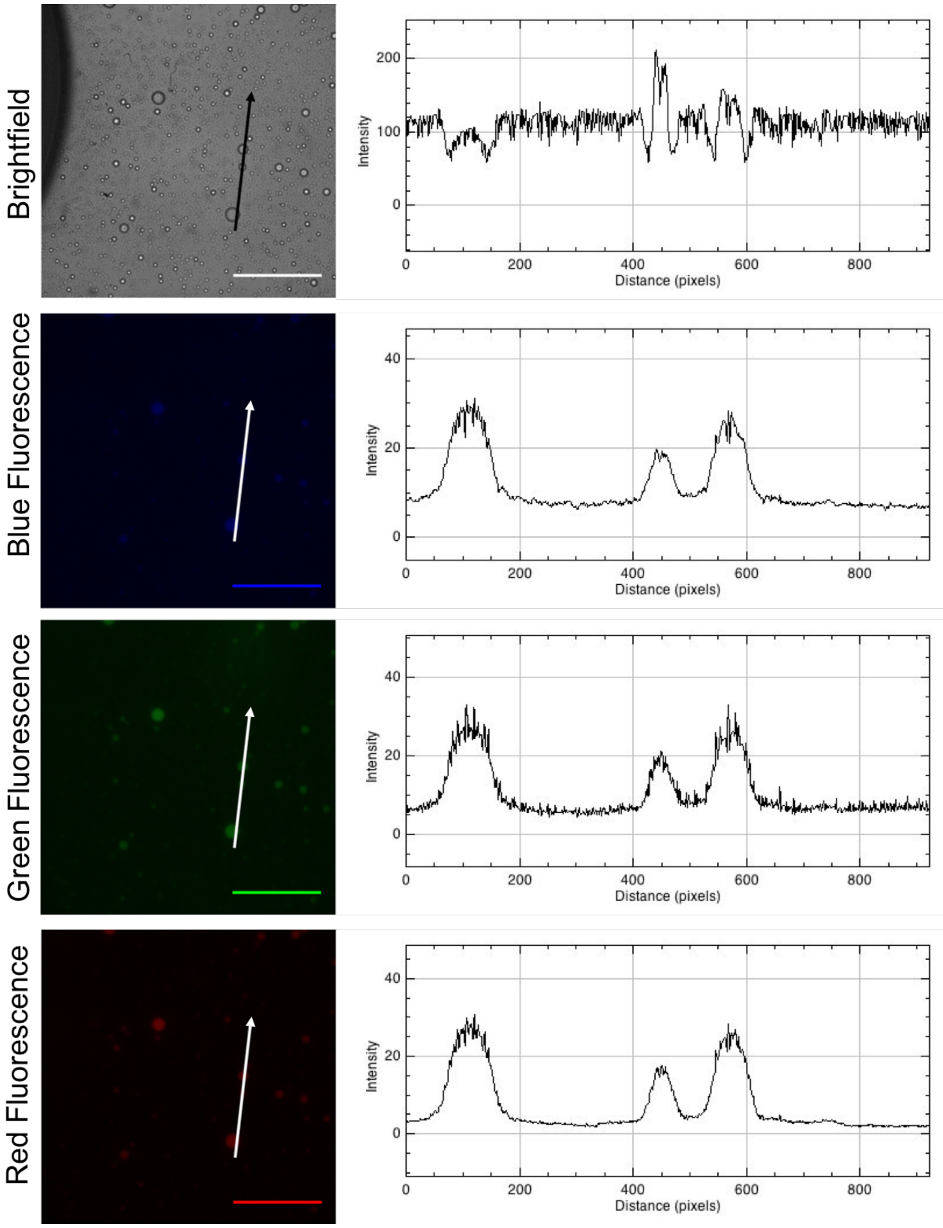
An overnight self-cleaving hammerhead ribozyme reaction was performed under a variety of conditions (4 µm HH1, 6 µm HH2, 200 mM MES pH 5.7, 100 mM $MgCl_2$) including in the various ratios of 4a2h:PA-containing polyester systems and polymerized pure poly(4a2h) and polyPA (the identical ribozyme reaction was observed to occur in the presence of polyPA previously[6]). The fraction of product accumulated for each of the hammerhead ribozyme reactions is presented above each respective lane. The representative gel-shift assay indicates that the reaction (fluorescent starting material band above, and fluorescent product band below) occurred under all conditions tested, suggesting that the presence of polyester samples (poly(4a2h), polyPA, and poly(4a2h-PA) with different 4a2h:PA ratios) does not completely inhibit the reaction from occurring.

Figure S27

	No Polyesters (Control)	1:4 polymerized 4a2h:PA	100% polymerized PA
Fraction of Product Accumulated	0.68 ± 0.04	0.61 ± 0.10	0.54 ± 0.12

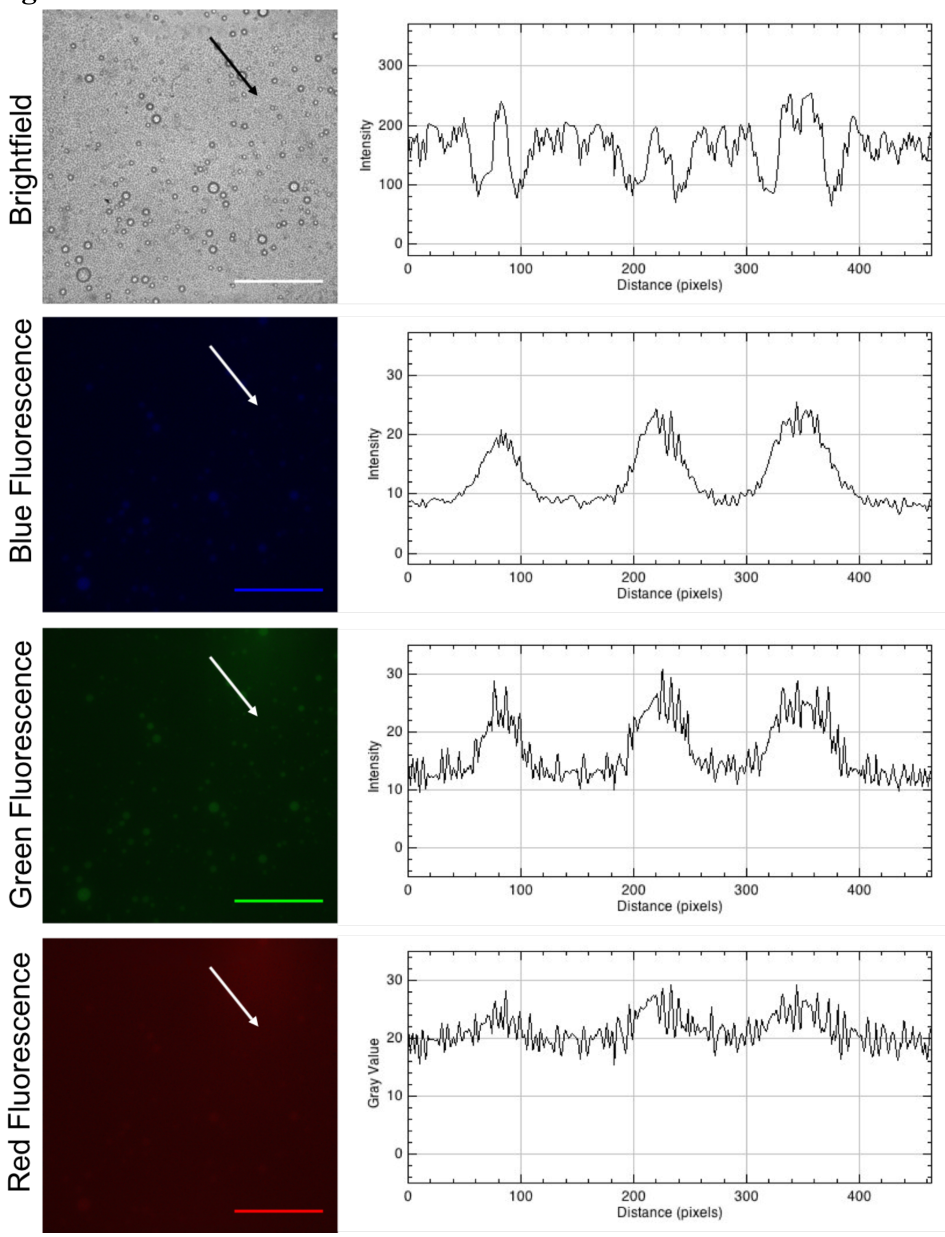
The mean and the standard error to the mean (n = 4) of the fraction of product accumulated for hammerhead ribozyme reactions without polyesters and in the presence of poly(4a2h-PA) (1:4 4a2h:PA ratio) and polyPA. The gel-shift assay indicates that the amount of product that accumulated in the presence of poly(4a2h-PA) (1:4 4a2h:PA ratio) was similar to that in the absence of any polyesters as well as that of polyPA (within error). This suggests that 4a2h-containing polyesters do not result in complete inhibition of the self-cleavage function of the hammerhead ribozyme, although we cannot make any statements about the potential inhibition of the reaction rate by polyesters (this study was an endpoint measurement and not a kinetic study). However, as this experiment was conducted on only one specific, simple ribozyme system, further studies regarding activity of other functional RNA (such as ribozyme-catalyzed nucleic acid ligation or nonenzymatic polymerization) within polyester microdroplet systems are still warranted to determine global patterns of RNA function in polyester microdroplets.

Figure S28



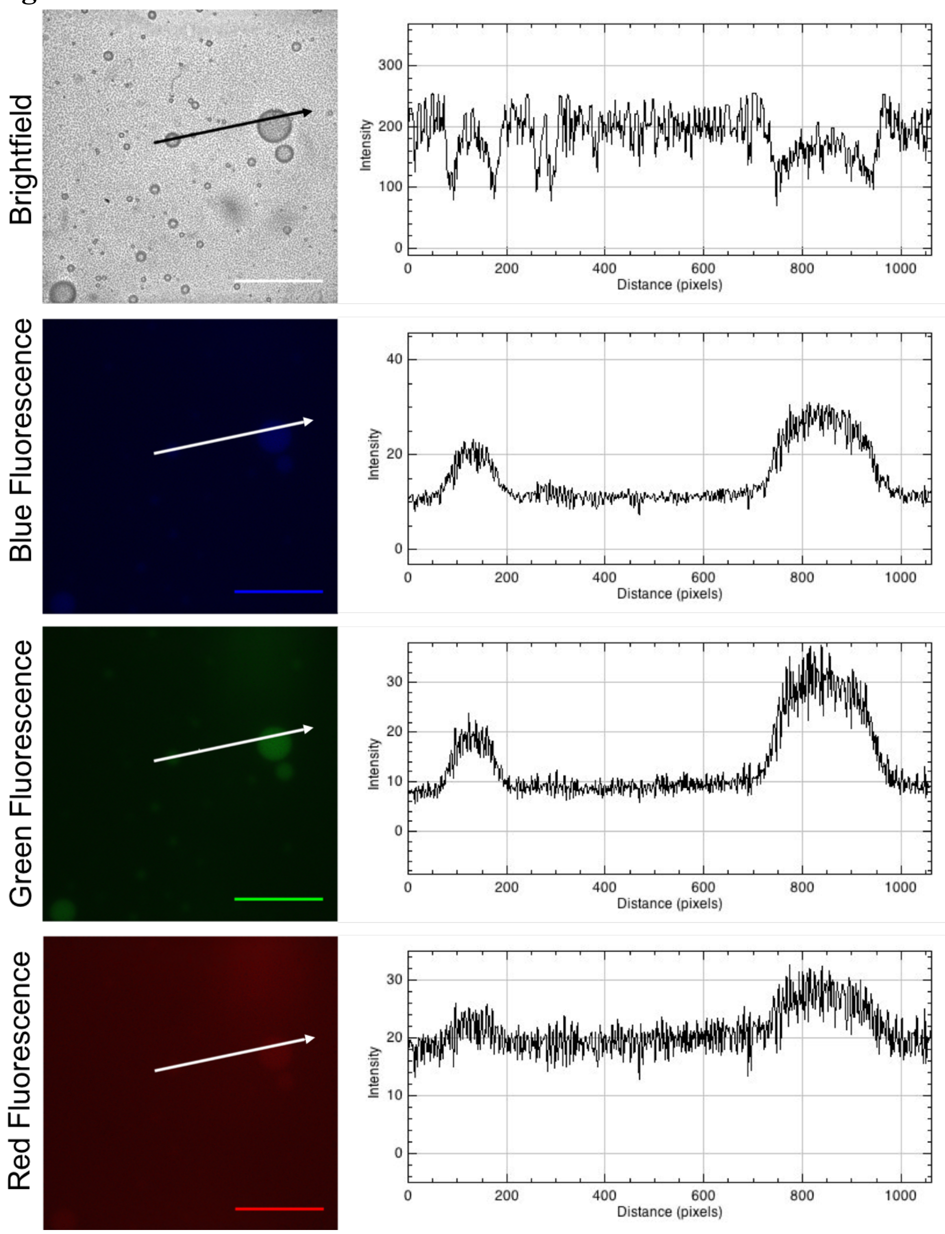
Representative brightfield and fluorescence microscopy images of poly(4a2h-LA) droplets (1:9 4a2h:LA; 500 mM total monomer concentration before synthesis) in blue (470 nm emission), green (527 nm emission), and red (585 nm emission) channels with accompanying kymographs. The region and direction of analysis for each image were identical (in black for brightfield image and in white for fluorescence images; arrows indicate direction of analysis). The column represents a single sample. poly(4a2h-LA) droplets may show intrinsic fluorescence in all channels. Scale bars are 100 µm (615.38 pixels). Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (contrast, brightness) parameters were constant down each column.

Figure S29



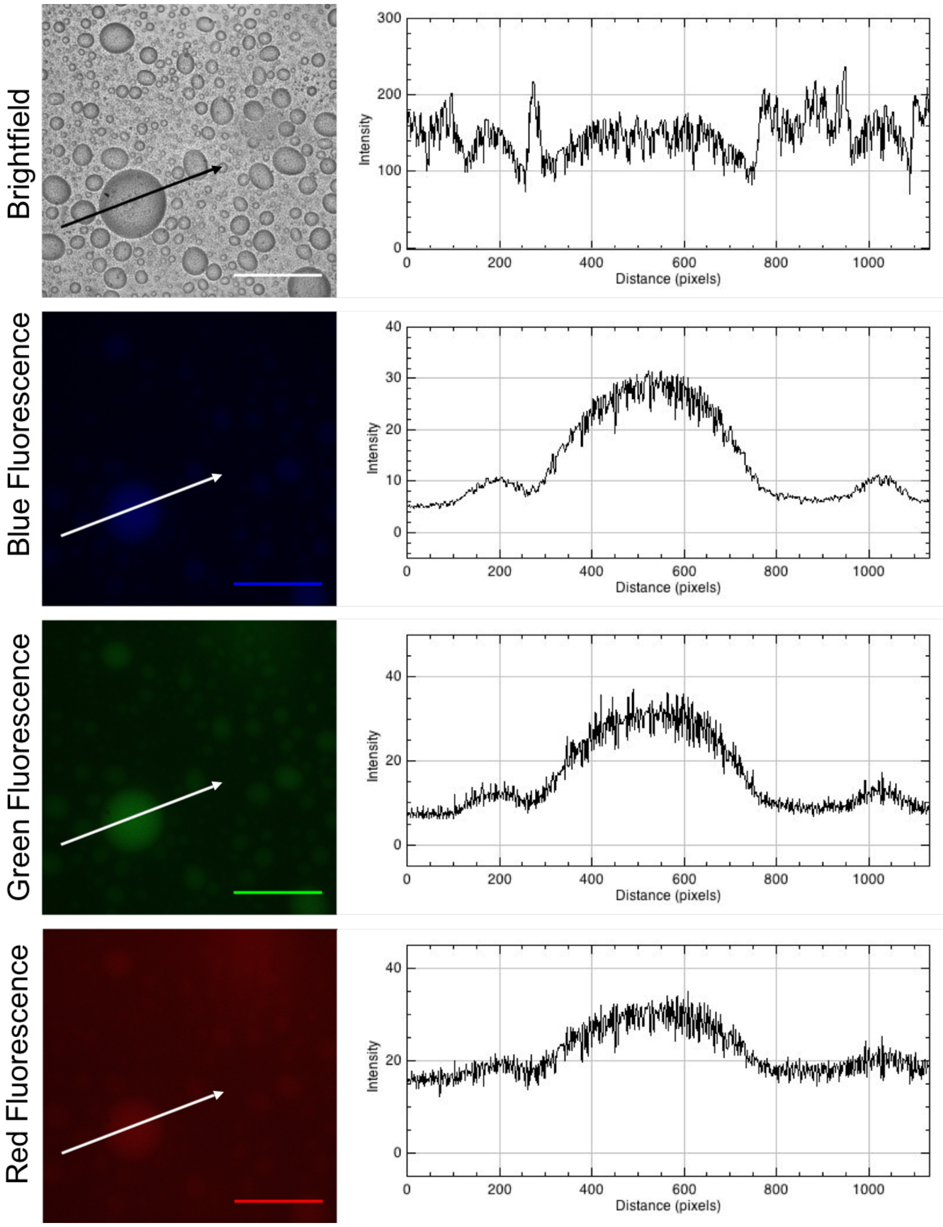
Representative brightfield and fluorescence microscopy images of poly(4a2h-PA) droplets (1:4 4a2h:PA; 500 mM total monomer concentration before synthesis) in blue (470 nm emission), green (527 nm emission), and red (585 nm emission) channels with accompanying kymographs. The region and direction of analysis for each image were identical (in black for brightfield image and in white for fluorescence images; arrows indicate direction of analysis). The column represents a single sample. poly(4a2h-PA) droplets may show intrinsic fluorescence in all channels, although the intensities may be variable. Scale bars are 100 µm (615.38 pixels). Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (contrast, brightness) parameters were constant down each column.

Figure S30



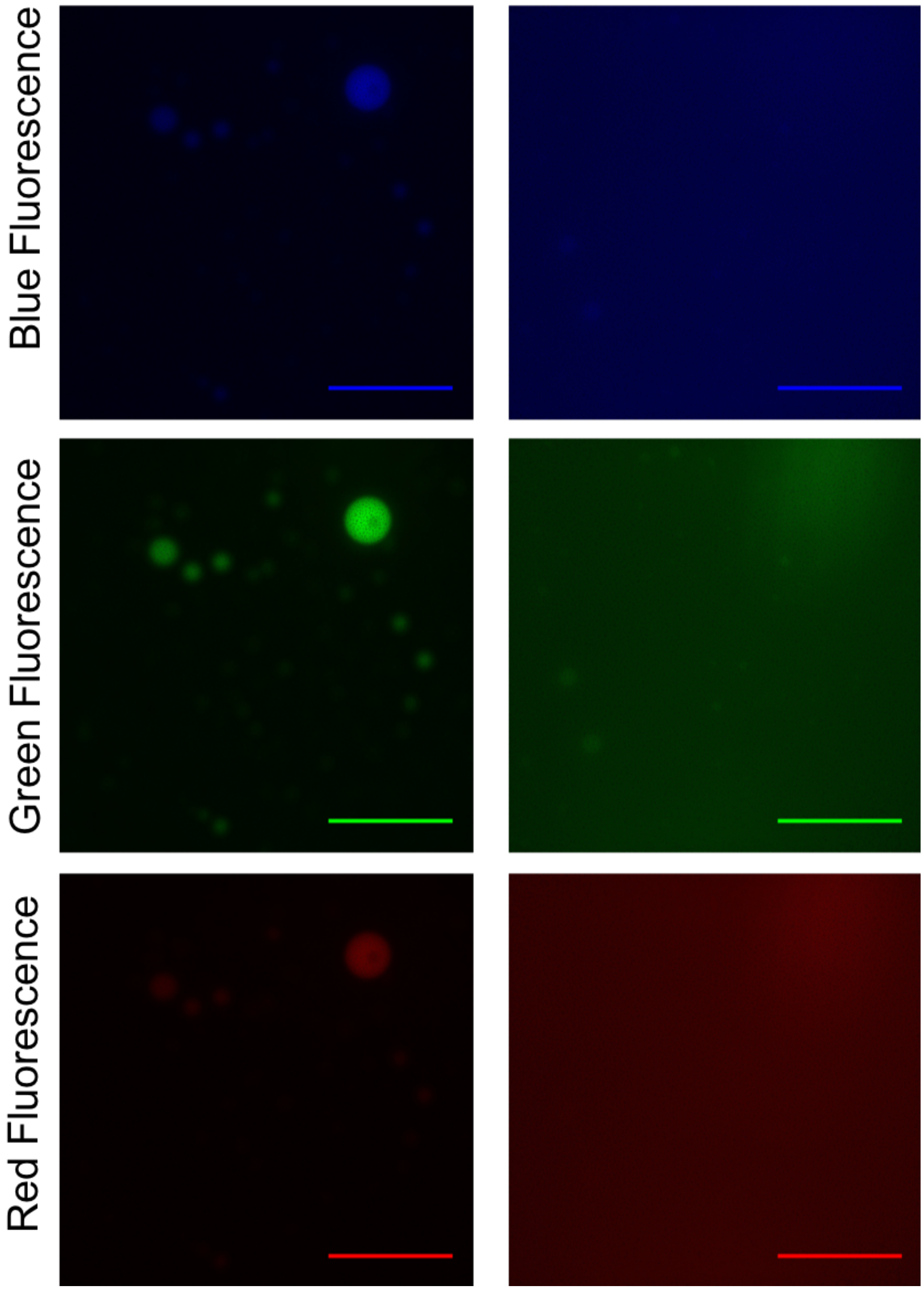
Representative brightfield and fluorescence microscopy images of poly(4a2h-MA) droplets (1:4 4a2h:MA; 500 mM total monomer concentration before synthesis) in blue (470 nm emission), green (527 nm emission), and red (585 nm emission) channels with accompanying kymographs. The region and direction of analysis for each image were identical (in black for brightfield image and in white for fluorescence images; arrows indicate direction of analysis). The column represents a single sample. poly(4a2h-MA) droplets may show intrinsic fluorescence in all channels, although the intensities may be variable. Scale bars are 100 μm (615.38 pixels). Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (contrast, brightness) parameters were constant down each column.

Figure S31



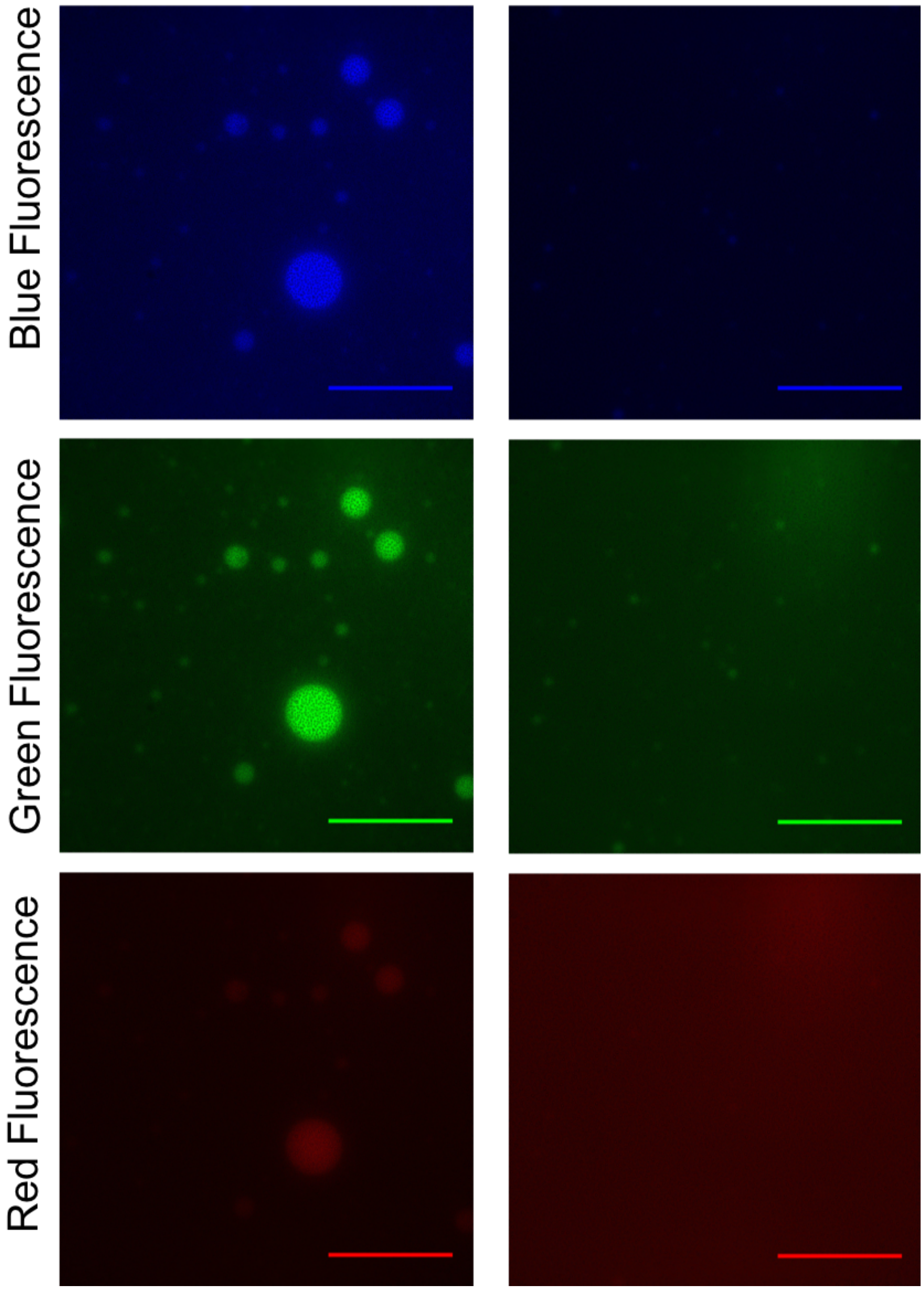
Representative brightfield and fluorescence microscopy images of poly(4a2h-SA) droplets (1:4 4a2h:SA; 500 mM total monomer concentration before synthesis) in blue (470 nm emission), green (527 nm emission), and red (585 nm emission) channels with accompanying kymographs. The region and direction of analysis for each image were identical (in black for brightfield image and in white for fluorescence images; arrows indicate direction of analysis). The column represents a single sample. poly(4a2h-SA) droplets may show intrinsic fluorescence in all channels, although the intensities may be variable. Scale bars are 100 µm (615.38 pixels). Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (contrast, brightness) parameters were constant down each column.

Figure S32



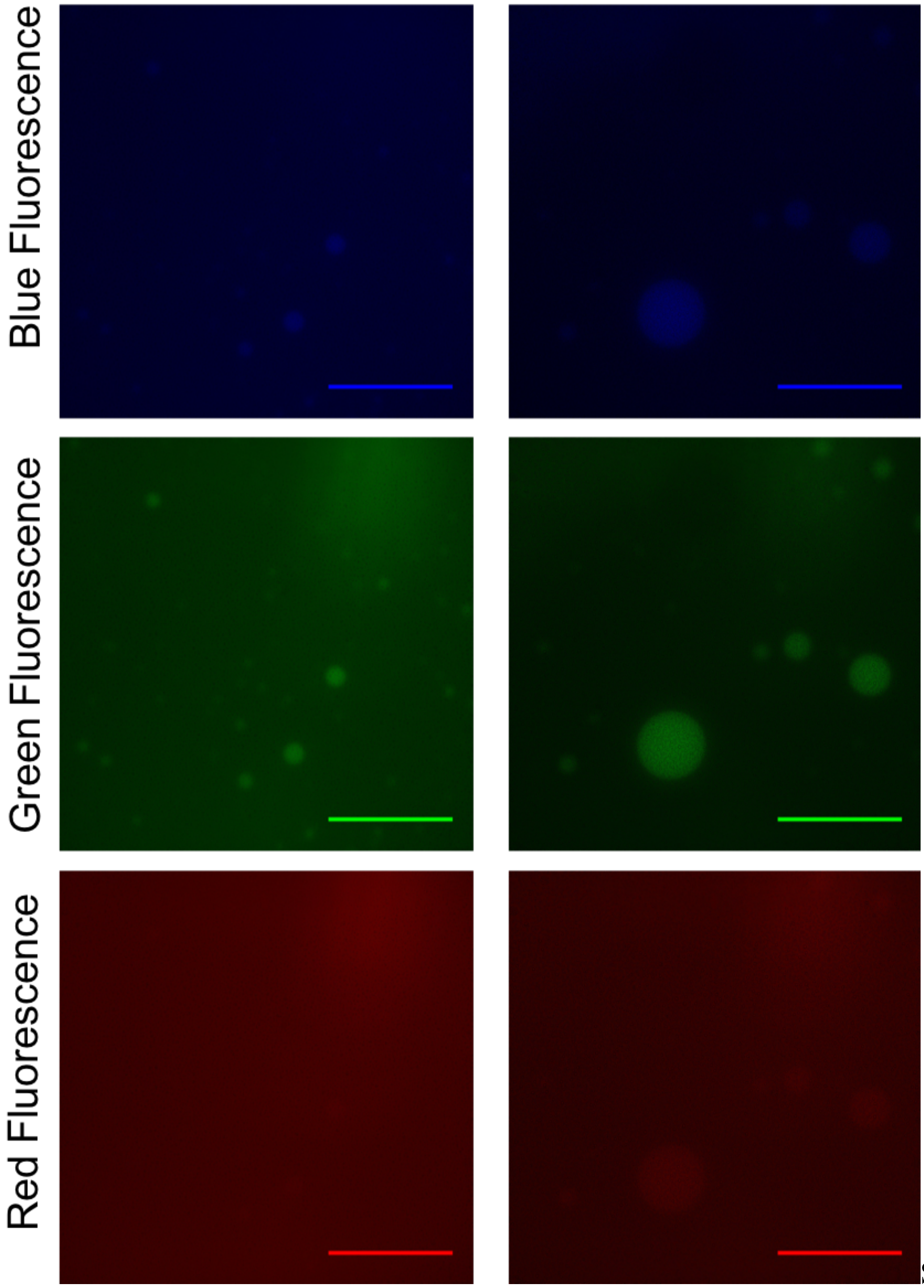
Additional fluorescence microscopy images of poly(4a2h-LA) droplets (1:9 4a2h:LA; 500 mM total monomer concentration before synthesis) in all emission channels. Each column represents a single sample. We observed some variability in the intrinsic fluorescence, and further detailed investigations are planned. Scale bars are 100 µm. Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (brightness, contrast) parameters were constant down each column.

Figure S33



Additional fluorescence microscopy images of poly(4a2h-PA) droplets (1:4 4a2h:PA; 500 mM total monomer concentration before synthesis) in all emission channels. Each column represents a single sample. We observed some variability in the intrinsic fluorescence, and further detailed investigations are planned. Scale bars are 100 µm. Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (brightness, contrast) parameters were constant down each column.

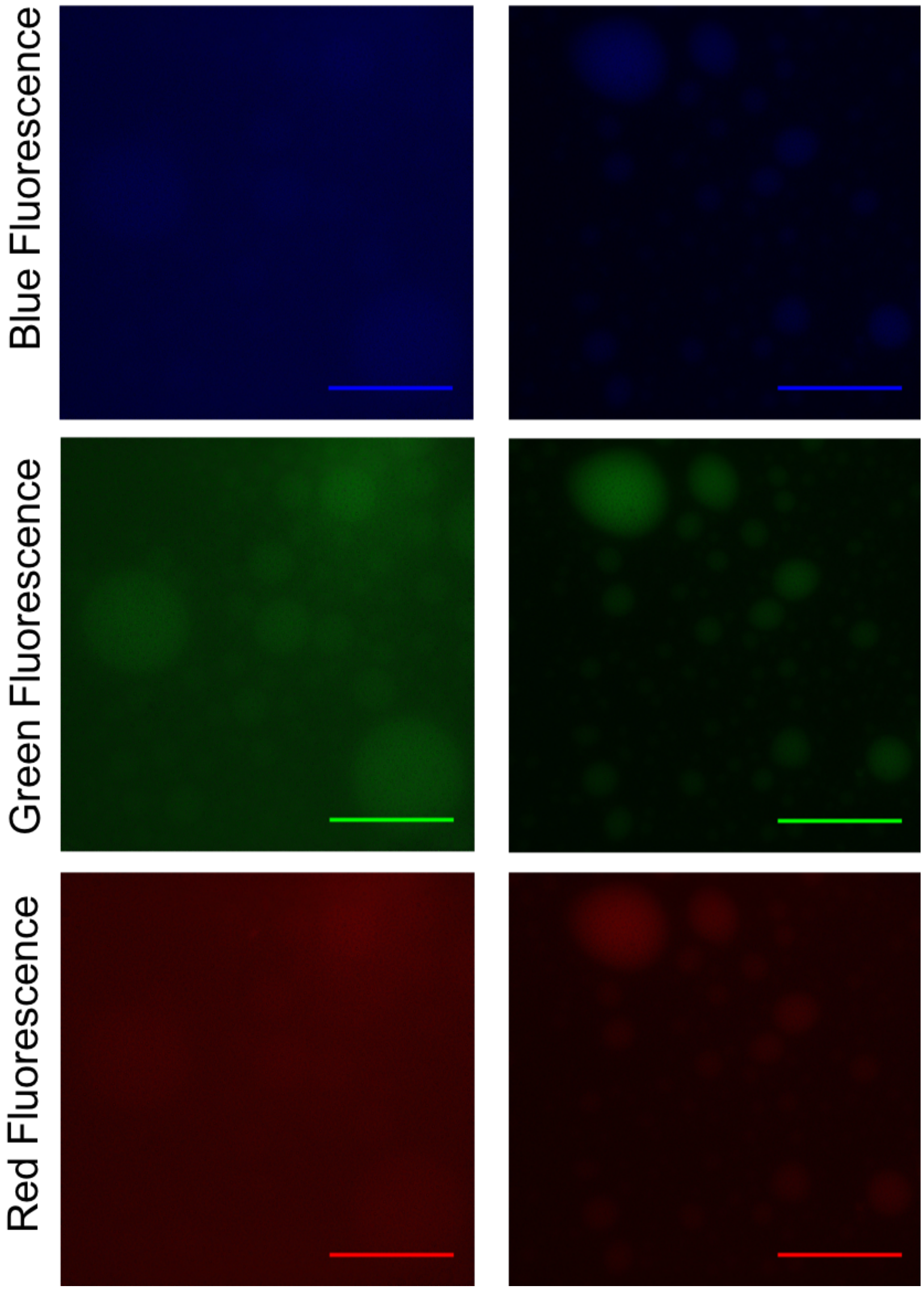
Figure S34



S41

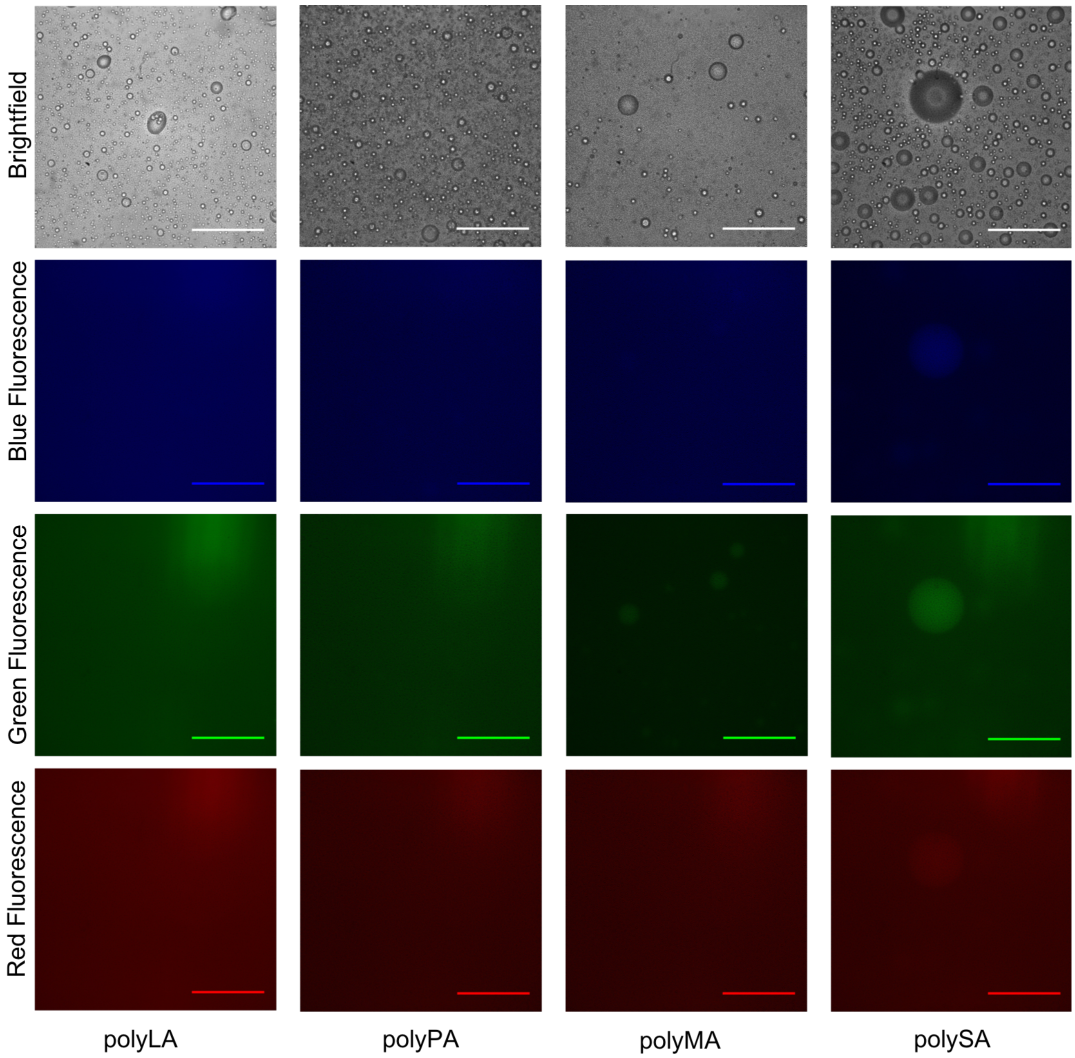
Additional fluorescence microscopy images of poly(4a2h-MA) droplets (1:4 4a2h:MA; 500 mM total monomer concentration before synthesis) in all emission channels. Each column represents a single sample. We observed some variability in the intrinsic fluorescence, and further detailed investigations are planned. Scale bars are 100 µm. Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (brightness, contrast) parameters were constant down each column.

Figure S35



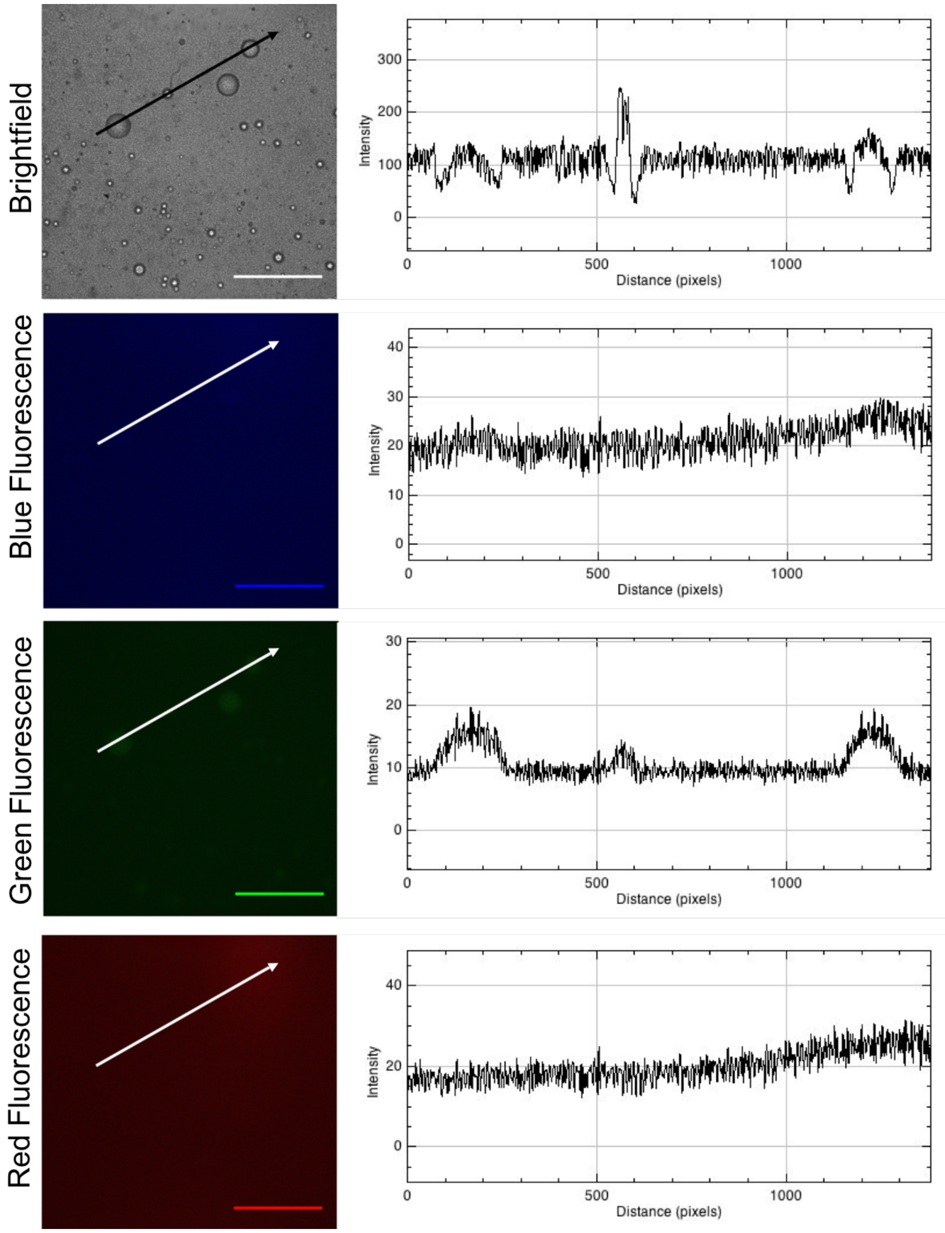
Additional fluorescence microscopy images of poly(4a2h-SA) droplets (1:4 4a2h:SA; 500 mM total monomer concentration before synthesis) in all emission channels. Each column represents a single sample. We observed some variability in the intrinsic fluorescence, and further detailed investigations are planned. Scale bars are 100 μm. Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (brightness, contrast) parameters were constant down each column.

Figure S36



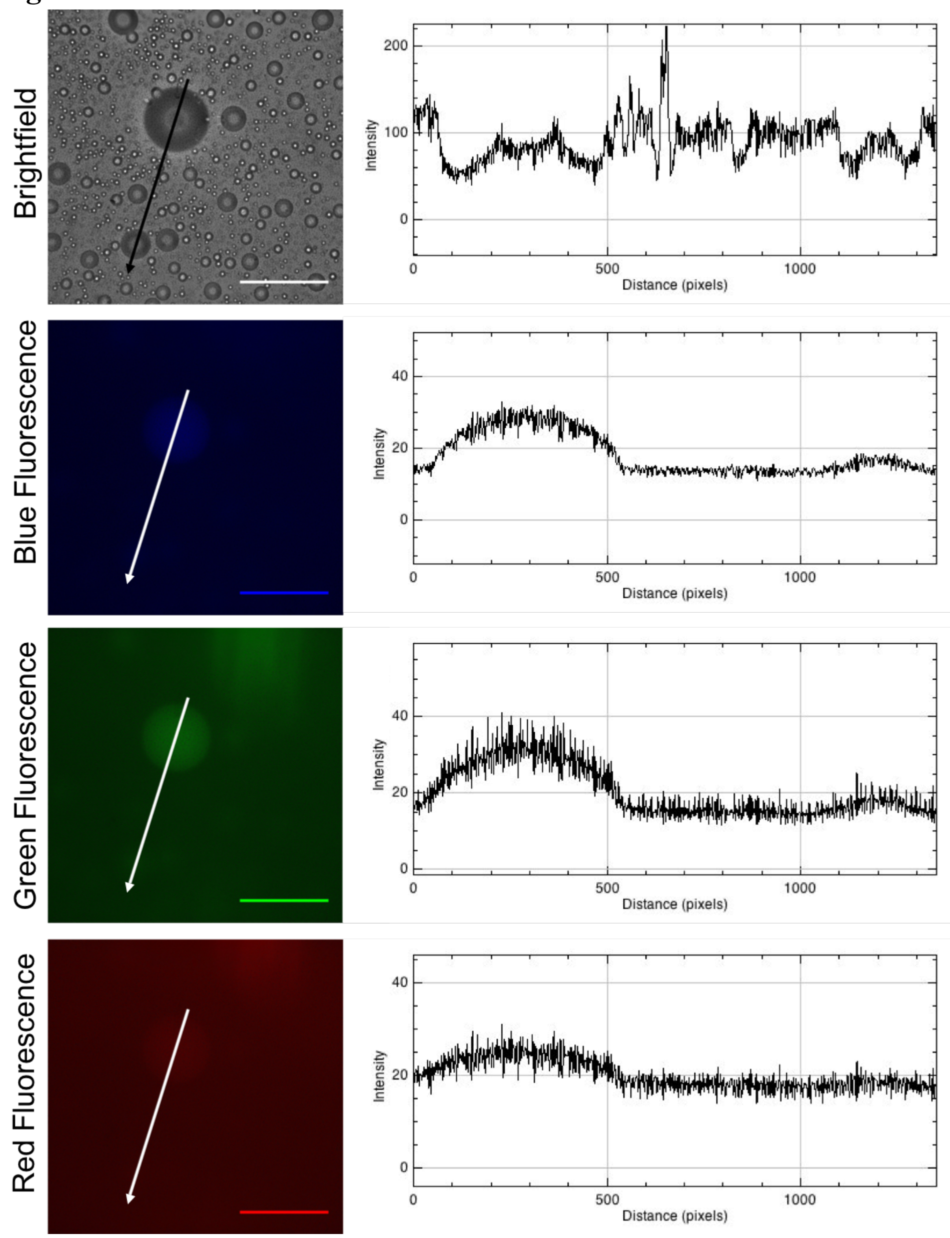
Representative brightfield and fluorescence microscopy images of homopolyester droplets in blue (470 nm emission), green (527 nm emission), and red (585 nm emission) channels. Each column represents a single sample. While polyMA and polySA show slight intrinsic fluorescence in one or more channels (**Figs. S36–S38**), polyLA and polyPA show little to no fluorescence (**Figs. S39–S40**). This suggests that incorporation of 4a2h into polyLA or polyPA systems may convey the emergence of fluorescent properties within 4a2h-containing heteropolyester droplets observed in **Figure 8**. Incorporation of 4a2h into the polyMA system in particular may expand the type of fluorescence exhibited, as potentially stronger blue fluorescence was observed (in addition to the green fluorescence originally observed in polyMA) in the poly(4a2h-MA) system (**Figs. 8** and **S34**). Scale bars are 100 µm. Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (brightness, contrast) parameters were constant down each column.

Figure S37



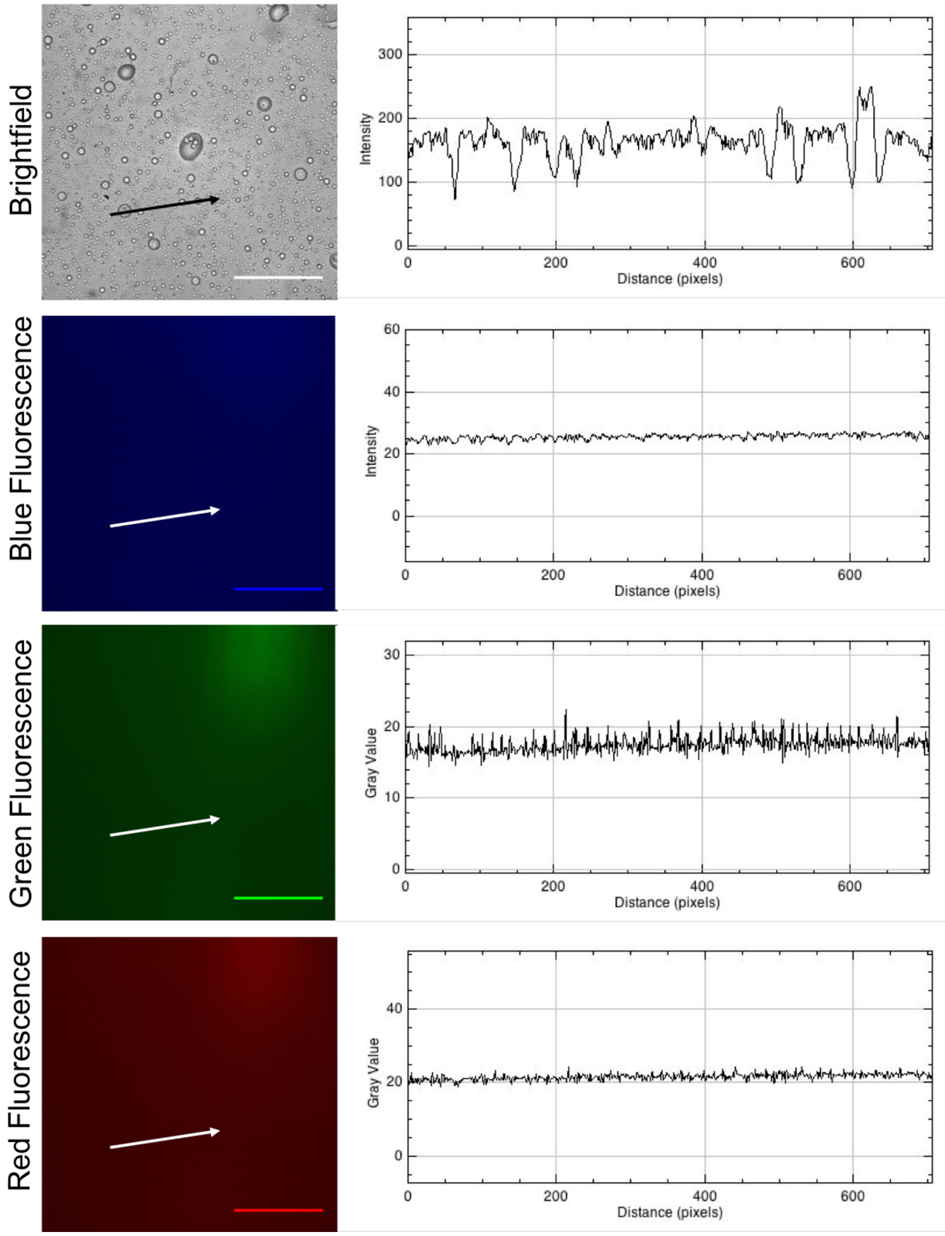
Representative brightfield and fluorescence microscopy images of polyMA droplets in blue (470 nm emission), green (527 nm emission), and red (585 nm emission) channels with accompanying kymographs. The region and direction of analysis for each image were identical (in black for brightfield image and in white for fluorescence images; arrows indicate direction of analysis). The column represents a single sample. polyMA apparently shows some intrinsic fluorescence (especially green fluorescence) based on kymograph analysis. Scale bars are 100 µm (615.38 pixels). Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (contrast, brightness) parameters were constant down the column.

Figure S38



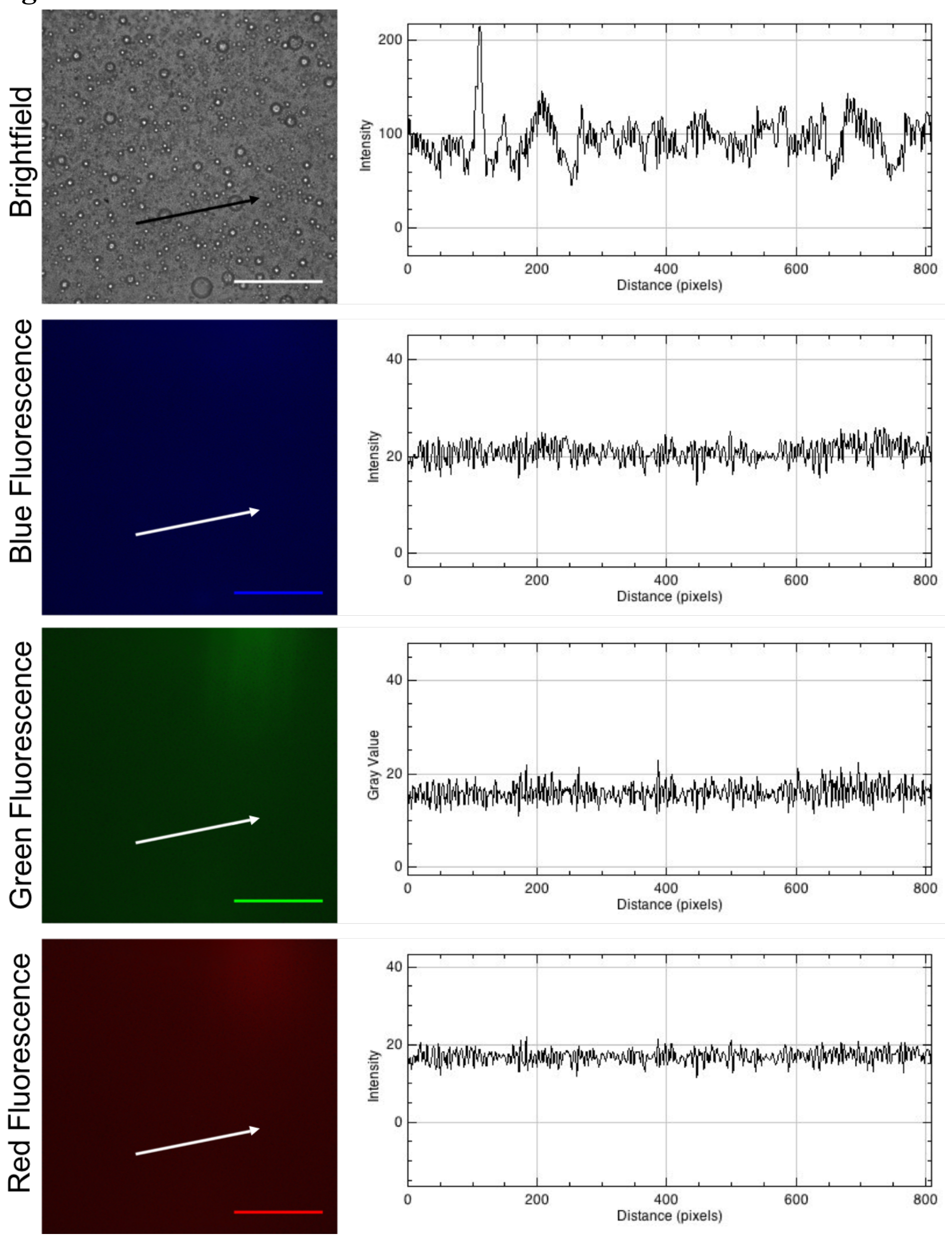
Representative brightfield and fluorescence microscopy images of polySA droplets in blue (470 nm emission), green (527 nm emission), and red (585 nm emission) channels with accompanying kymographs. The region and direction of analysis for each image were identical (in black for brightfield image and in white for fluorescence images; arrows indicate direction of analysis). The column represents a single sample. polySA shows some intrinsic fluorescence in all channels as evidenced by the kymograph analysis. Scale bars are 100 µm (615.38 pixels). Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (contrast, brightness) parameters were constant down the column.

Figure S39



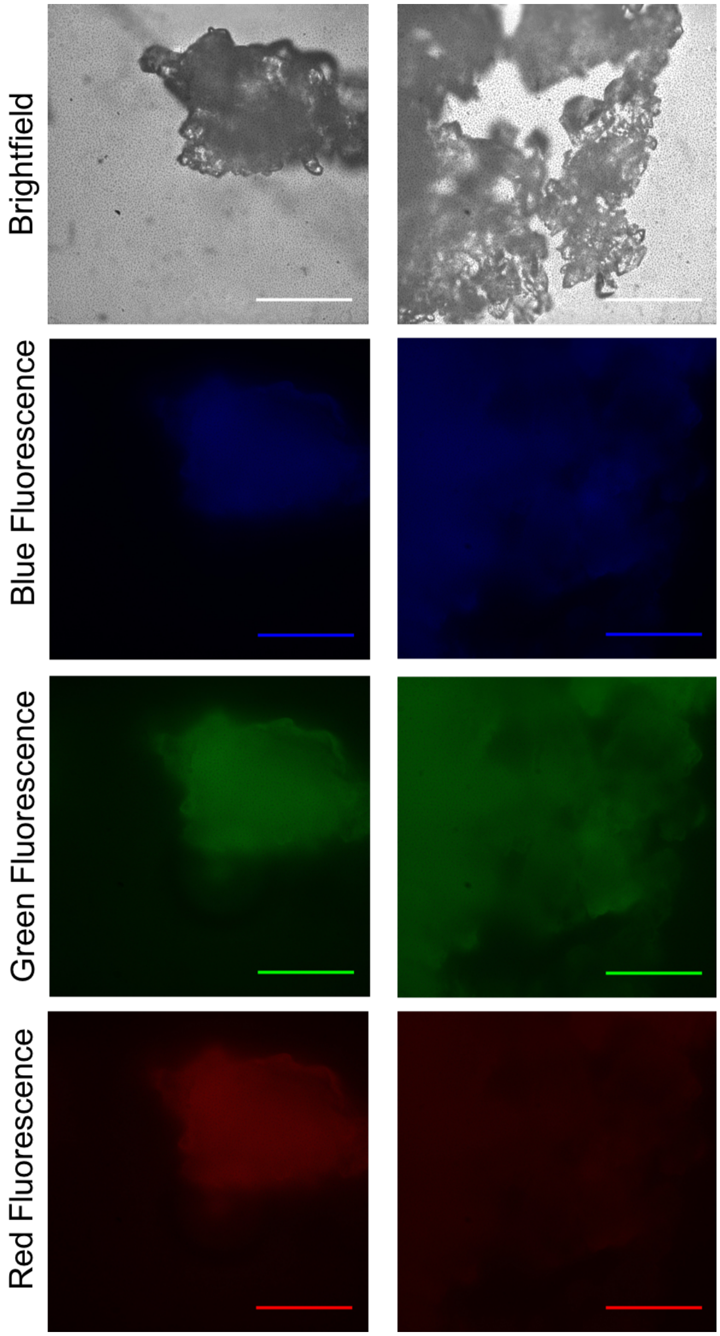
Representative brightfield and fluorescence microscopy images of polyLA droplets in blue (470 nm emission), green (527 nm emission), and red (585 nm emission) channels with accompanying kymographs. The region and direction of analysis for each image were identical (in black for brightfield image and in white for fluorescence images; arrows indicate direction of analysis). The column represents a single sample. polyLA shows little to no intrinsic fluorescence. Scale bars are 100 µm (615.38 pixels). Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (contrast, brightness) parameters were constant down the column.

Figure S40



Representative brightfield and fluorescence microscopy images of polyPA droplets in blue (470 nm emission), green (527 nm emission), and red (585 nm emission) channels with accompanying kymographs. The region and direction of analysis for each image were identical (in black for brightfield image and in white for fluorescence images; arrows indicate direction of analysis). The column represents a single sample. polyPA shows no clearly observable intrinsic fluorescence based on kymograph analysis. Scale bars are 100 µm (615.38 pixels). Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (contrast, brightness) parameters were constant down the column.

Figure S41



Representative brightfield and fluorescence microscopy images of the white powdery product from drying of 4a2h monomer solution (**Fig. S2**) in blue (470 nm emission), green (527 nm emission), and red (585 nm emission) channels. Each column represents a single sample. This product may show some apparent fluorescence. Scale bars are 100 µm (615.38 pixels). Fluorescence acquisition (excitation illumination strength and exposure time) and image processing (contrast, brightness) parameters were constant down the column; this acquisition and image analysis was performed once.

Table S1. Peak list sorted by mass for poly(4a2h) positive mode MALDI-TOF-MS (**Fig. S1**); protonated peaks. "M+H-H_2O (cyclic)": possibility of both dehydrated or cyclic species.

Observed Mass (m/z)	Intensity	Calculated Mass	Identity	Adduct	PPM
120.0731659	510367.5448	120.065519	4a2h	M+H	63.68934282
203.1046448	15413.79948	203.102637	$(4a2h)_2$	M+H-H_2O (cyclic)	9.885519113
221.1161804	69864.22229	221.113202	$(4a2h)_2$	M+H	13.47011383
304.1588745	10586.59585	304.15032	$(4a2h)_3$	M+H-H_2O (cyclic)	28.12593457
322.1725769	91069.28237	322.160885	$(4a2h)_3$	M+H	36.29212777
423.2255859	58388.26055	423.208568	$(4a2h)_4$	M+H	40.21170479
524.2819214	26539.99417	524.256251	$(4a2h)_5$	M+H	48.96534271
625.3421021	8320.135667	625.303934	$(4a2h)_6$	M+H	61.03919858

Table S2. Peak list sorted by adduct and then mass and also colorcoded (for ease of visualization) for poly(4a2h) positive mode MALDI-TOF-MS (**Fig. S1**); protonated peaks. "M+H-H_2O (cyclic)": possibility of both dehydrated or cyclic species.

Observed Mass (m/z)	Intensity	Calculated Mass	Identity	Adduct	PPM
120.0731659	510367.5448	120.065519	4a2h	M+H	63.68934282
221.1161804	69864.22229	221.113202	$(4a2h)_2$	M+H	13.47011383
322.1725769	91069.28237	322.160885	$(4a2h)_3$	M+H	36.29212777
423.2255859	58388.26055	423.208568	$(4a2h)_4$	M+H	40.21170479
524.2819214	26539.99417	524.256251	$(4a2h)_5$	M+H	48.96534271
625.3421021	8320.135667	625.303934	$(4a2h)_6$	M+H	61.03919858
203.1046448	15413.79948	203.102637	$(4a2h)_2$	M+H-H_2O (cyclic)	9.885519113
304.1588745	10586.59585	304.15032	$(4a2h)_3$	M+H-H_2O (cyclic)	28.12593457

Table S3. Peak list sorted by mass for poly(4a2h-GA) positive mode MALDI-TOF-MS (**Figs. 2** and **S6**); sodiated and protonated peaks. "M+H/Na-H_2O (cyclic)": possibility of both dehydrated or cyclic species.

Observed Mass (m/z)	Intensity	Calculated Mass	Identity	Adduct	PPM
124.0400009	**40223.07344**	**124.036896**	**4a2h**	**M+Na-H_2O (cyclic)**	**25.03219687**
182.0437775	**14999.38361**	**182.042376**	**(4a2h)GA**	**M+Na-H_2O (cyclic)**	**7.69857014**
200.0528717	**8975.386506**	**200.052941**	**(4a2h)GA**	**M+Na**	**0.346388309**
203.1046448	**335548.2198**	**203.102637**	**$(4a2h)_2$**	**M+H-H_2O (cyclic)**	**9.885519113**
221.1161804	**11685.60477**	**221.113202**	**$(4a2h)_2$**	**M+H**	**13.47011383**
225.0892334	**14974.01782**	**225.084579**	**$(4a2h)_2$**	**M+Na-H_2O (cyclic)**	**20.67844017**
261.1126099	**135610.0097**	**261.108117**	**$(4a2h)_2$GA**	**M+H-H_2O (cyclic)**	**17.20690667**
283.0907593	**82496.61156**	**283.090059**	**$(4a2h)_2$GA**	**M+Na-H_2O (cyclic)**	**2.47368983**
286.1491699	**441457.0766**	**286.13789**	**$(4a2h)_2$**	**M+ethanolamine+Na**	**39.42128042**
301.1065063	**19510.88378**	**301.100624**	**$(4a2h)_2$GA**	**M+Na**	**19.53615347**
304.1588745	**195246.9344**	**304.15032**	**$(4a2h)_3$**	**M+H-H_2O (cyclic)**	**28.12593457**
319.1213379	**17488.47027**	**319.113597**	**$(4a2h)_2GA_2$**	**M+H-H_2O (cyclic)**	**24.25747782**
326.1412048	**20728.48335**	**326.132262**	**$(4a2h)_3$**	**M+Na-H_2O (cyclic)**	**27.42088116**
341.1045532	**36320.30733**	**341.095539**	**$(4a2h)_2GA_2$**	**M+Na-H_2O (cyclic)**	**26.42726735**
344.1555176	**108391.6045**	**344.143365**	**$(4a2h)_2$GA**	**M+ethanolamine+Na**	**35.31254482**
359.1139221	**20225.99359**	**359.106104**	**$(4a2h)_2GA_2$**	**M+Na**	**21.77105572**
362.1670837	**191480.3936**	**362.1558**	**$(4a2h)_3$GA**	**M+H-H_2O (cyclic)**	**31.15714286**
384.1511536	**94434.368**	**384.137742**	**$(4a2h)_3$GA**	**M+Na-H_2O (cyclic)**	**34.91342436**
387.204071	**185011.0484**	**387.185568**	**$(4a2h)_3$**	**M+ethanolamine+Na**	**47.78857098**
399.1156616	**9479.577466**	**399.101019**	**$(4a2h)_2GA_3$**	**M+Na-H_2O (cyclic)**	**36.68900931**
402.1612854	**31872.25501**	**402.148845**	**$(4a2h)_2GA_2$**	**M+ethanolamine+Na**	**30.9348147**
402.1612854	**31872.25501**	**402.148307**	**$(4a2h)_3$GA**	**M+Na**	**32.27267099**
405.2134399	**74933.90811**	**405.198003**	**$(4a2h)_4$**	**M+H-H_2O (cyclic)**	**38.09727809**

417.1277466	**10683.35167**	**417.111584**	**$(4a2h)_2GA_3$**	**M+Na**	**38.74882075**
420.1789246	**61115.46674**	**420.16128**	**$(4a2h)_3GA_2$**	**M+H-H_2O (cyclic)**	**41.99473355**
427.1964722	**17597.17866**	**427.179945**	**$(4a2h)_4$**	**M+Na-H_2O (cyclic)**	**38.68900728**
442.1593018	**72077.419**	**442.143222**	**$(4a2h)_3GA_2$**	**M+Na-H_2O (cyclic)**	**36.36775868**
445.2150574	**158052.4843**	**445.191048**	**$(4a2h)_3GA$**	**M+ethanolamine+Na**	**53.93049368**
460.1722412	**31517.05646**	**460.154325**	**$(4a2h)_2GA_3$**	**M+ethanolamine+Na**	**38.93522244**
460.1722412	**31517.05646**	**460.153787**	**$(4a2h)_3GA_2$**	**M+Na**	**40.1044423**
463.2295227	**133427.5362**	**463.203483**	**$(4a2h)_4GA$**	**M+H-H_2O (cyclic)**	**56.21655699**
478.1901855	**12458.87168**	**478.16676**	**$(4a2h)_3GA_3$**	**M+H-H_2O (cyclic)**	**48.99032923**
485.2112732	**65778.20395**	**485.185425**	**$(4a2h)_4GA$**	**M+Na-H_2O (cyclic)**	**53.27487527**
488.2608948	**59412.83895**	**488.233251**	**$(4a2h)_4$**	**M+ethanolamine+Na**	**56.62001706**
500.1743164	**28151.63465**	**500.148702**	**$(4a2h)_3GA_3$**	**M+Na-H_2O (cyclic)**	**51.21358088**
503.2250366	**59062.58119**	**503.196528**	**$(4a2h)_3GA_2$**	**M+ethanolamine+Na**	**56.65504314**
503.2250366	**59062.58119**	**503.19599**	**$(4a2h)_4GA$**	**M+Na**	**57.72426962**
506.2736511	**24984.10188**	**506.245686**	**$(4a2h)_5$**	**M+H-H_2O (cyclic)**	**55.24021986**
518.1901245	**20255.6906**	**518.159805**	**$(4a2h)_2GA_4$**	**M+ethanolamine+Na**	**58.51382471**
518.1901245	**20255.6906**	**518.159267**	**$(4a2h)_3GA_3$**	**M+Na**	**59.55217626**
521.2373657	**78040.06133**	**521.208963**	**$(4a2h)_4GA_2$**	**M+H-H_2O (cyclic)**	**54.49392665**
528.2578735	**9805.778115**	**528.227628**	**$(4a2h)_5$**	**M+Na-H_2O (cyclic)**	**57.2585253**
543.2216797	**74038.11748**	**543.190905**	**$(4a2h)_4GA_2$**	**M+Na-H_2O (cyclic)**	**56.65538159**
546.2705078	**95953.86078**	**546.238731**	**$(4a2h)_4GA$**	**M+ethanolamine+Na**	**58.17385366**
558.190979	**7890.231182**	**558.154182**	**$(4a2h)_3GA_4$**	**M+Na-H_2O (cyclic)**	**65.92623541**
561.2334595	**35523.90839**	**561.202008**	**$(4a2h)_3GA_3$**	**M+ethanolamine+Na**	**56.04305144**
561.2334595	**35523.90839**	**561.20147**	**$(4a2h)_4GA_2$**	**M+Na**	**57.00176266**
564.2841797	**66350.08315**	**564.251166**	**$(4a2h)_5GA$**	**M+H-H_2O (cyclic)**	**58.50885207**
576.2038574	**8625.756098**	**576.165285**	**$(4a2h)_2GA_5$**	**M+ethanolamine+Na**	**66.94679982**

576.2038574	**8625.756098**	**576.164747**	**$(4a2h)_3GA_4$**	**M+Na**	**67.88062304**
579.2522583	**25827.92332**	**579.214443**	**$(4a2h)_4GA_3$**	**M+H-H_2O (cyclic)**	**65.2872204**
586.2652588	**35965.79904**	**586.233108**	**$(4a2h)_5GA$**	**M+Na-H_2O (cyclic)**	**54.84301136**
589.3154907	**18672.64635**	**589.280934**	**$(4a2h)_5$**	**M+ethanolamine+Na**	**58.64218746**
601.234314	**42399.11653**	**601.196385**	**$(4a2h)_4GA_3$**	**M+Na-H_2O (cyclic)**	**63.08914349**
604.2858276	**59753.9657**	**604.244211**	**$(4a2h)_4GA_2$**	**M+ethanolamine+Na**	**68.87386961**
604.2858276	**59753.9657**	**604.243673**	**$(4a2h)_5GA$**	**M+Na**	**69.7643002**
619.2484741	**26191.3836**	**619.207488**	**$(4a2h)_3GA_4$**	**M+ethanolamine+Na**	**66.19125543**
619.2484741	**26191.3836**	**619.20695**	**$(4a2h)_4GA_3$**	**M+Na**	**67.06016623**
622.3010254	**60049.53752**	**622.256646**	**$(4a2h)_5GA_2$**	**M+H-H_2O (cyclic)**	**71.32007554**
644.2799072	**51772.70637**	**644.238588**	**$(4a2h)_5GA_2$**	**M+Na-H_2O (cyclic)**	**64.13652918**
647.3355103	**42949.31003**	**647.286414**	**$(4a2h)_5GA$**	**M+ethanolamine+Na**	**75.84935036**
659.2451172	**16151.97222**	**659.201865**	**$(4a2h)_4GA_4$**	**M+Na-H_2O (cyclic)**	**65.61296364**
662.296814	**35461.14964**	**662.249691**	**$(4a2h)_4GA_3$**	**M+ethanolamine+Na**	**71.15588824**
662.296814	**35461.14964**	**662.249153**	**$(4a2h)_5GA_2$**	**M+Na**	**71.96832912**
665.3424072	**27933.75054**	**665.298849**	**$(4a2h)_6GA$**	**M+H-H_2O (cyclic)**	**65.47167046**
677.2575073	**13511.1714**	**677.212968**	**$(4a2h)_3GA_5$**	**M+ethanolamine+Na**	**65.76856337**
677.2575073	**13511.1714**	**677.21243**	**$(4a2h)_4GA_4$**	**M+Na**	**66.56304876**
680.3108521	**30417.34061**	**680.262126**	**$(4a2h)_5GA_3$**	**M+H-H_2O (cyclic)**	**71.6283461**
687.3244019	**16780.62446**	**687.280791**	**$(4a2h)_6GA$**	**M+Na-H_2O (cyclic)**	**63.45420325**
702.2949829	**39848.25195**	**702.244068**	**$(4a2h)_5GA_3$**	**M+Na-H_2O (cyclic)**	**72.50315427**
705.3435669	**40697.91891**	**705.291894**	**$(4a2h)_5GA_2$**	**M+ethanolamine+Na**	**73.26455251**
705.3435669	**40697.91891**	**705.291356**	**$(4a2h)_6GA$**	**M+Na**	**74.02741371**
717.263855	**5412.926919**	**717.207345**	**$(4a2h)_4GA_5$**	**M+Na-H_2O (cyclic)**	**78.79169168**
720.303894	**24036.04273**	**720.255171**	**$(4a2h)_4GA_4$**	**M+ethanolamine+Na**	**67.64691871**
720.303894	**24036.04273**	**720.254633**	**$(4a2h)_5GA_3$**	**M+Na**	**68.39392729**

723.3572388	**35069.74033**	**723.304329**	**$(4a2h)_6GA_2$**	**M+H-H_2O (cyclic)**	**73.15008065**
735.2769165	**5993.886221**	**735.218448**	**$(4a2h)_3GA_6$**	**M+ethanolamine+Na**	**79.52534945**
735.2769165	**5993.886221**	**735.21791**	**$(4a2h)_4GA_5$**	**M+Na**	**80.25716348**
738.3204346	**11056.77839**	**738.267606**	**$(4a2h)_5GA_4$**	**M+H-H_2O (cyclic)**	**71.55748074**
745.3424072	**28520.67782**	**745.286271**	**$(4a2h)_6GA_2$**	**M+Na-H_2O (cyclic)**	**75.32169743**
748.3928223	**17103.13495**	**748.334097**	**$(4a2h)_6GA$**	**M+ethanolamine+Na**	**78.4746629**
760.3064575	**20013.44797**	**760.249548**	**$(4a2h)_5GA_4$**	**M+Na-H_2O (cyclic)**	**74.85636808**
763.3522339	**28262.33855**	**763.297374**	**$(4a2h)_5GA_3$**	**M+ethanolamine+Na**	**71.87223338**
763.3522339	**28262.33855**	**763.296836**	**$(4a2h)_6GA_2$**	**M+Na**	**72.57712123**
766.4041748	**11138.89027**	**766.346532**	**$(4a2h)_7GA$**	**M+H-H_2O (cyclic)**	**75.21767581**
778.3182983	**15354.55148**	**778.260651**	**$(4a2h)_4GA_5$**	**M+ethanolamine+Na**	**74.07202192**
778.3182983	**15354.55148**	**778.260113**	**$(4a2h)_5GA_4$**	**M+Na**	**74.76335871**
781.3716431	**24798.47332**	**781.309809**	**$(4a2h)_6GA_3$**	**M+H-H_2O (cyclic)**	**79.14154576**
788.3884888	**7519.70457**	**788.328474**	**$(4a2h)_7GA$**	**M+Na-H_2O (cyclic)**	**76.12914157**
803.352478	**27697.001**	**803.291751**	**$(4a2h)_6GA_3$**	**M+Na-H_2O (cyclic)**	**75.59772265**
806.4040527	**21790.57475**	**806.339577**	**$(4a2h)_6GA_2$**	**M+ethanolamine+Na**	**79.96101871**
806.4040527	**21790.57475**	**806.339039**	**$(4a2h)_7GA$**	**M+Na**	**80.62828519**
818.3193359	**7880.62899**	**818.255028**	**$(4a2h)_5GA_5$**	**M+Na-H_2O (cyclic)**	**78.59155862**
821.362854	**19850.48399**	**821.302854**	**$(4a2h)_5GA_4$**	**M+ethanolamine+Na**	**73.05466395**
821.362854	**19850.48399**	**821.302316**	**$(4a2h)_6GA_3$**	**M+Na**	**73.70976901**
824.4120483	**17648.81544**	**824.352012**	**$(4a2h)_7GA_2$**	**M+H-H_2O (cyclic)**	**72.82852365**
836.3344727	**7486.395318**	**836.266131**	**$(4a2h)_4GA_6$**	**M+ethanolamine+Na**	**81.72237696**
836.3344727	**7486.395318**	**836.265593**	**$(4a2h)_5GA_5$**	**M+Na**	**82.36576582**
839.381897	**12227.83666**	**839.315289**	**$(4a2h)_6GA_4$**	**M+H-H_2O (cyclic)**	**79.35989475**
846.395874	**14387.72797**	**846.333954**	**$(4a2h)_7GA_2$**	**M+Na-H_2O (cyclic)**	**73.16263599**
861.3621826	**17605.83479**	**861.297231**	**$(4a2h)_6GA_4$**	**M+Na-H_2O (cyclic)**	**75.4113849**

864.4101563	**18499.07725**	**864.345057**	**$(4a2h)_6GA_3$**	**M+ethanolamine+Na**	**75.31627499**
864.4101563	**18499.07725**	**864.344519**	**$(4a2h)_7GA_2$**	**M+Na**	**75.93875886**
879.3763428	**13311.35027**	**879.308334**	**$(4a2h)_5GA_5$**	**M+ethanolamine+Na**	**77.34348734**
879.3763428	**13311.35027**	**879.307796**	**$(4a2h)_6GA_4$**	**M+Na**	**77.95537957**
882.4258423	**16284.32368**	**882.357492**	**$(4a2h)_7GA_3$**	**M+H-H_2O (cyclic)**	**77.46325681**
904.4099731	**16316.53843**	**904.339434**	**$(4a2h)_7GA_3$**	**M+Na-H_2O (cyclic)**	**78.00073993**
907.456665	**9863.059684**	**907.38726**	**$(4a2h)_7GA_2$**	**M+ethanolamine+Na**	**76.48888414**
907.456665	**9863.059684**	**907.386722**	**$(4a2h)_8GA$**	**M+Na**	**77.08184097**
919.3787231	**8939.006052**	**919.302711**	**$(4a2h)_6GA_5$**	**M+Na-H_2O (cyclic)**	**82.68456526**
922.4274292	**13749.00442**	**922.350537**	**$(4a2h)_6GA_4$**	**M+ethanolamine+Na**	**83.36548407**
922.4274292	**13749.00442**	**922.349999**	**$(4a2h)_7GA_3$**	**M+Na**	**83.94882537**
937.3886719	**7765.893903**	**937.313814**	**$(4a2h)_5GA_6$**	**M+ethanolamine+Na**	**79.86426091**
937.3886719	**7765.893903**	**937.313276**	**$(4a2h)_6GA_5$**	**M+Na**	**80.43828774**
940.4359741	**9876.554511**	**940.362972**	**$(4a2h)_7GA_4$**	**M+H-H_2O (cyclic)**	**77.63185405**
962.4266357	**13010.21676**	**962.344914**	**$(4a2h)_7GA_4$**	**M+Na-H_2O (cyclic)**	**84.91938889**
965.467041	**10383.62124**	**965.39274**	**$(4a2h)_7GA_3$**	**M+ethanolamine+Na**	**76.96454813**
965.467041	**10383.62124**	**965.392202**	**$(4a2h)_8GA_2$**	**M+Na**	**77.52187748**
980.4384766	**10019.87347**	**980.356017**	**$(4a2h)_6GA_5$**	**M+ethanolamine+Na**	**84.11185383**
980.4384766	**10019.87347**	**980.355479**	**$(4a2h)_7GA_4$**	**M+Na**	**84.66068052**
1020.439514	**7355.481173**	**1020.350394**	**$(4a2h)_7GA_5$**	**M+Na-H_2O (cyclic)**	**87.34270161**
1023.480896	**8763.829756**	**1023.39822**	**$(4a2h)_7GA_4$**	**M+ethanolamine+Na**	**80.78575708**
1023.480896	**8763.829756**	**1023.397682**	**$(4a2h)_8GA_3$**	**M+Na**	**81.31149939**
1038.444336	**6218.391766**	**1038.361497**	**$(4a2h)_6GA_6$**	**M+ethanolamine+Na**	**79.77851667**
1038.444336	**6218.391766**	**1038.360959**	**$(4a2h)_7GA_5$**	**M+Na**	**80.29668226**
1081.49353	**6526.155217**	**1081.4037**	**$(4a2h)_7GA_5$**	**M+ethanolamine+Na**	**83.06821033**
1081.49353	**6526.155217**	**1081.403162**	**$(4a2h)_8GA_4$**	**M+Na**	**83.56575344**

Table S4. Peak list sorted by adduct and then mass and also colorcoded (for ease of visualization) for poly(4a2h-GA) positive mode MALDI-TOF-MS (**Figs. 2** and **S6**); sodiated and protonated peaks. "M+H/Na-H_2O (cyclic)": possibility of both dehydrated or cyclic species.

Observed Mass (m/z)	Intensity	Calculated Mass	Identity	Adduct	PPM
286.1491699	441457.0766	286.13789	$(4a2h)_2$	M+ethanolamine+Na	39.42128042
344.1555176	108391.6045	344.143365	$(4a2h)_2GA$	M+ethanolamine+Na	35.31254482
387.204071	185011.0484	387.185568	$(4a2h)_3$	M+ethanolamine+Na	47.78857098
402.1612854	31872.25501	402.148845	$(4a2h)_2GA_2$	M+ethanolamine+Na	30.9348147
445.2150574	158052.4843	445.191048	$(4a2h)_3GA$	M+ethanolamine+Na	53.93049368
460.1722412	31517.05646	460.154325	$(4a2h)_2GA_3$	M+ethanolamine+Na	38.93522244
488.2608948	59412.83895	488.233251	$(4a2h)_4$	M+ethanolamine+Na	56.62001706
503.2250366	59062.58119	503.196528	$(4a2h)_3GA_2$	M+ethanolamine+Na	56.65504314
518.1901245	20255.6906	518.159805	$(4a2h)_2GA_4$	M+ethanolamine+Na	58.51382471
546.2705078	95953.86078	546.238731	$(4a2h)_4GA$	M+ethanolamine+Na	58.17385366
561.2334595	35523.90839	561.202008	$(4a2h)_3GA_3$	M+ethanolamine+Na	56.04305144
576.2038574	8625.756098	576.165285	$(4a2h)_2GA_5$	M+ethanolamine+Na	66.94679982
589.3154907	18672.64635	589.280934	$(4a2h)_5$	M+ethanolamine+Na	58.64218746
604.2858276	59753.9657	604.244211	$(4a2h)_4GA_2$	M+ethanolamine+Na	68.87386961
619.2484741	26191.3836	619.207488	$(4a2h)_3GA_4$	M+ethanolamine+Na	66.19125543
647.3355103	42949.31003	647.286414	$(4a2h)_5GA$	M+ethanolamine+Na	75.84935036
662.296814	35461.14964	662.249691	$(4a2h)_4GA_3$	M+ethanolamine+Na	71.15588824
677.2575073	13511.1714	677.212968	$(4a2h)_3GA_5$	M+ethanolamine+Na	65.76856337
705.3435669	40697.91891	705.291894	$(4a2h)_5GA_2$	M+ethanolamine+Na	73.26455251
720.303894	24036.04273	720.255171	$(4a2h)_4GA_4$	M+ethanolamine+Na	67.64691871
735.2769165	5993.886221	735.218448	$(4a2h)_3GA_6$	M+ethanolamine+Na	79.52534945
748.3928223	17103.13495	748.334097	$(4a2h)_6GA$	M+ethanolamine+Na	78.4746629
763.3522339	28262.33855	763.297374	$(4a2h)_5GA_3$	M+ethanolamine+Na	71.87223338

778.3182983	15354.55148	778.260651	$(4a2h)_4GA_5$	M+ethanolamine+Na	74.07202192
806.4040527	21790.57475	806.339577	$(4a2h)_6GA_2$	M+ethanolamine+Na	79.96101871
821.362854	19850.48399	821.302854	$(4a2h)_5GA_4$	M+ethanolamine+Na	73.05466395
836.3344727	7486.395318	836.266131	$(4a2h)_4GA_6$	M+ethanolamine+Na	81.72237696
864.4101563	18499.07725	864.345057	$(4a2h)_6GA_3$	M+ethanolamine+Na	75.31627499
879.3763428	13311.35027	879.308334	$(4a2h)_5GA_5$	M+ethanolamine+Na	77.34348734
907.456665	9863.059684	907.38726	$(4a2h)_7GA_2$	M+ethanolamine+Na	76.48888414
922.4274292	13749.00442	922.350537	$(4a2h)_6GA_4$	M+ethanolamine+Na	83.36548407
937.3886719	7765.893903	937.313814	$(4a2h)_5GA_6$	M+ethanolamine+Na	79.86426091
965.467041	10383.62124	965.39274	$(4a2h)_7GA_3$	M+ethanolamine+Na	76.96454813
980.4384766	10019.87347	980.356017	$(4a2h)_6GA_5$	M+ethanolamine+Na	84.11185383
1023.480896	8763.829756	1023.39822	$(4a2h)_7GA_4$	M+ethanolamine+Na	80.78575708
1038.444336	6218.391766	1038.361497	$(4a2h)_6GA_6$	M+ethanolamine+Na	79.77851667
1081.49353	6526.155217	1081.4037	$(4a2h)_7GA_5$	M+ethanolamine+Na	83.06821033
221.1161804	11685.60477	221.113202	$(4a2h)_2$	M+H	13.47011383
203.1046448	335548.2198	203.102637	$(4a2h)_2$	M+H-H_2O (cyclic)	9.885519113
261.1126099	135610.0097	261.108117	$(4a2h)_2GA$	M+H-H_2O (cyclic)	17.20690667
304.1588745	195246.9344	304.15032	$(4a2h)_3$	M+H-H_2O (cyclic)	28.12593457
319.1213379	17488.47027	319.113597	$(4a2h)_2GA_2$	M+H-H_2O (cyclic)	24.25747782
362.1670837	191480.3936	362.1558	$(4a2h)_3GA$	M+H-H_2O (cyclic)	31.15714286
405.2134399	74933.90811	405.198003	$(4a2h)_4$	M+H-H_2O (cyclic)	38.09727809
420.1789246	61115.46674	420.16128	$(4a2h)_3GA_2$	M+H-H_2O (cyclic)	41.99473355
463.2295227	133427.5362	463.203483	$(4a2h)_4GA$	M+H-H_2O (cyclic)	56.21655699
478.1901855	12458.87168	478.16676	$(4a2h)_3GA_3$	M+H-H_2O (cyclic)	48.99032923
506.2736511	24984.10188	506.245686	$(4a2h)_5$	M+H-H_2O (cyclic)	55.24021986
521.2373657	78040.06133	521.208963	$(4a2h)_4GA_2$	M+H-H_2O (cyclic)	54.49392665

564.2841797	66350.08315	564.251166	$(4a2h)_5GA$	M+H-H_2O (cyclic)	58.50885207
579.2522583	25827.92332	579.214443	$(4a2h)_4GA_3$	M+H-H_2O (cyclic)	65.2872204
622.3010254	60049.53752	622.256646	$(4a2h)_5GA_2$	M+H-H_2O (cyclic)	71.32007554
665.3424072	27933.75054	665.298849	$(4a2h)_6GA$	M+H-H_2O (cyclic)	65.47167046
680.3108521	30417.34061	680.262126	$(4a2h)_5GA_3$	M+H-H_2O (cyclic)	71.6283461
723.3572388	35069.74033	723.304329	$(4a2h)_6GA_2$	M+H-H_2O (cyclic)	73.15008065
738.3204346	11056.77839	738.267606	$(4a2h)_5GA_4$	M+H-H_2O (cyclic)	71.55748074
766.4041748	11138.89027	766.346532	$(4a2h)_7GA$	M+H-H_2O (cyclic)	75.21767581
781.3716431	24798.47332	781.309809	$(4a2h)_6GA_3$	M+H-H_2O (cyclic)	79.14154576
824.4120483	17648.81544	824.352012	$(4a2h)_7GA_2$	M+H-H_2O (cyclic)	72.82852365
839.381897	12227.83666	839.315289	$(4a2h)_6GA_4$	M+H-H_2O (cyclic)	79.35989475
882.4258423	16284.32368	882.357492	$(4a2h)_7GA_3$	M+H-H_2O (cyclic)	77.46325681
940.4359741	9876.554511	940.362972	$(4a2h)_7GA_4$	M+H-H_2O (cyclic)	77.63185405
200.0528717	8975.386506	200.052941	(4a2h)GA	M+Na	0.346388309
301.1065063	19510.88378	301.100624	$(4a2h)_2GA$	M+Na	19.53615347
359.1139221	20225.99359	359.106104	$(4a2h)_2GA_2$	M+Na	21.77105572
402.1612854	31872.25501	402.148307	$(4a2h)_3GA$	M+Na	32.27267099
417.1277466	10683.35167	417.111584	$(4a2h)_2GA_3$	M+Na	38.74882075
460.1722412	31517.05646	460.153787	$(4a2h)_3GA_2$	M+Na	40.1044423
503.2250366	59062.58119	503.19599	$(4a2h)_4GA$	M+Na	57.72426962
518.1901245	20255.6906	518.159267	$(4a2h)_3GA_3$	M+Na	59.55217626
561.2334595	35523.90839	561.20147	$(4a2h)_4GA_2$	M+Na	57.00176266
576.2038574	8625.756098	576.164747	$(4a2h)_3GA_4$	M+Na	67.88062304
604.2858276	59753.9657	604.243673	$(4a2h)_5GA$	M+Na	69.7643002
619.2484741	26191.3836	619.20695	$(4a2h)_4GA_3$	M+Na	67.06016623
662.296814	35461.14964	662.249153	$(4a2h)_5GA_2$	M+Na	71.96832912

677.2575073	13511.1714	677.21243	$(4a2h)_4GA_4$	M+Na	66.56304876
705.3435669	40697.91891	705.291356	$(4a2h)_6GA$	M+Na	74.02741371
720.303894	24036.04273	720.254633	$(4a2h)_5GA_3$	M+Na	68.39392729
735.2769165	5993.886221	735.21791	$(4a2h)_4GA_5$	M+Na	80.25716348
763.3522339	28262.33855	763.296836	$(4a2h)_6GA_2$	M+Na	72.57712123
778.3182983	15354.55148	778.260113	$(4a2h)_5GA_4$	M+Na	74.76335871
806.4040527	21790.57475	806.339039	$(4a2h)_7GA$	M+Na	80.62828519
821.362854	19850.48399	821.302316	$(4a2h)_6GA_3$	M+Na	73.70976901
836.3344727	7486.395318	836.265593	$(4a2h)_5GA_5$	M+Na	82.36576582
864.4101563	18499.07725	864.344519	$(4a2h)_7GA_2$	M+Na	75.93875886
879.3763428	13311.35027	879.307796	$(4a2h)_6GA_4$	M+Na	77.95537957
907.456665	9863.059684	907.386722	$(4a2h)_8GA$	M+Na	77.08184097
922.4274292	13749.00442	922.349999	$(4a2h)_7GA_3$	M+Na	83.94882537
937.3886719	7765.893903	937.313276	$(4a2h)_6GA_5$	M+Na	80.43828774
965.467041	10383.62124	965.392202	$(4a2h)_8GA_2$	M+Na	77.52187748
980.4384766	10019.87347	980.355479	$(4a2h)_7GA_4$	M+Na	84.66068052
1023.480896	8763.829756	1023.397682	$(4a2h)_8GA_3$	M+Na	81.31149939
1038.444336	6218.391766	1038.360959	$(4a2h)_7GA_5$	M+Na	80.29668226
1081.49353	6526.155217	1081.403162	$(4a2h)_8GA_4$	M+Na	83.56575344
124.0400009	40223.07344	124.036896	4a2h	M+Na-H_2O (cyclic)	25.03219687
182.0437775	14999.38361	182.042376	(4a2h)GA	M+Na-H_2O (cyclic)	7.69857014
225.0892334	14974.01782	225.084579	$(4a2h)_2$	M+Na-H_2O (cyclic)	20.67844017
283.0907593	82496.61156	283.090059	$(4a2h)_2GA$	M+Na-H_2O (cyclic)	2.47368983
326.1412048	20728.48335	326.132262	$(4a2h)_3$	M+Na-H_2O (cyclic)	27.42088116
341.1045532	36320.30733	341.095539	$(4a2h)_2GA_2$	M+Na-H_2O (cyclic)	26.42726735
384.1511536	94434.368	384.137742	$(4a2h)_3GA$	M+Na-H_2O (cyclic)	34.91342436

399.1156616	9479.577466	399.101019	$(4a2h)_2GA_3$	M+Na-H_2O (cyclic)	36.68900931
427.1964722	17597.17866	427.179945	$(4a2h)_4$	M+Na-H_2O (cyclic)	38.68900728
442.1593018	72077.419	442.143222	$(4a2h)_3GA_2$	M+Na-H_2O (cyclic)	36.36775868
485.2112732	65778.20395	485.185425	$(4a2h)_4GA$	M+Na-H_2O (cyclic)	53.27487527
500.1743164	28151.63465	500.148702	$(4a2h)_3GA_3$	M+Na-H_2O (cyclic)	51.21358088
528.2578735	9805.778115	528.227628	$(4a2h)_5$	M+Na-H_2O (cyclic)	57.2585253
543.2216797	74038.11748	543.190905	$(4a2h)_4GA_2$	M+Na-H_2O (cyclic)	56.65538159
558.190979	7890.231182	558.154182	$(4a2h)_3GA_4$	M+Na-H_2O (cyclic)	65.92623541
586.2652588	35965.79904	586.233108	$(4a2h)_5GA$	M+Na-H_2O (cyclic)	54.84301136
601.234314	42399.11653	601.196385	$(4a2h)_4GA_3$	M+Na-H_2O (cyclic)	63.08914349
644.2799072	51772.70637	644.238588	$(4a2h)_5GA_2$	M+Na-H_2O (cyclic)	64.13652918
659.2451172	16151.97222	659.201865	$(4a2h)_4GA_4$	M+Na-H_2O (cyclic)	65.61296364
687.3244019	16780.62446	687.280791	$(4a2h)_6GA$	M+Na-H_2O (cyclic)	63.45420325
702.2949829	39848.25195	702.244068	$(4a2h)_5GA_3$	M+Na-H_2O (cyclic)	72.50315427
717.263855	5412.926919	717.207345	$(4a2h)_4GA_5$	M+Na-H_2O (cyclic)	78.79169168
745.3424072	28520.67782	745.286271	$(4a2h)_6GA_2$	M+Na-H_2O (cyclic)	75.32169743
760.3064575	20013.44797	760.249548	$(4a2h)_5GA_4$	M+Na-H_2O (cyclic)	74.85636808
788.3884888	7519.70457	788.328474	$(4a2h)_7GA$	M+Na-H_2O (cyclic)	76.12914157
803.352478	27697.001	803.291751	$(4a2h)_6GA_3$	M+Na-H_2O (cyclic)	75.59772265
818.3193359	7880.62899	818.255028	$(4a2h)_5GA_5$	M+Na-H_2O (cyclic)	78.59155862
846.395874	14387.72797	846.333954	$(4a2h)_7GA_2$	M+Na-H_2O (cyclic)	73.16263599
861.3621826	17605.83479	861.297231	$(4a2h)_6GA_4$	M+Na-H_2O (cyclic)	75.4113849
904.4099731	16316.53843	904.339434	$(4a2h)_7GA_3$	M+Na-H_2O (cyclic)	78.00073993
919.3787231	8939.006052	919.302711	$(4a2h)_6GA_5$	M+Na-H_2O (cyclic)	82.68456526
962.4266357	13010.21676	962.344914	$(4a2h)_7GA_4$	M+Na-H_2O (cyclic)	84.91938889
1020.439514	7355.481173	1020.350394	$(4a2h)_7GA_5$	M+Na-H_2O (cyclic)	87.34270161

Table S5. Peak list sorted by mass for poly(4a2h-LA) positive mode MALDI-TOF-MS (**Figs. 2** and **S6**); sodiated and protonated peaks. "M+H-H_2O (cyclic)": possibility of both dehydrated or cyclic species.

Observed Mass (m/z)	Intensity	Calculated Mass	Identity	Adduct	PPM
203.1046448	310156.1954	203.102637	$(4a2h)_2$	M+H-H_2O (cyclic)	9.885519113
275.1292725	121712.8269	275.123747	$(4a2h)_2LA$	M+H-H_2O (cyclic)	20.08354808
286.1534729	399893.0661	286.13789	$(4a2h)_2$	M+ethanolamine+Na	54.45940767
304.1632996	219114.1385	304.15032	$(4a2h)_3$	M+H-H_2O (cyclic)	42.67482277
347.1585693	28440.59692	347.144857	$(4a2h)_2LA_2$	M+H-H_2O (cyclic)	39.50032882
358.1759644	130060.0404	358.158995	$(4a2h)_2LA$	M+ethanolamine+Na	47.37939082
376.1924133	222088.7496	376.17143	$(4a2h)_3LA$	M+H-H_2O (cyclic)	55.78129631
387.2090759	215042.5396	387.185568	$(4a2h)_3$	M+ethanolamine+Na	60.71488698
405.2236633	106882.5888	405.198003	$(4a2h)_4$	M+H-H_2O (cyclic)	63.32787874
419.190094	8245.149344	419.165967	$(4a2h)_2LA_3$	M+H-H_2O (cyclic)	57.5595251
430.2052612	31175.58651	430.180105	$(4a2h)_2LA_2$	M+ethanolamine+Na	58.47836687
448.222168	98427.2027	448.19254	$(4a2h)_3LA_2$	M+H-H_2O (cyclic)	66.10544879
459.2406921	204851.9006	459.206678	$(4a2h)_3LA$	M+ethanolamine+Na	74.07152515
477.2516174	178425.8422	477.219113	$(4a2h)_4LA$	M+H-H_2O (cyclic)	68.11217555
488.2664795	95265.03239	488.233251	$(4a2h)_4$	M+ethanolamine+Na	68.05864191
502.2393799	10106.00743	502.201215	$(4a2h)_2LA_3$	M+ethanolamine+Na	75.99520244
506.2850952	43273.87977	506.245686	$(4a2h)_5$	M+H-H_2O (cyclic)	77.84602633
520.2515259	35344.78352	520.21365	$(4a2h)_3LA_3$	M+H-H_2O (cyclic)	72.80831443
531.2701416	92994.80409	531.227788	$(4a2h)_3LA_2$	M+ethanolamine+Na	79.72776078
549.2802124	129416.6699	549.240223	$(4a2h)_4LA_2$	M+H-H_2O (cyclic)	72.80858234
560.3005981	147956.14	560.254361	$(4a2h)_4LA$	M+ethanolamine+Na	82.52884443
578.3167114	106401.573	578.266796	$(4a2h)_5LA$	M+H-H_2O (cyclic)	86.31902496
589.3216553	39550.91519	589.280934	$(4a2h)_5$	M+ethanolamine+Na	69.10332687

592.2870483	**13760.19135**	**592.23476**	**$(4a2h)_3LA_4$**	**M+H-H_2O (cyclic)**	**88.28988694**
603.2990112	**34314.20048**	**603.248898**	**$(4a2h)_3LA_3$**	**M+ethanolamine+Na**	**83.07222801**
607.3388672	**17711.5739**	**607.293369**	**$(4a2h)_6$**	**M+H-H_2O (cyclic)**	**74.91961929**
621.3122559	**64947.32759**	**621.261333**	**$(4a2h)_4LA_3$**	**M+H-H_2O (cyclic)**	**81.96688945**
632.3282471	**103996.2997**	**632.275471**	**$(4a2h)_4LA_2$**	**M+ethanolamine+Na**	**83.47005763**
650.3464355	**106994.1225**	**650.287906**	**$(4a2h)_5LA_2$**	**M+H-H_2O (cyclic)**	**90.00559054**
661.3550415	**81982.80034**	**661.302044**	**$(4a2h)_5LA$**	**M+ethanolamine+Na**	**80.14114652**
664.326416	**6966.899115**	**664.25587**	**$(4a2h)_3LA_5$**	**M+H-H_2O (cyclic)**	**106.203075**
675.3336792	**12023.88379**	**675.270008**	**$(4a2h)_3LA_4$**	**M+ethanolamine+Na**	**94.28998511**
679.3762207	**52742.31982**	**679.314479**	**$(4a2h)_6LA$**	**M+H-H_2O (cyclic)**	**90.88824824**
690.3737183	**17061.40467**	**690.328617**	**$(4a2h)_6$**	**M+ethanolamine+Na**	**65.33303254**
693.3427734	**27939.0476**	**693.282443**	**$(4a2h)_4LA_4$**	**M+H-H_2O (cyclic)**	**87.02144214**
704.3581543	**52496.08738**	**704.296581**	**$(4a2h)_4LA_3$**	**M+ethanolamine+Na**	**87.42523911**
708.3920898	**7487.961148**	**708.341052**	**$(4a2h)_7$**	**M+H-H_2O (cyclic)**	**72.05264167**
722.3729248	**71394.94506**	**722.309016**	**$(4a2h)_5LA_3$**	**M+H-H_2O (cyclic)**	**88.47848163**
733.3890991	**77791.51538**	**733.323154**	**$(4a2h)_5LA_2$**	**M+ethanolamine+Na**	**89.92641326**
736.3734741	**5038.285162**	**736.27698**	**$(4a2h)_3LA_6$**	**M+H-H_2O (cyclic)**	**131.0568218**
747.3637695	**5890.81099**	**747.291118**	**$(4a2h)_3LA_5$**	**M+ethanolamine+Na**	**97.21985081**
751.4077148	**68382.78517**	**751.335589**	**$(4a2h)_6LA_2$**	**M+H-H_2O (cyclic)**	**95.99684223**
762.4111938	**40423.64349**	**762.349727**	**$(4a2h)_6LA$**	**M+ethanolamine+Na**	**80.62814982**
765.3768311	**12201.02662**	**765.303553**	**$(4a2h)_4LA_5$**	**M+H-H_2O (cyclic)**	**95.75031334**
776.3899536	**21872.28955**	**776.317691**	**$(4a2h)_4LA_4$**	**M+ethanolamine+Na**	**93.08381586**
780.4337158	**23835.15482**	**780.362162**	**$(4a2h)_7LA$**	**M+H-H_2O (cyclic)**	**91.69309262**
791.4186401	**8773.753124**	**791.3763**	**$(4a2h)_7$**	**M+ethanolamine+Na**	**53.50190169**
794.40448	**37760.8861**	**794.330126**	**$(4a2h)_5LA_4$**	**M+H-H_2O (cyclic)**	**93.60589202**
805.4151001	**51204.31114**	**805.344264**	**$(4a2h)_5LA_3$**	**M+ethanolamine+Na**	**87.95753713**

823.43396	57880.14138	823.356699	$(4a2h)_6LA_3$	M+H-H_2O (cyclic)	93.83656087
834.4454956	48137.42963	834.370837	$(4a2h)_6LA_2$	M+ethanolamine+Na	89.47892435
837.4158936	6953.435255	837.324663	$(4a2h)_4LA_6$	M+H-H_2O (cyclic)	108.9548165
848.4168701	9679.751505	848.338801	$(4a2h)_4LA_5$	M+ethanolamine+Na	92.02587092
852.4661255	37074.11195	852.383272	$(4a2h)_7LA_2$	M+H-H_2O (cyclic)	97.20215157
863.4682617	19473.37411	863.39741	$(4a2h)_7LA$	M+ethanolamine+Na	82.06153757
866.4376221	18277.77089	866.351236	$(4a2h)_5LA_5$	M+H-H_2O (cyclic)	99.71252583
877.4467163	25930.19433	877.365374	$(4a2h)_5LA_4$	M+ethanolamine+Na	92.71201191
881.4817505	10476.86646	881.409845	$(4a2h)_8LA$	M+H-H_2O (cyclic)	81.58008265
892.4644165	5588.566316	892.423983	$(4a2h)_8$	M+ethanolamine+Na	45.30750492
895.4604492	36897.1879	895.377809	$(4a2h)_6LA_4$	M+H-H_2O (cyclic)	92.29647884
906.4762573	37945.76358	906.391947	$(4a2h)_6LA_3$	M+ethanolamine+Na	93.01751221
924.4910889	38167.21718	924.404382	$(4a2h)_7LA_3$	M+H-H_2O (cyclic)	93.79755082
935.505127	26021.91744	935.41852	$(4a2h)_7LA_2$	M+ethanolamine+Na	92.5863142
938.463623	9315.307001	938.372346	$(4a2h)_5LA_6$	M+H-H_2O (cyclic)	97.27167194
949.4743652	12739.08974	949.386484	$(4a2h)_5LA_5$	M+ethanolamine+Na	92.56634203
953.5228271	17961.87844	953.430955	$(4a2h)_8LA_2$	M+H-H_2O (cyclic)	96.35951877
964.5188599	9479.26976	964.445093	$(4a2h)_8LA$	M+ethanolamine+Na	76.48632725
967.491333	20212.78028	967.398919	$(4a2h)_6LA_5$	M+H-H_2O (cyclic)	95.52833499
978.5040283	23606.18319	978.413057	$(4a2h)_6LA_4$	M+ethanolamine+Na	92.97844029
996.520874	28319.96781	996.425492	$(4a2h)_7LA_4$	M+H-H_2O (cyclic)	95.72418988
1007.528015	24642.33925	1007.43963	$(4a2h)_7LA_3$	M+ethanolamine+Na	87.73244308
1009.531433	6000.015279	1010.393456	$(4a2h)_5LA_7$	M+H-H_2O (cyclic)	853.1556542
1021.504334	6606.929504	1021.407594	$(4a2h)_5LA_6$	M+ethanolamine+Na	94.71194513
1025.549072	21264.62702	1025.452065	$(4a2h)_8LA_3$	M+H-H_2O (cyclic)	94.59951695
1036.551514	13597.46102	1036.466203	$(4a2h)_8LA_2$	M+ethanolamine+Na	82.3091672

1039.526733	**10551.73249**	**1039.420029**	**$(4a2h)_6LA_6$**	**M+H-H_2O (cyclic)**	**102.6576331**
1050.529785	**12881.88462**	**1050.434167**	**$(4a2h)_6LA_5$**	**M+ethanolamine+Na**	**91.0272752**
1065.556641	**5067.830871**	**1065.492776**	**$(4a2h)_9LA$**	**M+ethanolamine+Na**	**59.93904552**
1068.548218	**17510.4293**	**1068.446602**	**$(4a2h)_7LA_5$**	**M+H-H_2O (cyclic)**	**95.10608187**
1079.56189	**16979.74775**	**1079.46074**	**$(4a2h)_7LA_4$**	**M+ethanolamine+Na**	**93.70387106**
1081.560547	**5295.226308**	**1082.414566**	**$(4a2h)_5LA_8$**	**M+H-H_2O (cyclic)**	**788.9944822**
1097.582886	**18080.18737**	**1097.473175**	**$(4a2h)_8LA_4$**	**M+H-H_2O (cyclic)**	**99.96667117**
1108.584229	**13885.34982**	**1108.487313**	**$(4a2h)_8LA_3$**	**M+ethanolamine+Na**	**87.43042781**
1111.551025	**5835.771056**	**1111.441139**	**$(4a2h)_6LA_7$**	**M+H-H_2O (cyclic)**	**98.86838461**
1122.5625	**6667.675158**	**1122.455277**	**$(4a2h)_6LA_6$**	**M+ethanolamine+Na**	**95.52540952**
1137.598022	**7258.682181**	**1137.513886**	**$(4a2h)_9LA_2$**	**M+ethanolamine+Na**	**73.96521575**
1140.577637	**9875.486724**	**1140.467712**	**$(4a2h)_7LA_6$**	**M+H-H_2O (cyclic)**	**96.38564849**
1151.593872	**10620.58957**	**1151.48185**	**$(4a2h)_7LA_5$**	**M+ethanolamine+Na**	**97.28513741**
1169.605347	**13049.81845**	**1169.494285**	**$(4a2h)_8LA_5$**	**M+H-H_2O (cyclic)**	**94.96556026**
1180.612427	**11601.27408**	**1180.508423**	**$(4a2h)_8LA_4$**	**M+ethanolamine+Na**	**88.10081993**
1209.63916	**7651.434319**	**1209.534996**	**$(4a2h)_9LA_3$**	**M+ethanolamine+Na**	**86.11917832**
1212.605591	**5658.185677**	**1212.488822**	**$(4a2h)_7LA_7$**	**M+H-H_2O (cyclic)**	**96.30506928**
1223.617432	**6097.388143**	**1223.50296**	**$(4a2h)_7LA_6$**	**M+ethanolamine+Na**	**93.56057463**
1252.644043	**8275.685694**	**1252.529533**	**$(4a2h)_8LA_5$**	**M+ethanolamine+Na**	**91.42297006**
1281.665894	**7024.973073**	**1281.556106**	**$(4a2h)_9LA_4$**	**M+ethanolamine+Na**	**85.66737694**
1324.674805	**5106.571028**	**1324.550643**	**$(4a2h)_8LA_6$**	**M+ethanolamine+Na**	**93.73872615**

Table S6. Peak list sorted by adduct and then mass and also colorcoded (for ease of visualization) for poly(4a2h-LA) positive mode MALDI-TOF-MS (**Figs. 2** and **S6**); sodiated and protonated peaks. “M+H-H_2O (cyclic)”: possibility of both dehydrated or cyclic species.

Observed Mass (m/z)	Intensity	Calculated Mass	Identity	Adduct	PPM
286.1534729	399893.0661	286.13789	$(4a2h)_2$	M+ethanolamine+Na	54.45940767
358.1759644	130060.0404	358.158995	$(4a2h)_2LA$	M+ethanolamine+Na	47.37939082
387.2090759	215042.5396	387.185568	$(4a2h)_3$	M+ethanolamine+Na	60.71488698
430.2052612	31175.58651	430.180105	$(4a2h)_2LA_2$	M+ethanolamine+Na	58.47836687
459.2406921	204851.9006	459.206678	$(4a2h)_3LA$	M+ethanolamine+Na	74.07152515
488.2664795	95265.03239	488.233251	$(4a2h)_4$	M+ethanolamine+Na	68.05864191
502.2393799	10106.00743	502.201215	$(4a2h)_2LA_3$	M+ethanolamine+Na	75.99520244
531.2701416	92994.80409	531.227788	$(4a2h)_3LA_2$	M+ethanolamine+Na	79.72776078
560.3005981	147956.14	560.254361	$(4a2h)_4LA$	M+ethanolamine+Na	82.52884443
589.3216553	39550.91519	589.280934	$(4a2h)_5$	M+ethanolamine+Na	69.10332687
603.2990112	34314.20048	603.248898	$(4a2h)_3LA_3$	M+ethanolamine+Na	83.07222801
632.3282471	103996.2997	632.275471	$(4a2h)_4LA_2$	M+ethanolamine+Na	83.47005763
661.3550415	81982.80034	661.302044	$(4a2h)_5LA$	M+ethanolamine+Na	80.14114652
675.3336792	12023.88379	675.270008	$(4a2h)_3LA_4$	M+ethanolamine+Na	94.28998511
690.3737183	17061.40467	690.328617	$(4a2h)_6$	M+ethanolamine+Na	65.33303254
704.3581543	52496.08738	704.296581	$(4a2h)_4LA_3$	M+ethanolamine+Na	87.42523911
733.3890991	77791.51538	733.323154	$(4a2h)_5LA_2$	M+ethanolamine+Na	89.92641326
747.3637695	5890.81099	747.291118	$(4a2h)_3LA_5$	M+ethanolamine+Na	97.21985081
762.4111938	40423.64349	762.349727	$(4a2h)_6LA$	M+ethanolamine+Na	80.62814982
776.3899536	21872.28955	776.317691	$(4a2h)_4LA_4$	M+ethanolamine+Na	93.08381586
791.4186401	8773.753124	791.3763	$(4a2h)_7$	M+ethanolamine+Na	53.50190169
805.4151001	51204.31114	805.344264	$(4a2h)_5LA_3$	M+ethanolamine+Na	87.95753713
834.4454956	48137.42963	834.370837	$(4a2h)_6LA_2$	M+ethanolamine+Na	89.47892435

848.4168701	9679.751505	848.338801	$(4a2h)_4LA_5$	M+ethanolamine+Na	92.02587092
863.4682617	19473.37411	863.39741	$(4a2h)_7LA$	M+ethanolamine+Na	82.06153757
877.4467163	25930.19433	877.365374	$(4a2h)_5LA_4$	M+ethanolamine+Na	92.71201191
892.4644165	5588.566316	892.423983	$(4a2h)_8$	M+ethanolamine+Na	45.30750492
906.4762573	37945.76358	906.391947	$(4a2h)_6LA_3$	M+ethanolamine+Na	93.01751221
935.505127	26021.91744	935.41852	$(4a2h)_7LA_2$	M+ethanolamine+Na	92.5863142
949.4743652	12739.08974	949.386484	$(4a2h)_5LA_5$	M+ethanolamine+Na	92.56634203
964.5188599	9479.26976	964.445093	$(4a2h)_8LA$	M+ethanolamine+Na	76.48632725
978.5040283	23606.18319	978.413057	$(4a2h)_6LA_4$	M+ethanolamine+Na	92.97844029
1007.528015	24642.33925	1007.43963	$(4a2h)_7LA_3$	M+ethanolamine+Na	87.73244308
1021.504334	6606.929504	1021.407594	$(4a2h)_5LA_6$	M+ethanolamine+Na	94.71194513
1036.551514	13597.46102	1036.466203	$(4a2h)_8LA_2$	M+ethanolamine+Na	82.3091672
1050.529785	12881.88462	1050.434167	$(4a2h)_6LA_5$	M+ethanolamine+Na	91.0272752
1065.556641	5067.830871	1065.492776	$(4a2h)_9LA$	M+ethanolamine+Na	59.93904552
1079.56189	16979.74775	1079.46074	$(4a2h)_7LA_4$	M+ethanolamine+Na	93.70387106
1108.584229	13885.34982	1108.487313	$(4a2h)_8LA_3$	M+ethanolamine+Na	87.43042781
1122.5625	6667.675158	1122.455277	$(4a2h)_6LA_6$	M+ethanolamine+Na	95.52540952
1137.598022	7258.682181	1137.513886	$(4a2h)_9LA_2$	M+ethanolamine+Na	73.96521575
1151.593872	10620.58957	1151.48185	$(4a2h)_7LA_5$	M+ethanolamine+Na	97.28513741
1180.612427	11601.27408	1180.508423	$(4a2h)_8LA_4$	M+ethanolamine+Na	88.10081993
1209.63916	7651.434319	1209.534996	$(4a2h)_9LA_3$	M+ethanolamine+Na	86.11917832
1223.617432	6097.388143	1223.50296	$(4a2h)_7LA_6$	M+ethanolamine+Na	93.56057463
1252.644043	8275.685694	1252.529533	$(4a2h)_8LA_5$	M+ethanolamine+Na	91.42297006
1281.665894	7024.973073	1281.556106	$(4a2h)_9LA_4$	M+ethanolamine+Na	85.66737694
1324.674805	5106.571028	1324.550643	$(4a2h)_8LA_6$	M+ethanolamine+Na	93.73872615
203.1046448	310156.1954	203.102637	$(4a2h)_2$	M+H-H_2O (cyclic)	9.885519113

275.1292725	121712.8269	275.123747	$(4a2h)_2LA$	M+H-H_2O (cyclic)	20.08354808
304.1632996	219114.1385	304.15032	$(4a2h)_3$	M+H-H_2O (cyclic)	42.67482277
347.1585693	28440.59692	347.144857	$(4a2h)_2LA_2$	M+H-H_2O (cyclic)	39.50032882
376.1924133	222088.7496	376.17143	$(4a2h)_3LA$	M+H-H_2O (cyclic)	55.78129631
405.2236633	106882.5888	405.198003	$(4a2h)_4$	M+H-H_2O (cyclic)	63.32787874
419.190094	8245.149344	419.165967	$(4a2h)_2LA_3$	M+H-H_2O (cyclic)	57.5595251
448.222168	98427.2027	448.19254	$(4a2h)_3LA_2$	M+H-H_2O (cyclic)	66.10544879
477.2516174	178425.8422	477.219113	$(4a2h)_4LA$	M+H-H_2O (cyclic)	68.11217555
506.2850952	43273.87977	506.245686	$(4a2h)_5$	M+H-H_2O (cyclic)	77.84602633
520.2515259	35344.78352	520.21365	$(4a2h)_3LA_3$	M+H-H_2O (cyclic)	72.80831443
549.2802124	129416.6699	549.240223	$(4a2h)_4LA_2$	M+H-H_2O (cyclic)	72.80858234
578.3167114	106401.573	578.266796	$(4a2h)_5LA$	M+H-H_2O (cyclic)	86.31902496
592.2870483	13760.19135	592.23476	$(4a2h)_3LA_4$	M+H-H_2O (cyclic)	88.28988694
607.3388672	17711.5739	607.293369	$(4a2h)_6$	M+H-H_2O (cyclic)	74.91961929
621.3122559	64947.32759	621.261333	$(4a2h)_4LA_3$	M+H-H_2O (cyclic)	81.96688945
650.3464355	106994.1225	650.287906	$(4a2h)_5LA_2$	M+H-H_2O (cyclic)	90.00559054
664.326416	6966.899115	664.25587	$(4a2h)_3LA_5$	M+H-H_2O (cyclic)	106.203075
679.3762207	52742.31982	679.314479	$(4a2h)_6LA$	M+H-H_2O (cyclic)	90.88824824
693.3427734	27939.0476	693.282443	$(4a2h)_4LA_4$	M+H-H_2O (cyclic)	87.02144214
708.3920898	7487.961148	708.341052	$(4a2h)_7$	M+H-H_2O (cyclic)	72.05264167
722.3729248	71394.94506	722.309016	$(4a2h)_5LA_3$	M+H-H_2O (cyclic)	88.47848163
736.3734741	5038.285162	736.27698	$(4a2h)_3LA_6$	M+H-H_2O (cyclic)	131.0568218
751.4077148	68382.78517	751.335589	$(4a2h)_6LA_2$	M+H-H_2O (cyclic)	95.99684223
765.3768311	12201.02662	765.303553	$(4a2h)_4LA_5$	M+H-H_2O (cyclic)	95.75031334
780.4337158	23835.15482	780.362162	$(4a2h)_7LA$	M+H-H_2O (cyclic)	91.69309262
794.40448	37760.8861	794.330126	$(4a2h)_5LA_4$	M+H-H_2O (cyclic)	93.60589202

823.43396	**57880.14138**	**823.356699**	**$(4a2h)_6LA_3$**	**M+H-H_2O (cyclic)**	**93.83656087**
837.4158936	**6953.435255**	**837.324663**	**$(4a2h)_4LA_6$**	**M+H-H_2O (cyclic)**	**108.9548165**
852.4661255	**37074.11195**	**852.383272**	**$(4a2h)_7LA_2$**	**M+H-H_2O (cyclic)**	**97.20215157**
866.4376221	**18277.77089**	**866.351236**	**$(4a2h)_5LA_5$**	**M+H-H_2O (cyclic)**	**99.71252583**
881.4817505	**10476.86646**	**881.409845**	**$(4a2h)_8LA$**	**M+H-H_2O (cyclic)**	**81.58008265**
895.4604492	**36897.1879**	**895.377809**	**$(4a2h)_6LA_4$**	**M+H-H_2O (cyclic)**	**92.29647884**
924.4910889	**38167.21718**	**924.404382**	**$(4a2h)_7LA_3$**	**M+H-H_2O (cyclic)**	**93.79755082**
938.463623	**9315.307001**	**938.372346**	**$(4a2h)_5LA_6$**	**M+H-H_2O (cyclic)**	**97.27167194**
953.5228271	**17961.87844**	**953.430955**	**$(4a2h)_8LA_2$**	**M+H-H_2O (cyclic)**	**96.35951877**
967.491333	**20212.78028**	**967.398919**	**$(4a2h)_6LA_5$**	**M+H-H_2O (cyclic)**	**95.52833499**
996.520874	**28319.96781**	**996.425492**	**$(4a2h)_7LA_4$**	**M+H-H_2O (cyclic)**	**95.72418988**
1009.531433	**6000.015279**	**1010.393456**	**$(4a2h)_5LA_7$**	**M+H-H_2O (cyclic)**	**853.1556542**
1025.549072	**21264.62702**	**1025.452065**	**$(4a2h)_8LA_3$**	**M+H-H_2O (cyclic)**	**94.59951695**
1039.526733	**10551.73249**	**1039.420029**	**$(4a2h)_6LA_6$**	**M+H-H_2O (cyclic)**	**102.6576331**
1068.548218	**17510.4293**	**1068.446602**	**$(4a2h)_7LA_5$**	**M+H-H_2O (cyclic)**	**95.10608187**
1081.560547	**5295.226308**	**1082.414566**	**$(4a2h)_5LA_8$**	**M+H-H_2O (cyclic)**	**788.9944822**
1097.582886	**18080.18737**	**1097.473175**	**$(4a2h)_8LA_4$**	**M+H-H_2O (cyclic)**	**99.96667117**
1111.551025	**5835.771056**	**1111.441139**	**$(4a2h)_6LA_7$**	**M+H-H_2O (cyclic)**	**98.86838461**
1140.577637	**9875.486724**	**1140.467712**	**$(4a2h)_7LA_6$**	**M+H-H_2O (cyclic)**	**96.38564849**
1169.605347	**13049.81845**	**1169.494285**	**$(4a2h)_8LA_5$**	**M+H-H_2O (cyclic)**	**94.96556026**
1212.605591	**5658.185677**	**1212.488822**	**$(4a2h)_7LA_7$**	**M+H-H_2O (cyclic)**	**96.30506928**

Table S7. Peak list sorted by mass for poly(4a2h-PA) positive mode MALDI-TOF-MS (**Figs. 3** and **S7**); sodiated and protonated peaks. "M+H/Na-H_2O (cyclic)": possibility of both dehydrated or cyclic species.

Observed Mass (m/z)	Intensity	Calculated Mass	Identity	Adduct	PPM
203.1010284	137059.9526	203.102637	$(4a2h)_2$	M+H-H_2O (cyclic)	7.919926712
286.1448669	187418.8148	286.13789	$(4a2h)_2$	M+ethanolamine+Na	24.38314968
304.1588745	75173.2404	304.15032	$(4a2h)_3$	M+H-H_2O (cyclic)	28.12593457
351.1687317	135816.358	351.155067	$(4a2h)_2$PA	M+H-H_2O (cyclic)	38.91354642
373.1539917	12961.63055	373.137009	$(4a2h)_2$PA	M+Na-H_2O (cyclic)	45.51330635
387.204071	48415.42214	387.185568	$(4a2h)_3$	M+ethanolamine+Na	47.78857098
405.2185669	28441.91319	405.198003	$(4a2h)_4$	M+H-H_2O (cyclic)	50.75023778
434.2140503	100207.6384	434.190315	$(4a2h)_2$PA	M+ethanolamine+Na	54.66564357
452.2330322	140878.5462	452.20275	$(4a2h)_3$PA	M+H-H_2O (cyclic)	66.96603902
474.2145996	15305.32683	474.184692	$(4a2h)_3$PA	M+Na-H_2O (cyclic)	63.07164593
488.2664795	18613.46149	488.233251	$(4a2h)_4$	M+ethanolamine+Na	68.05864191
499.2427368	84734.30597	499.207497	$(4a2h)_2PA_2$	M+H-H_2O (cyclic)	70.59151998
506.2736511	10785.32174	506.245686	$(4a2h)_5$	M+H-H_2O (cyclic)	55.24021986
521.225769	17451.59261	521.189439	$(4a2h)_2PA_2$	M+Na-H_2O (cyclic)	69.70602296
535.2783813	78575.30583	535.237998	$(4a2h)_3$PA	M+ethanolamine+Na	75.44932937
553.2901611	86865.58201	553.250433	$(4a2h)_4$PA	M+H-H_2O (cyclic)	71.80858908
568.239502	9981.198548	568.194186	$(4a2h)PA_3$	M+Na-H_2O (cyclic)	79.75434124
575.2769165	11680.47309	575.232375	$(4a2h)_4$PA	M+Na-H_2O (cyclic)	77.43219251
582.2903442	63748.79773	582.242745	$(4a2h)_2PA_2$	M+ethanolamine+Na	81.75153475
589.3216553	7628.842563	589.280934	$(4a2h)_5$	M+ethanolamine+Na	69.10332687
600.3060913	119488.2189	600.25518	$(4a2h)_3PA_2$	M+H-H_2O (cyclic)	84.81610938
622.2883301	20752.57418	622.237122	$(4a2h)_3PA_2$	M+Na-H_2O (cyclic)	82.2967261
636.3359985	41665.89492	636.285681	$(4a2h)_4$PA	M+ethanolamine+Na	79.08009956

647.3161011	**56645.12028**	**647.259927**	**$(4a2h)_2PA_3$**	**M+H-H_2O (cyclic)**	**86.78750477**
654.352478	**42251.91545**	**654.298116**	**$(4a2h)_5PA$**	**M+H-H_2O (cyclic)**	**83.08449264**
669.2957764	**19558.7082**	**669.241869**	**$(4a2h)_2PA_3$**	**M+Na-H_2O (cyclic)**	**80.54990206**
676.331604	**7467.884307**	**676.280058**	**$(4a2h)_5PA$**	**M+Na-H_2O (cyclic)**	**76.21990829**
683.3511963	**62198.33413**	**683.290428**	**$(4a2h)_3PA_2$**	**M+ethanolamine+Na**	**88.93478748**
701.3654785	**94700.75957**	**701.302863**	**$(4a2h)_4PA_2$**	**M+H-H_2O (cyclic)**	**89.28455779**
723.3504028	**17013.52254**	**723.284805**	**$(4a2h)_4PA_2$**	**M+Na-H_2O (cyclic)**	**90.69433167**
730.3626099	**30695.39719**	**730.295175**	**$(4a2h)_2PA_3$**	**M+ethanolamine+Na**	**92.33918737**
737.3949585	**19879.16011**	**737.333364**	**$(4a2h)_5PA$**	**M+ethanolamine+Na**	**83.53683559**
748.3719482	**97161.30323**	**748.30761**	**$(4a2h)_3PA_3$**	**M+H-H_2O (cyclic)**	**85.9783345**
755.4136353	**18682.30459**	**755.345799**	**$(4a2h)_6PA$**	**M+H-H_2O (cyclic)**	**89.80820982**
770.3582764	**23621.76205**	**770.289552**	**$(4a2h)_3PA_3$**	**M+Na-H_2O (cyclic)**	**89.21887467**
784.4096069	**41680.91185**	**784.338111**	**$(4a2h)_4PA_2$**	**M+ethanolamine+Na**	**91.15448172**
795.3866577	**12735.68778**	**795.312357**	**$(4a2h)_2PA_4$**	**M+H-H_2O (cyclic)**	**93.42331267**
802.4229736	**56445.73916**	**802.350546**	**$(4a2h)_5PA_2$**	**M+H-H_2O (cyclic)**	**90.26931353**
817.3812256	**7418.371807**	**817.294299**	**$(4a2h)_2PA_4$**	**M+Na-H_2O (cyclic)**	**106.3589776**
824.4047241	**11305.92803**	**824.332488**	**$(4a2h)_5PA_2$**	**M+Na-H_2O (cyclic)**	**87.62983632**
831.4217529	**47071.89637**	**831.342858**	**$(4a2h)_3PA_3$**	**M+ethanolamine+Na**	**94.90059275**
838.4538574	**9516.653737**	**838.381047**	**$(4a2h)_6PA$**	**M+ethanolamine+Na**	**86.84645515**
849.4319458	**89008.77399**	**849.355293**	**$(4a2h)_4PA_3$**	**M+H-H_2O (cyclic)**	**90.24821724**
856.4654541	**8301.332901**	**856.393482**	**$(4a2h)_7PA$**	**M+H-H_2O (cyclic)**	**84.04092688**
871.4228516	**21206.89675**	**871.337235**	**$(4a2h)_4PA_3$**	**M+Na-H_2O (cyclic)**	**98.2588125**
878.4338379	**6997.332038**	**878.347605**	**$(4a2h)_2PA_4$**	**M+ethanolamine+Na**	**98.17626929**
885.4654541	**23825.25791**	**885.385794**	**$(4a2h)_5PA_2$**	**M+ethanolamine+Na**	**89.97219352**
896.4425049	**37989.79361**	**896.36004**	**$(4a2h)_3PA_4$**	**M+H-H_2O (cyclic)**	**91.99973149**
903.4847412	**29744.27566**	**903.398229**	**$(4a2h)_6PA_2$**	**M+H-H_2O (cyclic)**	**95.76309563**

918.4304199	12478.51659	918.341982	$(4a2h)_3PA_4$	M+Na-H_2O (cyclic)	96.30173044
925.4657593	7209.437315	925.380171	$(4a2h)_6PA_2$	M+Na-H_2O (cyclic)	92.4898541
932.4813843	40030.55625	932.390541	$(4a2h)_4PA_3$	M+ethanolamine+Na	97.43050042
939.4924316	5238.321615	939.42873	$(4a2h)_7PA$	M+ethanolamine+Na	67.80891298
943.4725952	5709.115833	943.364787	$(4a2h)_2PA_5$	M+H-H_2O (cyclic)	114.2805164
950.4935303	59568.77598	950.402976	$(4a2h)_5PA_3$	M+H-H_2O (cyclic)	95.27987105
972.4821167	14865.20188	972.384918	$(4a2h)_5PA_3$	M+Na-H_2O (cyclic)	99.95907711
979.4909058	14764.80323	979.395288	$(4a2h)_3PA_4$	M+ethanolamine+Na	97.62938741
986.5249023	12427.25465	986.433477	$(4a2h)_6PA_2$	M+ethanolamine+Na	92.68272634
997.5007324	52151.51073	997.407723	$(4a2h)_4PA_4$	M+H-H_2O (cyclic)	93.25115482
1004.534729	14309.10144	1004.445912	$(4a2h)_7PA_2$	M+H-H_2O (cyclic)	88.42387523
1019.489014	14606.61892	1019.389665	$(4a2h)_4PA_4$	M+Na-H_2O (cyclic)	97.45897316
1033.539795	25627.29835	1033.438224	$(4a2h)_5PA_3$	M+ethanolamine+Na	98.28446214
1044.519409	8049.175896	1044.41247	$(4a2h)_3PA_5$	M+H-H_2O (cyclic)	102.3917112
1051.55249	33206.36071	1051.450659	$(4a2h)_6PA_3$	M+H-H_2O (cyclic)	96.84832011
1073.535278	8977.046764	1073.432601	$(4a2h)_6PA_3$	M+Na-H_2O (cyclic)	95.65325285
1080.548462	19051.87764	1080.442971	$(4a2h)_4PA_4$	M+ethanolamine+Na	97.636722
1087.57605	6355.580857	1087.48116	$(4a2h)_7PA_2$	M+ethanolamine+Na	87.25650015
1098.560791	45769.06684	1098.455406	$(4a2h)_5PA_4$	M+H-H_2O (cyclic)	95.9392793
1105.587646	6610.105902	1105.493595	$(4a2h)_8PA_2$	M+H-H_2O (cyclic)	85.07645854
1120.551636	12461.83988	1120.437348	$(4a2h)_5PA_4$	M+Na-H_2O (cyclic)	102.002794
1134.596558	13748.86947	1134.485907	$(4a2h)_6PA_3$	M+ethanolamine+Na	97.53371048
1145.575317	12678.41333	1145.460153	$(4a2h)_4PA_5$	M+H-H_2O (cyclic)	100.5398396
1152.604248	15819.89438	1152.498342	$(4a2h)_7PA_3$	M+H-H_2O (cyclic)	91.89258339
1174.587891	5035.794002	1174.480284	$(4a2h)_7PA_3$	M+Na-H_2O (cyclic)	91.62062698
1181.609253	15856.70201	1181.490654	$(4a2h)_5PA_4$	M+ethanolamine+Na	100.3807602

1199.615845	**29918.04387**	**1199.503089**	**$(4a2h)_6PA_4$**	**M+H-H_2O (cyclic)**	**94.00203387**
1221.606689	**8716.703415**	**1221.485031**	**$(4a2h)_6PA_4$**	**M+Na-H_2O (cyclic)**	**99.59880548**
1235.64502	**6982.360499**	**1235.53359**	**$(4a2h)_7PA_3$**	**M+ethanolamine+Na**	**90.18737402**
1246.626343	**15159.01792**	**1246.507836**	**$(4a2h)_5PA_5$**	**M+H-H_2O (cyclic)**	**95.07101887**
1253.661987	**7539.637977**	**1253.546025**	**$(4a2h)_8PA_3$**	**M+H-H_2O (cyclic)**	**92.50741312**
1268.61731	**5055.243486**	**1268.489778**	**$(4a2h)_5PA_5$**	**M+Na-H_2O (cyclic)**	**100.5381141**
1282.659058	**10846.77469**	**1282.538337**	**$(4a2h)_6PA_4$**	**M+ethanolamine+Na**	**94.12632474**
1300.675781	**16468.14796**	**1300.550772**	**$(4a2h)_7PA_4$**	**M+H-H_2O (cyclic)**	**96.1202382**
1322.665771	**5318.028955**	**1322.532714**	**$(4a2h)_7PA_4$**	**M+Na-H_2O (cyclic)**	**100.6080822**
1347.688599	**13565.55857**	**1347.555519**	**$(4a2h)_6PA_5$**	**M+H-H_2O (cyclic)**	**98.75632441**
1383.717651	**6322.22457**	**1383.58602**	**$(4a2h)_7PA_4$**	**M+ethanolamine+Na**	**95.13782887**
1401.734741	**8172.217933**	**1401.598455**	**$(4a2h)_8PA_4$**	**M+H-H_2O (cyclic)**	**97.236273**
1448.746338	**9724.808944**	**1448.603202**	**$(4a2h)_7PA_5$**	**M+H-H_2O (cyclic)**	**98.80959106**
1549.799072	**5826.728473**	**1549.650885**	**$(4a2h)_8PA_5$**	**M+H-H_2O (cyclic)**	**95.62622874**

Table S8. Peak list sorted by adduct and then mass and also colorcoded (for ease of visualization) for poly(4a2h-PA) positive mode MALDI-TOF-MS (**Figs. 3** and **S7**); sodiated and protonated peaks. "M+H/Na-H_2O (cyclic)": possibility of both dehydrated or cyclic species.

Observed Mass (m/z)	Intensity	Calculated Mass	Identity	Adduct	PPM
286.1448669	187418.8148	286.13789	$(4a2h)_2$	M+ethanolamine+Na	24.38314968
387.204071	48415.42214	387.185568	$(4a2h)_3$	M+ethanolamine+Na	47.78857098
434.2140503	100207.6384	434.190315	$(4a2h)_2PA$	M+ethanolamine+Na	54.66564357
488.2664795	18613.46149	488.233251	$(4a2h)_4$	M+ethanolamine+Na	68.05864191
535.2783813	78575.30583	535.237998	$(4a2h)_3PA$	M+ethanolamine+Na	75.44932937
582.2903442	63748.79773	582.242745	$(4a2h)_2PA_2$	M+ethanolamine+Na	81.75153475
589.3216553	7628.842563	589.280934	$(4a2h)_5$	M+ethanolamine+Na	69.10332687
636.3359985	41665.89492	636.285681	$(4a2h)_4PA$	M+ethanolamine+Na	79.08009956
683.3511963	62198.33413	683.290428	$(4a2h)_3PA_2$	M+ethanolamine+Na	88.93478748
730.3626099	30695.39719	730.295175	$(4a2h)_2PA_3$	M+ethanolamine+Na	92.33918737
737.3949585	19879.16011	737.333364	$(4a2h)_5PA$	M+ethanolamine+Na	83.53683559
784.4096069	41680.91185	784.338111	$(4a2h)_4PA_2$	M+ethanolamine+Na	91.15448172
831.4217529	47071.89637	831.342858	$(4a2h)_3PA_3$	M+ethanolamine+Na	94.90059275
838.4538574	9516.653737	838.381047	$(4a2h)_6PA$	M+ethanolamine+Na	86.84645515
878.4338379	6997.332038	878.347605	$(4a2h)_2PA_4$	M+ethanolamine+Na	98.17626929
885.4654541	23825.25791	885.385794	$(4a2h)_5PA_2$	M+ethanolamine+Na	89.97219352
932.4813843	40030.55625	932.390541	$(4a2h)_4PA_3$	M+ethanolamine+Na	97.43050042
939.4924316	5238.321615	939.42873	$(4a2h)_7PA$	M+ethanolamine+Na	67.80891298
979.4909058	14764.80323	979.395288	$(4a2h)_3PA_4$	M+ethanolamine+Na	97.62938741
986.5249023	12427.25465	986.433477	$(4a2h)_6PA_2$	M+ethanolamine+Na	92.68272634
1033.539795	25627.29835	1033.438224	$(4a2h)_5PA_3$	M+ethanolamine+Na	98.28446214
1080.548462	19051.87764	1080.442971	$(4a2h)_4PA_4$	M+ethanolamine+Na	97.636722
1087.57605	6355.580857	1087.48116	$(4a2h)_7PA_2$	M+ethanolamine+Na	87.25650015

1134.596558	13748.86947	1134.485907	$(4a2h)_6PA_3$	M+ethanolamine+Na	97.53371048
1181.609253	15856.70201	1181.490654	$(4a2h)_5PA_4$	M+ethanolamine+Na	100.3807602
1235.64502	6982.360499	1235.53359	$(4a2h)_7PA_3$	M+ethanolamine+Na	90.18737402
1282.659058	10846.77469	1282.538337	$(4a2h)_6PA_4$	M+ethanolamine+Na	94.12632474
1383.717651	6322.22457	1383.58602	$(4a2h)_7PA_4$	M+ethanolamine+Na	95.13782887
203.1010284	137059.9526	203.102637	$(4a2h)_2$	M+H-H_2O (cyclic)	7.919926712
304.1588745	75173.2404	304.15032	$(4a2h)_3$	M+H-H_2O (cyclic)	28.12593457
351.1687317	135816.358	351.155067	$(4a2h)_2PA$	M+H-H_2O (cyclic)	38.91354642
405.2185669	28441.91319	405.198003	$(4a2h)_4$	M+H-H_2O (cyclic)	50.75023778
452.2330322	140878.5462	452.20275	$(4a2h)_3PA$	M+H-H_2O (cyclic)	66.96603902
499.2427368	84734.30597	499.207497	$(4a2h)_2PA_2$	M+H-H_2O (cyclic)	70.59151998
506.2736511	10785.32174	506.245686	$(4a2h)_5$	M+H-H_2O (cyclic)	55.24021986
553.2901611	86865.58201	553.250433	$(4a2h)_4PA$	M+H-H_2O (cyclic)	71.80858908
600.3060913	119488.2189	600.25518	$(4a2h)_3PA_2$	M+H-H_2O (cyclic)	84.81610938
647.3161011	56645.12028	647.259927	$(4a2h)_2PA_3$	M+H-H_2O (cyclic)	86.78750477
654.352478	42251.91545	654.298116	$(4a2h)_5PA$	M+H-H_2O (cyclic)	83.08449264
701.3654785	94700.75957	701.302863	$(4a2h)_4PA_2$	M+H-H_2O (cyclic)	89.28455779
748.3719482	97161.30323	748.30761	$(4a2h)_3PA_3$	M+H-H_2O (cyclic)	85.9783345
755.4136353	18682.30459	755.345799	$(4a2h)_6PA$	M+H-H_2O (cyclic)	89.80820982
795.3866577	12735.68778	795.312357	$(4a2h)_2PA_4$	M+H-H_2O (cyclic)	93.42331267
802.4229736	56445.73916	802.350546	$(4a2h)_5PA_2$	M+H-H_2O (cyclic)	90.26931353
849.4319458	89008.77399	849.355293	$(4a2h)_4PA_3$	M+H-H_2O (cyclic)	90.24821724
856.4654541	8301.332901	856.393482	$(4a2h)_7PA$	M+H-H_2O (cyclic)	84.04092688
896.4425049	37989.79361	896.36004	$(4a2h)_3PA_4$	M+H-H_2O (cyclic)	91.99973149
903.4847412	29744.27566	903.398229	$(4a2h)_6PA_2$	M+H-H_2O (cyclic)	95.76309563
943.4725952	5709.115833	943.364787	$(4a2h)_2PA_5$	M+H-H_2O (cyclic)	114.2805164

950.4935303	59568.77598	950.402976	$(4a2h)_5PA_3$	M+H-H_2O (cyclic)	95.27987105
997.5007324	52151.51073	997.407723	$(4a2h)_4PA_4$	M+H-H_2O (cyclic)	93.25115482
1004.534729	14309.10144	1004.445912	$(4a2h)_7PA_2$	M+H-H_2O (cyclic)	88.42387523
1044.519409	8049.175896	1044.41247	$(4a2h)_3PA_5$	M+H-H_2O (cyclic)	102.3917112
1051.55249	33206.36071	1051.450659	$(4a2h)_6PA_3$	M+H-H_2O (cyclic)	96.84832011
1098.560791	45769.06684	1098.455406	$(4a2h)_5PA_4$	M+H-H_2O (cyclic)	95.9392793
1105.587646	6610.105902	1105.493595	$(4a2h)_8PA_2$	M+H-H_2O (cyclic)	85.07645854
1145.575317	12678.41333	1145.460153	$(4a2h)_4PA_5$	M+H-H_2O (cyclic)	100.5398396
1152.604248	15819.89438	1152.498342	$(4a2h)_7PA_3$	M+H-H_2O (cyclic)	91.89258339
1199.615845	29918.04387	1199.503089	$(4a2h)_6PA_4$	M+H-H_2O (cyclic)	94.00203387
1246.626343	15159.01792	1246.507836	$(4a2h)_5PA_5$	M+H-H_2O (cyclic)	95.07101887
1253.661987	7539.637977	1253.546025	$(4a2h)_8PA_3$	M+H-H_2O (cyclic)	92.50741312
1300.675781	16468.14796	1300.550772	$(4a2h)_7PA_4$	M+H-H_2O (cyclic)	96.1202382
1347.688599	13565.55857	1347.555519	$(4a2h)_6PA_5$	M+H-H_2O (cyclic)	98.75632441
1401.734741	8172.217933	1401.598455	$(4a2h)_8PA_4$	M+H-H_2O (cyclic)	97.236273
1448.746338	9724.808944	1448.603202	$(4a2h)_7PA_5$	M+H-H_2O (cyclic)	98.80959106
1549.799072	5826.728473	1549.650885	$(4a2h)_8PA_5$	M+H-H_2O (cyclic)	95.62622874
373.1539917	12961.63055	373.137009	$(4a2h)_2PA$	M+Na-H_2O (cyclic)	45.51330635
474.2145996	15305.32683	474.184692	$(4a2h)_3PA$	M+Na-H_2O (cyclic)	63.07164593
521.225769	17451.59261	521.189439	$(4a2h)_2PA_2$	M+Na-H_2O (cyclic)	69.70602296
568.239502	9981.198548	568.194186	$(4a2h)PA_3$	M+Na-H_2O (cyclic)	79.75434124
575.2769165	11680.47309	575.232375	$(4a2h)_4PA$	M+Na-H_2O (cyclic)	77.43219251
622.2883301	20752.57418	622.237122	$(4a2h)_3PA_2$	M+Na-H_2O (cyclic)	82.2967261
669.2957764	19558.7082	669.241869	$(4a2h)_2PA_3$	M+Na-H_2O (cyclic)	80.54990206
676.331604	7467.884307	676.280058	$(4a2h)_5PA$	M+Na-H_2O (cyclic)	76.21990829
723.3504028	17013.52254	723.284805	$(4a2h)_4PA_2$	M+Na-H_2O (cyclic)	90.69433167

770.3582764	23621.76205	770.289552	$(4a2h)_3PA_3$	M+Na-H_2O (cyclic)	89.21887467
817.3812256	7418.371807	817.294299	$(4a2h)_2PA_4$	M+Na-H_2O (cyclic)	106.3589776
824.4047241	11305.92803	824.332488	$(4a2h)_5PA_2$	M+Na-H_2O (cyclic)	87.62983632
871.4228516	21206.89675	871.337235	$(4a2h)_4PA_3$	M+Na-H_2O (cyclic)	98.2588125
918.4304199	12478.51659	918.341982	$(4a2h)_3PA_4$	M+Na-H_2O (cyclic)	96.30173044
925.4657593	7209.437315	925.380171	$(4a2h)_6PA_2$	M+Na-H_2O (cyclic)	92.4898541
972.4821167	14865.20188	972.384918	$(4a2h)_5PA_3$	M+Na-H_2O (cyclic)	99.95907711
1019.489014	14606.61892	1019.389665	$(4a2h)_4PA_4$	M+Na-H_2O (cyclic)	97.45897316
1073.535278	8977.046764	1073.432601	$(4a2h)_6PA_3$	M+Na-H_2O (cyclic)	95.65325285
1120.551636	12461.83988	1120.437348	$(4a2h)_5PA_4$	M+Na-H_2O (cyclic)	102.002794
1174.587891	5035.794002	1174.480284	$(4a2h)_7PA_3$	M+Na-H_2O (cyclic)	91.62062698
1221.606689	8716.703415	1221.485031	$(4a2h)_6PA_4$	M+Na-H_2O (cyclic)	99.59880548
1268.61731	5055.243486	1268.489778	$(4a2h)_5PA_5$	M+Na-H_2O (cyclic)	100.5381141
1322.665771	5318.028955	1322.532714	$(4a2h)_7PA_4$	M+Na-H_2O (cyclic)	100.6080822

Table S9. Peak list sorted by mass for poly(4a2h-SA) positive mode MALDI-TOF-MS (**Figs. 3** and **S7**); sodiated and protonated peaks. "M+H-H_2O (cyclic)": possibility of both dehydrated or cyclic species.

Observed Mass (m/z)	Intensity	Calculated Mass	Identity	Adduct	PPM
203.1082611	119627.7243	203.102637	$(4a2h)_2$	M+H-H_2O (cyclic)	27.69096494
286.1534729	138296.5019	286.13789	$(4a2h)_2$	M+ethanolamine+Na	54.45940767
304.1632996	79547.49402	304.15032	$(4a2h)_3$	M+H-H_2O (cyclic)	42.67482277
335.145752	45208.77016	335.127147	$(4a2h)_2$SA	M+H-H_2O (cyclic)	55.51610237
387.2140808	64667.31716	387.185568	$(4a2h)_3$	M+ethanolamine+Na	73.64120297
405.2236633	31962.4951	405.198003	$(4a2h)_4$	M+H-H_2O (cyclic)	63.32787874
418.1920471	34312.11079	418.162395	$(4a2h)_2$SA	M+ethanolamine+Na	70.91053465
436.2015381	61431.72595	436.17483	$(4a2h)_3$SA	M+H-H_2O (cyclic)	61.23252458
467.1861877	10903.82403	467.151657	$(4a2h)_2SA_2$	M+H-H_2O (cyclic)	73.91763142
488.2720947	24187.12329	488.233251	$(4a2h)_4$	M+ethanolamine+Na	79.55977378
506.2850952	10026.07337	506.245686	$(4a2h)_5$	M+H-H_2O (cyclic)	77.84602633
519.2550659	37057.09256	519.210078	$(4a2h)_3$SA	M+ethanolamine+Na	86.64685049
537.2675781	36690.33756	537.222513	$(4a2h)_4$SA	M+H-H_2O (cyclic)	83.88539927
550.2336426	7235.814997	550.186905	$(4a2h)_2SA_2$	M+ethanolamine+Na	84.94854671
568.2455444	21107.43784	568.19934	$(4a2h)_3SA_2$	M+H-H_2O (cyclic)	81.31729614
589.3278198	7174.857536	589.280934	$(4a2h)_5$	M+ethanolamine+Na	79.56446797
620.3115845	20729.73856	620.2578	$(4a2h)_4$SA	M+ethanolamine+Na	86.77597667
638.3253784	16077.44795	638.270196	$(4a2h)_5$SA	M+H-H_2O (cyclic)	86.45620357
651.2932739	12060.34898	651.234588	$(4a2h)_3SA_2$	M+ethanolamine+Na	90.11487885
669.3023071	17325.23547	669.247023	$(4a2h)_4SA_2$	M+H-H_2O (cyclic)	82.60646234
700.2886353	5774.033225	700.22385	$(4a2h)_3SA_3$	M+H-H_2O (cyclic)	92.52077603
721.3756104	8676.655065	721.305444	$(4a2h)_5$SA	M+ethanolamine+Na	97.27689231
739.3847046	6555.611082	739.317879	(4a2h)6SA1	M+H-H_2O (cyclic)	90.38816982

752.355896	**8958.850791**	**752.2823**	**$(4a2h)_4SA_2$**	**M+ethanolamine+Na**	**97.8688437**
770.3652954	**10377.94951**	**770.294706**	**(4a2h)5SA2**	**M+H-H_2O (cyclic)**	**91.6394848**
801.3500977	**6084.155758**	**801.271533**	**$(4a2h)_4SA_3$**	**M+H-H_2O (cyclic)**	**98.04997777**

Table S10. Peak list sorted by adduct and then mass and also colorcoded (for ease of visualization) for poly(4a2h-SA) positive mode MALDI-TOF-MS (**Figs. 3** and **S7**); sodiated and protonated peaks. "M+H-H_2O (cyclic)": possibility of both dehydrated or cyclic species.

Observed Mass (m/z)	Intensity	Calculated Mass	Identity	Adduct	PPM
286.1534729	138296.5019	286.13789	$(4a2h)_2$	M+ethanolamine+Na	54.45940767
387.2140808	64667.31716	387.185568	$(4a2h)_3$	M+ethanolamine+Na	73.64120297
418.1920471	34312.11079	418.162395	$(4a2h)_2$SA	M+ethanolamine+Na	70.91053465
488.2720947	24187.12329	488.233251	$(4a2h)_4$	M+ethanolamine+Na	79.55977378
519.2550659	37057.09256	519.210078	$(4a2h)_3$SA	M+ethanolamine+Na	86.64685049
550.2336426	7235.814997	550.186905	$(4a2h)_2SA_2$	M+ethanolamine+Na	84.94854671
589.3278198	7174.857536	589.280934	$(4a2h)_5$	M+ethanolamine+Na	79.56446797
620.3115845	20729.73856	620.2578	$(4a2h)_4$SA	M+ethanolamine+Na	86.77597667
651.2932739	12060.34898	651.234588	$(4a2h)_3SA_2$	M+ethanolamine+Na	90.11487885
721.3756104	8676.655065	721.305444	$(4a2h)_5$SA	M+ethanolamine+Na	97.27689231
752.355896	8958.850791	752.2823	$(4a2h)_4SA_2$	M+ethanolamine+Na	97.8688437
203.1082611	119627.7243	203.102637	$(4a2h)_2$	M+H-H_2O (cyclic)	27.69096494
304.1632996	79547.49402	304.15032	$(4a2h)_3$	M+H-H_2O (cyclic)	42.67482277
335.145752	45208.77016	335.127147	$(4a2h)_2$SA	M+H-H_2O (cyclic)	55.51610237
405.2236633	31962.4951	405.198003	$(4a2h)_4$	M+H-H_2O (cyclic)	63.32787874
436.2015381	61431.72595	436.17483	$(4a2h)_3$SA	M+H-H_2O (cyclic)	61.23252458
467.1861877	10903.82403	467.151657	$(4a2h)_2SA_2$	M+H-H_2O (cyclic)	73.91763142
506.2850952	10026.07337	506.245686	$(4a2h)_5$	M+H-H_2O (cyclic)	77.84602633
537.2675781	36690.33756	537.222513	$(4a2h)_4$SA	M+H-H_2O (cyclic)	83.88539927
568.2455444	21107.43784	568.19934	$(4a2h)_3SA_2$	M+H-H_2O (cyclic)	81.31729614
638.3253784	16077.44795	638.270196	$(4a2h)_5$SA	M+H-H_2O (cyclic)	86.45620357
669.3023071	17325.23547	669.247023	$(4a2h)_4SA_2$	M+H-H_2O (cyclic)	82.60646234
700.2886353	5774.033225	700.22385	$(4a2h)_3SA_3$	M+H-H_2O (cyclic)	92.52077603

739.3847046	6555.611082	739.317879	(4a2h)6SA1	M+H-H_2O (cyclic)	90.38816982
770.3652954	10377.94951	770.294706	(4a2h)5SA2	M+H-H_2O (cyclic)	91.6394848
801.3500977	6084.155758	801.271533	$(4a2h)_4SA_3$	M+H-H_2O (cyclic)	98.04997777

Table S11. Peak list sorted by mass for poly(4a2h-MA) positive mode MALDI-TOF-MS (**Figs. 3** and **S7**)); sodiated and protonated peaks. "M+H-H_2O (cyclic)": possibility of both dehydrated or cyclic species.

Observed Mass (m/z)	Intensity	Calculated Mass	Identity	Adduct	PPM
203.1118774	61217.23984	203.102637	$(4a2h)_2$	M+H-H_2O (cyclic)	45.49641076
286.1534729	59098.51242	286.13789	$(4a2h)_2$	M+ethanolamine+Na	54.45940767
304.1677246	38826.89896	304.15032	$(4a2h)_3$	M+H-H_2O (cyclic)	57.22370767
317.1872253	46808.71956	317.170717	$(4a2h)_2MA$	M+H-H_2O (cyclic)	52.04875833
387.2140808	21416.12425	387.185568	$(4a2h)_3$	M+ethanolamine+Na	73.64120297
400.2329102	22744.67772	400.205965	$(4a2h)_2MA$	M+ethanolamine+Na	67.32822186
405.2236633	15895.80825	405.198003	$(4a2h)_4$	M+H-H_2O (cyclic)	63.32787874
418.2492065	51464.6359	418.2184	$(4a2h)_3MA$	M+H-H_2O (cyclic)	73.66137645
431.2703247	25806.98307	431.238797	$(4a2h)_2MA_2$	M+H-H_2O (cyclic)	73.10962562
488.2720947	7823.612667	488.233251	$(4a2h)_4$	M+ethanolamine+Na	79.55977378
501.2944946	19271.03419	501.253648	$(4a2h)_3MA$	M+ethanolamine+Na	81.4889411
506.2850952	5339.720985	506.245686	$(4a2h)_5$	M+H-H_2O (cyclic)	77.84602633
514.3158569	10465.10194	514.274045	$(4a2h)_2MA_2$	M+ethanolamine+Na	81.30282756
519.3071899	30128.49217	519.266083	$(4a2h)_4MA$	M+H-H_2O (cyclic)	79.16353936
532.3309326	33528.91296	532.28648	$(4a2h)_3MA_2$	M+H-H_2O (cyclic)	83.51257954
545.3502197	12750.27915	545.306877	$(4a2h)_2MA_3$	M+H-H_2O (cyclic)	79.48318429
602.3504639	10335.776	602.301331	$(4a2h)_4MA$	M+ethanolamine+Na	81.57522567
615.3770752	10687.08136	615.321728	$(4a2h)_3MA_2$	M+ethanolamine+Na	89.94838388
620.3622437	14124.68433	620.313766	$(4a2h)_5MA$	M+H-H_2O (cyclic)	78.15021149
633.3897705	25799.72225	633.334163	$(4a2h)_4MA_2$	M+H-H_2O (cyclic)	87.8012134

646.4109497	19576.36245	646.35456	$(4a2h)_3MA_3$	M+H-H_2O (cyclic)	87.24268457
716.4333496	7321.153815	716.369411	$(4a2h)_4MA_2$	M+ethanolamine+Na	89.25368395
721.4234009	5715.255404	721.361449	$(4a2h)_6MA$	M+H-H_2O (cyclic)	85.88188222
734.4498291	14634.74789	734.381846	$(4a2h)_5MA_2$	M+H-H_2O (cyclic)	92.57187166
747.4680176	16847.41138	747.402243	$(4a2h)_4MA_3$	M+H-H_2O (cyclic)	88.00425556
760.4887085	7543.129313	760.42264	$(4a2h)_3MA_4$	M+H-H_2O (cyclic)	86.88391498
835.5036621	7313.521706	835.429529	$(4a2h)_6MA_2$	M+H-H_2O (cyclic)	88.73651987
848.5279541	11279.42892	848.449926	$(4a2h)_5MA_3$	M+H-H_2O (cyclic)	91.96547682
949.5841064	6558.255092	949.497609	$(4a2h)_6MA_3$	M+H-H_2O (cyclic)	91.09811776
962.6081543	6296.545552	962.518006	$(4a2h)_5MA_4$	M+H-H_2O (cyclic)	93.65881619

Table S12. Peak list sorted by adduct and then mass and also colorcoded (for ease of visualization) for poly(4a2h-MA) positive mode MALDI-TOF-MS (**Figs. 3** and **S7**)); sodiated and protonated peaks. "M+H-H_2O (cyclic)": possibility of both dehydrated or cyclic species.

Observed Mass (m/z)	Intensity	Calculated Mass	Identity	Adduct	PPM
286.1534729	59098.51242	286.13789	$(4a2h)_2$	M+ethanolamine+Na	54.45940767
387.2140808	21416.12425	387.185568	$(4a2h)_3$	M+ethanolamine+Na	73.64120297
400.2329102	22744.67772	400.205965	$(4a2h)_2MA$	M+ethanolamine+Na	67.32822186
488.2720947	7823.612667	488.233251	$(4a2h)_4$	M+ethanolamine+Na	79.55977378
501.2944946	19271.03419	501.253648	$(4a2h)_3MA$	M+ethanolamine+Na	81.4889411
514.3158569	10465.10194	514.274045	$(4a2h)_2MA_2$	M+ethanolamine+Na	81.30282756
602.3504639	10335.776	602.301331	$(4a2h)_4MA$	M+ethanolamine+Na	81.57522567
615.3770752	10687.08136	615.321728	$(4a2h)_3MA_2$	M+ethanolamine+Na	89.94838388
716.4333496	7321.153815	716.369411	$(4a2h)_4MA_2$	M+ethanolamine+Na	89.25368395
203.1118774	61217.23984	203.102637	$(4a2h)_2$	M+H-H_2O (cyclic)	45.49641076
304.1677246	38826.89896	304.15032	$(4a2h)_3$	M+H-H_2O (cyclic)	57.22370767
317.1872253	46808.71956	317.170717	$(4a2h)_2MA$	M+H-H_2O (cyclic)	52.04875833
405.2236633	15895.80825	405.198003	$(4a2h)_4$	M+H-H_2O (cyclic)	63.32787874

418.2492065	51464.6359	418.2184	$(4a2h)_3MA$	M+H-H_2O (cyclic)	73.66137645
431.2703247	25806.98307	431.238797	$(4a2h)_2MA_2$	M+H-H_2O (cyclic)	73.10962562
506.2850952	5339.720985	506.245686	$(4a2h)_5$	M+H-H_2O (cyclic)	77.84602633
519.3071899	30128.49217	519.266083	$(4a2h)_4MA$	M+H-H_2O (cyclic)	79.16353936
532.3309326	33528.91296	532.28648	$(4a2h)_3MA_2$	M+H-H_2O (cyclic)	83.51257954
545.3502197	12750.27915	545.306877	$(4a2h)_2MA_3$	M+H-H_2O (cyclic)	79.48318429
620.3622437	14124.68433	620.313766	$(4a2h)_5MA$	M+H-H_2O (cyclic)	78.15021149
633.3897705	25799.72225	633.334163	$(4a2h)_4MA_2$	M+H-H_2O (cyclic)	87.8012134
646.4109497	19576.36245	646.35456	$(4a2h)_3MA_3$	M+H-H_2O (cyclic)	87.24268457
721.4234009	5715.255404	721.361449	$(4a2h)_6MA$	M+H-H_2O (cyclic)	85.88188222
734.4498291	14634.74789	734.381846	$(4a2h)_5MA_2$	M+H-H_2O (cyclic)	92.57187166
747.4680176	16847.41138	747.402243	$(4a2h)_4MA_3$	M+H-H_2O (cyclic)	88.00425556
760.4887085	7543.129313	760.42264	$(4a2h)_3MA_4$	M+H-H_2O (cyclic)	86.88391498
835.5036621	7313.521706	835.429529	$(4a2h)_6MA_2$	M+H-H_2O (cyclic)	88.73651987
848.5279541	11279.42892	848.449926	$(4a2h)_5MA_3$	M+H-H_2O (cyclic)	91.96547682
949.5841064	6558.255092	949.497609	$(4a2h)_6MA_3$	M+H-H_2O (cyclic)	91.09811776
962.6081543	6296.545552	962.518006	$(4a2h)_5MA_4$	M+H-H_2O (cyclic)	93.65881619

Table S13. Compositional ratios of polyesters containing 4a2h and one other αHA which assemble into droplets. Cells with "X" indicate that the conditions were not tested in this study, as these conditions were generally not near the "Droplet"/"No Droplet" transition. Relevant microscopy images can be found in **Figs. 4, 5, S11, S12, and S23** and in reference[6]; the associated phase diagram is depicted as **Fig. 6.**

	4a2h:GA	**4a2h:LA**	**4a2h:PA**	**4a2h:SA**	**4a2h:MA**
0% 4a2h	*No* Droplets	Droplets	Droplets	Droplets	Droplets
10% 4a2h	X	Droplets	X	X	X
20% 4a2h	X	*No* Droplets	Droplets	Droplets	Droplets
40% 4a2h	X	X	Droplets	X	Droplets
50% 4a2h	*No* Droplets	*No* Droplets	Droplets	*No* Droplets	Droplets
60% 4a2h	X	X	Droplets	X	*No* Droplets
80% 4a2h	X	X	*No* Droplets	X	*No* Droplets

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