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Emulsion Polymerization of Acrylonitrile in Aqueous Methanol†

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Polyacrylonitrile (PAN) is the most widely utilized precursor for carbon fiber (CF) production. Though the CF market is growing, increased adoption is impeded by the high cost of the primary raw material, acrylonitrile (AN). AN is manufactured today *via* propylene ammoxidation, which produces several byproducts (hydrogen cyanide, acetonitrile, acrolein) that require multi-step separations to produce polymerization-grade AN. Recently, a new approach to manufacture bio-based AN from sugars was proposed based on catalytic nitrilation, which produces AN from C3-acrylate esters at >98% yield with alcohol and water as coproducts. The proposed nitrilation process included a 2-stage separation and purification scheme for AN recovery. Here, we hypothesize that in addition to offering a green alternative to propylene ammoxidation with higher product yield, nitrilation of methyl acrylate to produce AN could also enable direct AN polymerization without the proposed separation steps, since water can act as the solvent and MeOH as the chain transfer agent (CTA). Because AN, water, and MeOH form a ternary azeotrope, the heat duty required for separation is substantial and removal of this separation step reduces the heat demand significantly. To that end, we report AN polymerization *via* emulsion polymerization in aqueous methanol at varying concentrations of CTA. High molecular weight, low polydispersity (*e.g.*, 331.7 kDa, PDI = 1.88) PAN copolymers were produced from AN-MeOH-water emulsions, in the absence of additional CTAs. These PAN copolymers demonstrated thermal properties and carbon mass yields comparable to PAN copolymers prepared *via* conventional emulsion polymerization. By polymerizing AN in aqueous MeOH, the alcohol acts as the CTA, obviating the need for toxic, malodorous thiol-based CTAs (mercaptans). Utilizing the MeOH coproduct as the CTA results in a substantial heat demand reduction for the overall nitrilation process by 35%, leading to a 40% reduction imported process electricity demand, as the heat-intensive distillation steps required post-ammoxidation and previously proposed post-nitrilation are avoided. This polymerization method offers the opportunity to reduce the energy requirements of renewable AN production to improve both the sustainability and overall economics of bio-based CF precursor production.

Introduction

Carbon fiber (CF) is a high-performance material of increasing importance for designing lightweight, strong materials. CFs contain at least 90% carbon obtained by controlled pyrolysis of appropriate fiber precursors and have high tensile strengths (up to 7 GPa), excellent creep resistance, low densities, and high thermal and chemical resistance in the absence of oxidizers.[1-2] These ideal material properties make CF attractive for use in composites as continuous or chopped fibers or as woven textiles.[2] The CF sector is projected to grow substantially, with an expected annual increase of 11-18%,[3] driven by the need to make automotive vehicles more fuel efficient through lightweighting, as improved fuel economy offers significant potential for reducing greenhouse gas emissions and mitigating the harmful effects of global climate change.[4]

The greatest obstacle for CF technology is the high precursor cost, and polyacrylonitrile (PAN) is the most widely utilized precursor in the market.[2, 5-6] Acrylonitrile (AN) is commercially produced *via* propylene ammoxidation, a technology originally developed in the 1950s by the SOHIO company.[7-8] Although AN product yields have improved significantly since the 1950s, the chemistry produces significant quantities of hydrogen cyanide, acetonitrile, and acrolein, co-products that require use of five separation columns to yield polymerization-grade AN.[8] Propane ammoxidation as a route to AN has also garnered interest, because propane is cheaper and potentially of lesser environmental impact relative to propylene.[9] Still, the volatility of petroleum, propylene, and propane prices leads to volatility in the AN market, presenting a significant problem for CF manufacturers, as approximately 50% of the manufacturing cost of CF is due to AN costs.[6, 10]

Due to apprehension concerning propylene price volatility and environmental safety and sustainability issues, multiple non-petroleum routes to AN have been explored. Grasselli and

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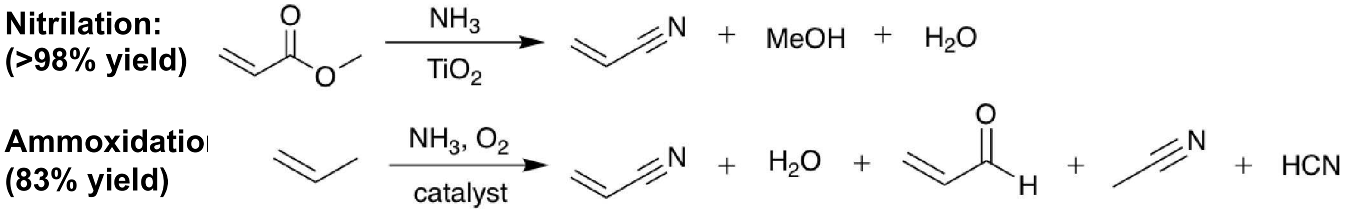
Trifirò summarized recent efforts to produce AN from alternative feedstocks such as glycerol[11-13] and glutamic acid.[14] Glycerol dehydration to acrolein followed by ammoxidation to AN was then deemed the most promising route, achieving AN yields of 60% on 5 cc microreactor scale.[11] Overall, the yields of AN from biomass feeds were not competitive with commercial routes to AN by ammoxidation of propylene or propane.

Driven by the need for new, sustainable, cost-effective processes for bio-derived AN, we recently reported quantitative conversion of acrylate esters, which can be derived from 3-hydroxypropionic acid[15] to AN *via* ester aminolysis to an amide followed by amide dehydration to nitriles, which we refer to as catalytic nitrilation. Specifically, we presented a route from ethyl 3-hydroxy-propanoate (ethyl 3-HP, derived from biologically-produced 3-hydroxypropionic acid, 3-HP) to AN at molar yields exceeding 90%, which included a 2-stage separation and purification process that recovers AN from residual solvents at a purity of >97%. Methyl acrylate is directly obtainable from ethyl 3-HP through reactive distillation, which combines esterification, alcohol dehydration, and product separation into a single unit operation. Building on this initial work, we now present a route from methyl acrylate (MA) to AN via nitrilation, at >90% yield. Using this nitrilation chemistry depicted in **Scheme 1**, an acrylate ester is passed over a TiO_2 catalyst with excess ammonia at 310-315°C, to produce stoichiometric amounts of AN, water, and alcohol (*e.g.*, methanol for MA nitrilation).

Nitrilation offers multiple green chemistry advantages over propylene ammoxidation (**Scheme 1**), which requires oxidation of propylene passed over a bismuth molybdate-based catalyst with O_2, an exothermic reaction that is inherently more hazardous and difficult to control than acrylate ester nitrilation.[16] AN yields *via* nitrilation of >98% already exceed the maximum AN yields achievable by ammoxidation chemistry, which currently peaks at 83%.[3, 16] Additionally, the ammoxidation byproducts, hydrogen cyanide (HCN), acetonitrile, and acrolein complicate product separation and require considerations for safe handling of HCN and acrolein, while nitrilation byproducts, water and methanol (MeOH), are relatively harmless. We also hypothesize that while AN produced from ammoxidation must be separated from reaction byproducts which are detrimental to polymerization, nitrilation byproducts would make a suitable solvent basis for PAN synthesis *via* emulsion polymerization, effectively removing the need to purify AN after producing it. Preliminary analysis (*vide infra*) of removing the process operations for recovery and purification of the AN product indicate promise of significant energy savings. Thus, nitrilation of acrylate esters offers an efficient pathway to cost competitive, sustainable AN from renewably-sourced intermediates, and may also obviate the need for expensive, energy intensive distillation steps required for producing polymerization-grade AN. Our previous work producing renewable AN through nitrilation chemistry made numerous strides in addressing the principles of green chemistry relative to propylene ammoxidation: the endothermic reaction eliminates runaway reaction hazards, higher product yields can be achieved, the toxic byproducts hydrogen cyanide and acrolein were avoided to improve process safety, and a renewable feedstock was utilized in an economical fashion. The novel polymerization technique reported herein maintains these original advantages over propylene ammoxidation, while also offering additional green chemistry improvements to the originally proposed nitrilation scheme and typical industrial AN polymerization process: removal of separation steps can greatly reduce heat and energy demands to the process, MeOH and water byproducts are utilized within the polymerization, and relatively benign MeOH is used as a substitute for dodecyl mercaptan, a corrosive liquid considered highly hazardous to water. Overall, the novel technique of polymerization AN in MeOH post-nitrilation affords the opportunity for significantly reducing both the cost and environmental impact of CF manufacturing.



Scheme 1. Nitrilation is a new process that can be employed to convert methyl acrylate to acrylonitrile (top). Ammoxidation is the conventional process to convert propylene to acrylonitrile (bottom).

Industrially, PAN copolymers are prepared in aqueous systems by free-radical mechanisms, such as suspension or emulsion polymerization.[1, 17-18] It has been shown that PAN CF precursor of very high molecular weights exceeding 1,000 kDa can be synthesized by emulsion polymerization.[19-20] Currently, most CF is produced from precursor fiber with ~95 wt% AN, with ~5 wt% of bulky acrylic comonomer (*e.g.*, MA) to improve spinnability and drawability, at molecular weights ranging from 70 to 200 kDa[5, 21] Polymers in this range yield precursor fibers with sufficient strength for textile applications, but it is known that further increasing the molecular weight can improve mechanical properties to reach an optimal strength and modulus for high performance CF.[2] **Figure 1** illustrates the approach proposed in this work whereby bio-derived AN is produced *via* nitrilation and polymerized, without further purification, in the presence of reaction coproducts, to yield the optimal molecular weight and material properties of a high performance CF precursor.

In this study, we aimed to determine if AN produced *via* nitrilation could be polymerized directly in reaction coproducts with no further separation, to demonstrate a significant advantage over the nitrilation method we previously proposed which included a 2-stage separation[15] and over the current industrial procedures whereby AN produced *via* propylene ammoxidation must subsequently be separated from reaction byproducts that are detrimental to polymerization. To demonstrate potential for direct polymerization of AN from nitrilation (without separating the monomer from coproduct solvent mixture), we synthesized ten PAN-based copolymers using commercial AN: one with no chain transfer agent (CTA) or MeOH, five with increasing levels of MeOH to act as a replacement CTA (including one which is a near-stoichiometric equivalent of the nitrilation product mixture), and four with increasing levels of dodecyl mercaptan (DDM) CTA. The chemical structure, molecular weight, and thermal properties of these copolymers were evaluated for their suitability as CF precursors. These results indicate that AN can be successfully polymerized at high, controlled molecular weights without separation from MeOH and water. PAN copolymers synthesized in aqueous MeOH demonstrated thermal properties and carbon mass yields comparable to PAN copolymers prepared *via* conventional emulsion polymerization both herein and reported in literature, suggesting optimal CF precursor properties. We also show experimental product flowrates with time-on-stream data, demonstrating the stoichiometric production of AN, MeOH, and water during MA nitrilation, to determine the actual ratio of AN and byproducts produced, and to establish there are no additional byproducts produced from side reactions. The primary goal of this research is to develop a technique for polymerizing renewable AN, produced from methyl acrylate nitrilation, within reaction coproducts, to yield high performance CF precursor comparable to or better than CF precursor produced from high purity, petroleum-derived AN polymerized by conventional emulsion polymerization.

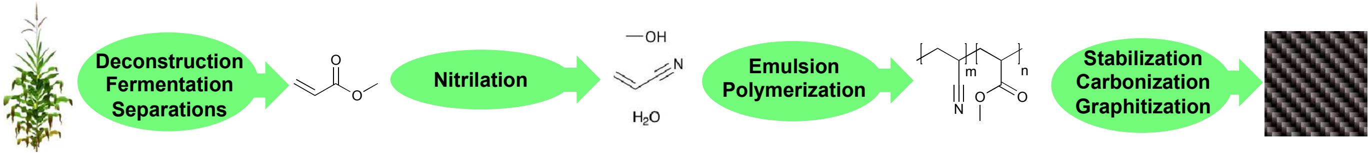


Figure 1. Methodology of current work. Bio-derived acrylonitrile is produced via nitrilation and polymerized in the presence of the reaction coproducts to yield a renewable carbon fiber precursor.

Results

Expanding on our initial work reporting quantitative production of bio-derived acrylate esters to AN[15], we now present a route to AN from methyl acrylate (MA), another biologically-derivable acrylate ester, at >98% yield. Using the "nitrilation" chemistry depicted in **Scheme 1**, AN was produced by passing MA over a TiO_2 catalyst with excess ammonia at 310-315°C to quantitatively produce stoichiometric yields of AN, water, and MeOH. Experimental product flowrates with time-on-stream are shown in **Figure 2**. AN yield is 97% ± 3% between 1 hour and 10.6 hours on stream. The total amount of product generated can be calculated by integrating product flowrates from **Figure 2**, giving total amounts of 0.52 mol AN (27.8 g), 0.56 moles MeOH (17.9 g), and 0.48 moles water (8.7 g).

With new processes developed to produce renewable AN with the coproducts of only water and alcohol, new procedures to polymerize in the presence of these coproducts are warranted to avoid the expensive separations needed to yield high purity AN. We hypothesized that AN could be polymerized by aqueous emulsion polymerization in the presence of MeOH, by foregoing the typical mercaptan-based CTA, allowing MeOH to control the reaction instead. Herein, AN was polymerized *via* emulsion polymerization with varying concentrations of MeOH or DDM. In all runs, the amount of the surfactant (alkyldiphenyloxide disulfonate; DOWFAX^{TM} 8390) remained constant.

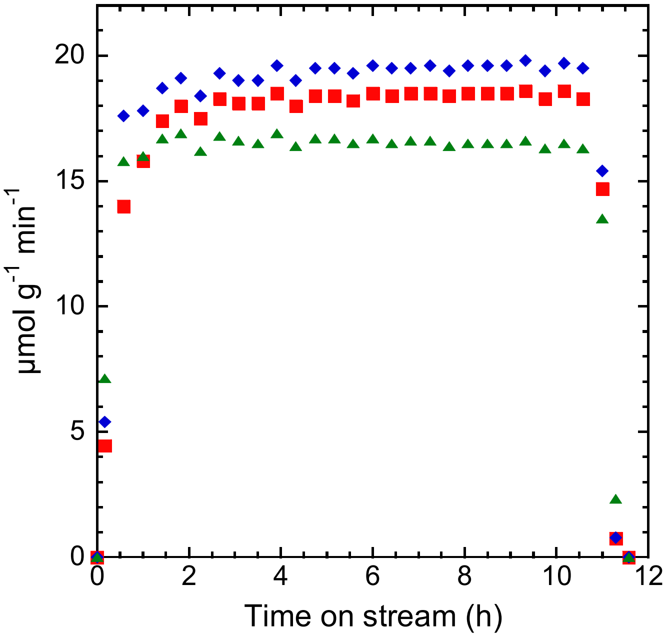


Figure 2. Product flowrates as a function of time-on-stream for methyl acrylate nitrilation over TiO_2. Legend: acrylonitrile (red squares), methanol (blue diamonds), and water (green triangles). Conditions: 45 g TiO_2, 315⁰C, 1923 sccm N_2, 128 sccm NH_3, 0.077 mL min^{-1} methyl acrylate. Acrylonitrile flowrate is equivalent to 97% between t = 1 and 10.6 hours.

Table 1 shows the results of synthesizing PAN copolymers with no CTA (Sample 1), MeOH CTA (Samples 2-6), or DDM CTA (Samples 7-10). When no CTA (Sample 1) or minimal MeOH (Sample 2) is used, the product yield is sufficiently high, but the M_N is not well controlled; it is noted in **Table 1** that these experiments resulted in undesirable bimodal molecular weight distributions, which are further discussed in the Supporting Information (SI). Sample 3, which used slightly more than equimolar MeOH to AN, is readily accessible by addition of slight excess of MeOH to the expected composition of AN and MeOH resulting from nitrilation reactions (**Figure 2**) and was successful in yielding an ideal polymer for CF precursor. Sample 3 exhibited high M_N, low PDI, and unimodal distribution, such that the methyl acrylate nitrilation products herein are at an ideal composition for direct copolymerization of AN in coproducts to yield high quality CF precursor. Samples 4-6 are also accessible post-nitrilation by excess MeOH addition, allowing for facile targeting of desired molecular weight. It may be noted here that the lower-molecular weight precursors are often desired for production of filaments via solvent-plasticized melt-spinning.[22]

Figure 3 compares the molecular weights of copolymers as a function of the concentration of MeOH or DDM CTA used. As expected because of the lower chain transfer constant of MeOH, a significantly higher concentration of MeOH is required to control the molecular weight distribution than if DDM were used. At the bench-scale (50 g), the molecular weight region of >150 kDa is not easily accessible with DDM, because an exceedingly small amount of the liquid CTA (<50 mg) would have to be measured accurately. At industrial scale, DDM would be scaled up to higher volumes that would make higher molecular weight more accessible. However, MeOH is shown to produce lower PDIs at similar M_N (see Table 1, Sample 5 and Sample 9), which is highly desirable for CF precursor. Overall, these data demonstrate that MeOH provides a readily accessible, broad window of PAN molecular weight, and provides improved control over polydispersity.

Table 1. Summary of PAN-*r*-PMA synthesized with various CTAs and CTA concentrations.

Sample	Mol fed AN:MeOH	MeOH (M)	DDM ($Mx10^{-3}$)	Yield (wt%)	PAN:MA (mol%)[a]	M_N (kDa)	PDI
1	1.00:0.00	0	0	92.9	97:3	726.3[b]	13.30[b]
2	1.00:0.58	2.3	0	79.7	97:3	507.7[b]	13.50[b]
3[c]	**1.00:1.14**	**4.6**	**0**	**79.5**	**97:3**	**331.7**	**1.88**
4	1.00:2.29	9.3	0	63.9	97:3	226.3	2.07
5	1.00:3.44	13.7	0	34.9	97:3	82.5	2.10
6	1.00:4.46	17.7	0	21.0	97:3	50.4	1.99
7	1.00:0.00	0	2.5	88.6	96:4	150.9	2.29
8	1.00:0.00	0	5.0	90.8	97:3	117.5	2.47
9	1.00:0.00	0	10.0	88.6	96:4	85.8	2.84
10	1.00:0.00	0	15.1	94.3	97:3	38.9	2.28

[a] Molar composition of polymer as determined by ^1H NMR spectroscopy. All reactions were fed a ratio of 97 moles AN:3 moles MA and reacted for 24 h at 65°C. [b] An additional lower molecular weight shoulder peak was detected in the eluogram. The higher molecular weight peak is reported here; molecular weight analysis of the lower molecular weight peak is provided in Table S1. The PDI reported here is representative of the overall M_N, including the lower molecular weight peak. [c] Sample 3 composition is readily accessible directly from the product mixture resulting from nitrilation of MA.

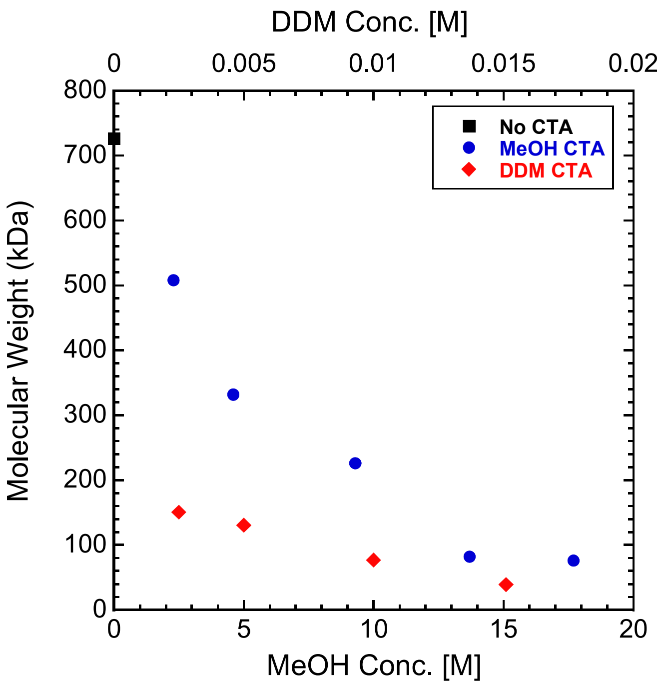


Figure 3. Molecular weight of PAN-*r*-PMA copolymer as a function of **(bottom)** MeOH CTA concentration and **(top)** dodecyl mercaptan CTA concentration.

The chemical structure, composition, and purity of the ten PAN copolymer samples was investigated by ^{1}H NMR spectroscopy. **Figure 4** shows ^{1}H NMR spectra of the ten samples. Copolymer molar compositions were determined by comparing the integral of the methine (CH) protons from PAN and PMA units at 3.2 ppm (b; integrated from 3.28 ppm to 2.66 ppm) to the integral of the methyl (CH_3) protons of the PMA units at 3.7 ppm (c; integrated from 3.80 ppm to 3.53 ppm), such that the molar ratio of MA in the copolymer was calculated from the integral values of the methyl protons relative to the methine protons (*i.e.*, (c/3)/b). The acrylate co-monomer in the PAN precursor markedly influences the microstructure of resultant precursor fibers, with ~3 mol% MA incorporation being found suitable for precursor development, and increased MA interfering with cyclization.[23] Because AN is the product of MA nitrilation, running at 97% nitrilation conversion would even allow use of the mixture directly without adding 3 mol% MA. All samples fall within this narrow range of ideal composition (3-4 mol% MA). As expected, end groups make up a greater proportion of the polymer composition (*i.e.,* are more evident in ^{1}H NMR at 1.3 to 0.8 ppm) in samples employing a dodecyl end group from DDM (Samples 7-10), and in samples with a lower degree of polymerization relative to the methoxyl end group from MeOH (Samples 5-6). In industrial PAN CF precursors, a small quantity (<1 mol%) of stabilization accelerant monomer (such as itaconic acid or acrylic acid) may also be included.[2, 10] We aimed to keep the composition as a copolymer, mimicking industrial textile PAN copolymer that has promise as CF precursors, but the chemistry presented herein could readily incorporate such an accelerant.

The effect of altering the PAN copolymer architectures and end groups on the thermal stabilization process was investigated by DSC, TGA, and FTIR spectroscopy to evaluate the copolymers potential as CF precursors, relative to their preparation technique. The exothermic events evidenced by DSC analysis in **Figure 5** indicate cyclization reactions.[24] Thermal characterization by DSC was performed under nitrogen at a ramp rate of 10°C/min to investigate the extent of thermal cyclization reactions. In contrast to PAN homopolymer cyclization which is initiated in the amorphous phase through a radical mechanism yielding a sharp intense exotherm, PAN co-monomers exert a diluent effect such that the copolymer exotherms are broadened and have a lower energy peak release.[25-27] PAN homopolymer exotherms typically have peak temperatures of 260-280°C depending on heating rate, while increasing MA content in PAN copolymers results in an increase of exothermic peak temperatures.[27-29] All of the PAN copolymer samples exhibited relatively symmetric, narrow exotherms, with peaks centered between 309 and 329°C. Peak temperatures and the corresponding maximum heat flows are listed in **Table 2**. The samples with thiol-based end groups (Samples 7-10) exhibit slightly higher peak temperatures relative to the samples with methoxyl-based end groups (Samples 2-6), indicating that end-group effects cannot be neglected. Samples with thiol-based end groups (Samples 7-10) also generally reached a higher peak heat flow; these differences can likely be attributed to the higher reactivity of thiol groups relative to methoxyl groups. All samples have maximum heat flows of <10 W/g, which is an appropriately low amount of energy released over the narrow temperature range to avoid prematurely degrading the polymer backbone. Interestingly, Sample 2 has a notably lower peak cyclization temperature relative to all other samples. This lower cyclization temperature is in agreement with previous studies that lower M_n leads to lower T_p, as the bimodal molecular weight distribution of Sample 2 (Table S1) results in the lowest M_n of samples synthesized in MeOH.[30-31] Thermal properties of the PAN copolymers were further investigated by TGA, shown in **Figure 5**. Final mass yields from TGA are summarized in **Table 2**. Mass loss post-cyclization is an indicator of carbon content, where greater mass retention suggests formation of a more complete ladder structure.[29] TGA thermogram regions are as follows:

(1) Cyclization: the exothermic cyclization reaction, which occurs during the plateau between 200 and 300°C, represents the formation of the aromatic ladder structure and should theoretically not include weight loss.[32]

(2) Dehydration: rapid weight loss between 300 and 350°C during the conversion of C—C bonds to C=C bonds due to the heat generated during cyclization, accompanied by release of small molecules such as water and carbon dioxide.[33-34]

(3) Steady weight loss between 350 and 450°C due to continued removal of small molecules from the cyclized ladder structure such as methane, ammonia, hydrogen cyanide, water, and carbon dioxide.[35]

(4) Weight loss in the stabilized structure plateaus between 450 and 600°C.[29]

(5) Carbonization: steady weight loss above 600°C from release of hydrogen cyanide, ammonia, nitrogen, and hydrogen.[35]

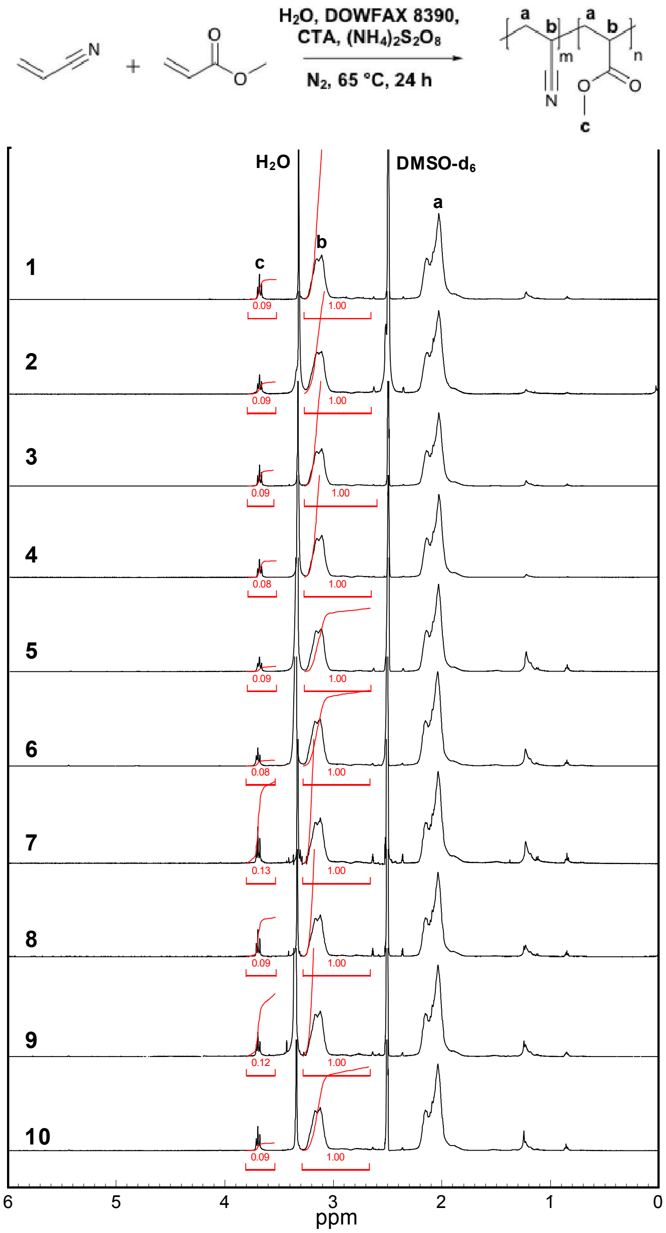


Figure 4. ^{1}H NMR spectra of PAN-*r*-PMA samples.

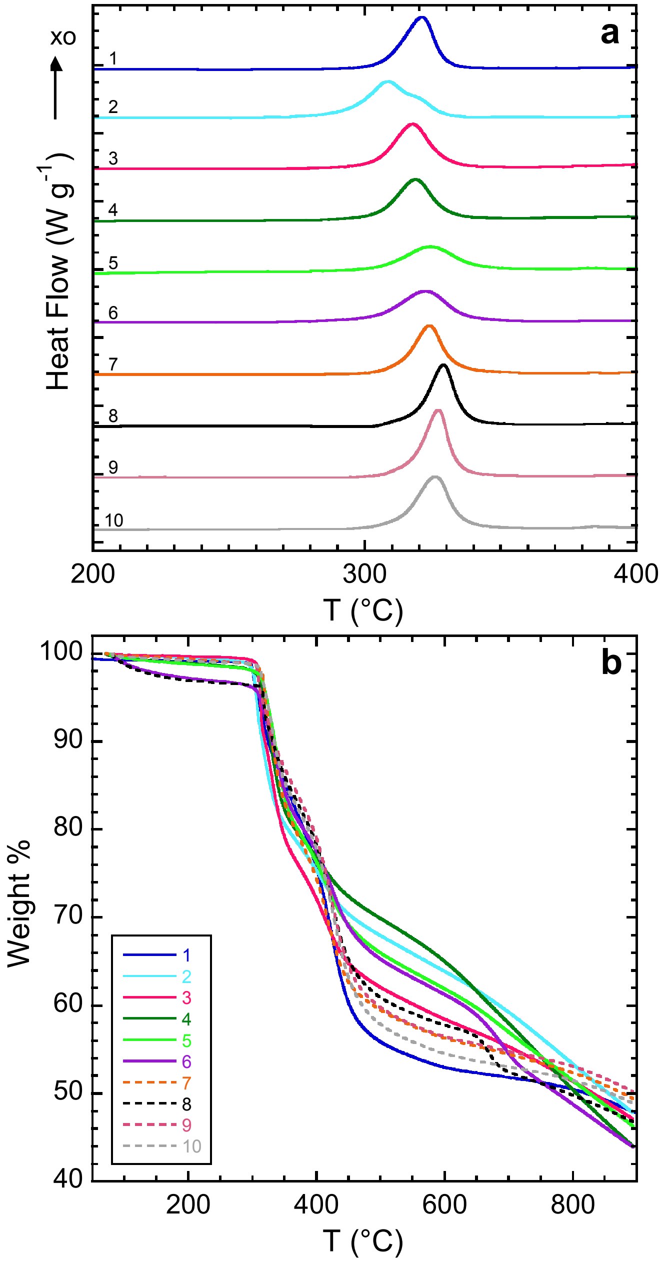


Figure 5. Thermal characterization of PAN-r-PMA samples: (**top**) DSC and (**bottom**) TGA thermograms.

It is apparent in **Figure 5** that the mass loss for the methoxyl group end-capped polymers is not as steep between 300 and 400°C as for those with thiol end groups. This is in agreement with the greater heat flow generated during cyclization observed in the DSC of Samples 7-10, which would cause more rapid mass loss. However, Samples 7-10 show more weight loss after 400°C such that the final residual mass content for all samples at 900°C falls within a range of 44-50 wt%, suggesting that end group and molecular weight effects are negligible in the overall goal of creating a ladder structure capable to withstand carbonization.

As cyclization and dehydrogenation reactions of CF precursor are essential steps in the successful conversion of precursor to graphitic carbon, the chemical structures of the ten samples were analyzed by FTIR spectroscopy prior to heat treatment and during the cyclization/dehydrogenation reactions, to determine their suitability as CF precursor and evaluate potential differences in thermal behavior arising from preparation method **Figure 6** shows the FTIR spectra of untreated PAN-r-PMA samples and samples after being heated to 500°C at 10°C/min under nitrogen with TGA. The FTIR spectra of the pristine PAN-*r*-PMA samples exhibited characteristic peaks of the vibrations of nitrile groups (C≡N at

2243 cm^{-1}), a hydrocarbon backbone (C-H in CH_2 at 2940 cm^{-1} and 1454 cm^{-1}, C-H in CH at 1360 cm^{-1}), and an ester group (C=O at 1732 cm^{-1}, C-O-C at 1171 cm^{-1}).[36-38] The peak at 1073 cm^{-1} is associated with the PAN fingerprint region, where assignment is uncertain.[20] Minimal differences are noted between samples; all samples contain the major peaks associated with PAN and PMA (C≡N, C-H, C=O) in the expected relative ratios, with variation in the fingerprint region, likely associated with residual water or end groups.

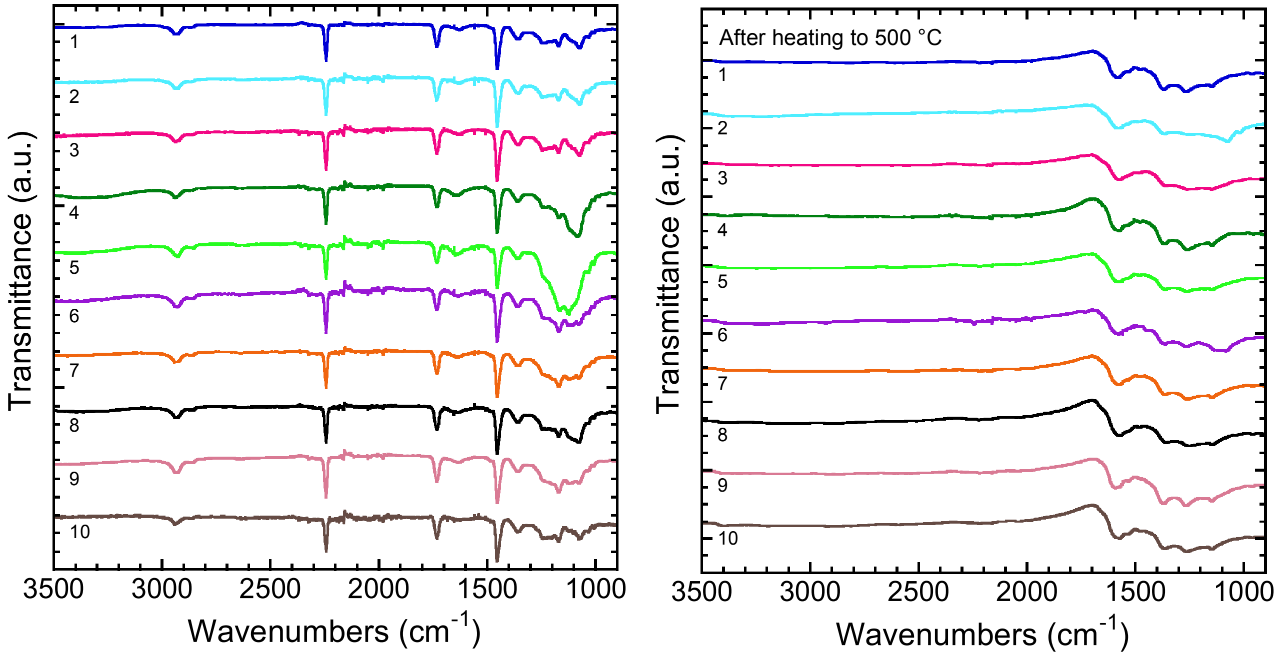


Figure 6. FTIR spectra of PAN-*r*-PMA samples (**left**) before heat treatment and (**right**) after heating to 500 ˚C by TGA.

Table 2. Summary of PAN-r-PMA thermal properties.

Sample	Peak Temperature (°C)[a]	Heat Flow (W/g)[b]	Mass Yield (wt%)[c]
1	321	5.6	47.8
2	309	4.1	47.8
3	317	5.0	47.1
4	318	4.6	44.0
5	325	2.7	46.3
6	324	3.4	43.9
7	323	5.4	49.4
8	329	6.8	46.8
9	327	7.5	50.2
10	325	5.7	48.8

[a] Temperature at maximum heat flow from DSC under N_2 at ramp rate of 10 °C/min

[b] Maximum heat flow at peak temperature from DSC under N_2 at ramp rate of 10 °C/min

[c] Final mass from TGA under N_2 at ramp rate of 10 °C/min

Evidence of cyclization can be clearly observed after heat treatment in **Figure 6**. The cyclization reaction converted –C≡N groups into cyclic –C=N- and –C-N- groups, as demonstrated by the disappearance of the nitrile peak at 2243 cm^{-1}. The peak at 1587 cm^{-1} represents cyclic –C=C– and –C=N– groups and the peak at 1267 cm^{-1} represents cyclic –C-N- group resulting from successful cyclization.[36-39] Minimal difference is noted across samples, indicating negligible interference of end groups with cyclization. **Table 3** summarizes the characteristic FTIR peak frequencies and functional groups of PAN before and after heat treatment.

Table 3. FTIR peaks of PAN-r-PMA before and after heat treatment.

Before Heat Treatment		After Heat Treatment	
Peak frequency (cm^{-1})	Functional Group	Peak frequency (cm^{-1})	Functional Group
2940	C-H	1587	C=C, C=N
2243	C≡N	1370	C-H
1732	C=O	1267	C-N, C-C
1454	C-H	-	-
1360	C-H	-	-
1247	C-O	-	-
1171	C-O-C	-	-
1073	Fingerprint	-	-

Discussion

In this study, new procedures to polymerize AN in the presence of water and MeOH were developed as a complement to recently developed processes for yielding renewable AN with water and alcohol byproducts. This novel chemistry is particularly advantageous over ammoxidation, the current standard for producing AN; ammoxidation yields byproducts of hydrogen cyanide, acetonitrile, and acrolein which are toxic and detrimental to polymerization, and thus require expensive separations to acquire polymerization-grade AN. Additionally, direct polymerization of nitrilation products gives the option to recover methanol post-polymerization for subsequent industrial use. Emulsion polymerization of nitrilation products was of particular interest because it is already a common industrial route for synthesizing PAN copolymers for CF precursor in water.[1, 17-18] Although this process already makes use of the water coproduct, alcohol is not regularly incorporated into this polymerization technique. However, emulsion polymerization does require use of a CTA, and it is a well-documented phenomenon in polymer chemistry that solvents with at least one weak chemical bond, such as alcohols, may act as CTAs, controlling the average molecular weight and polydispersity of the final polymer. In a typical emulsion polymerization of acrylic monomers, DDM is the most commonly employed CTA, with a relatively high chain transfer constant.[40-41] There is interest in substituting DDM with a more benign CTA, as it is highly toxic and exhibits a strongly repulsive odor.[42-44] Herein, we hypothesized that MeOH could replace DDM in the emulsion polymerization of AN at higher concentrations due to the lower chain transfer constant of MeOH.

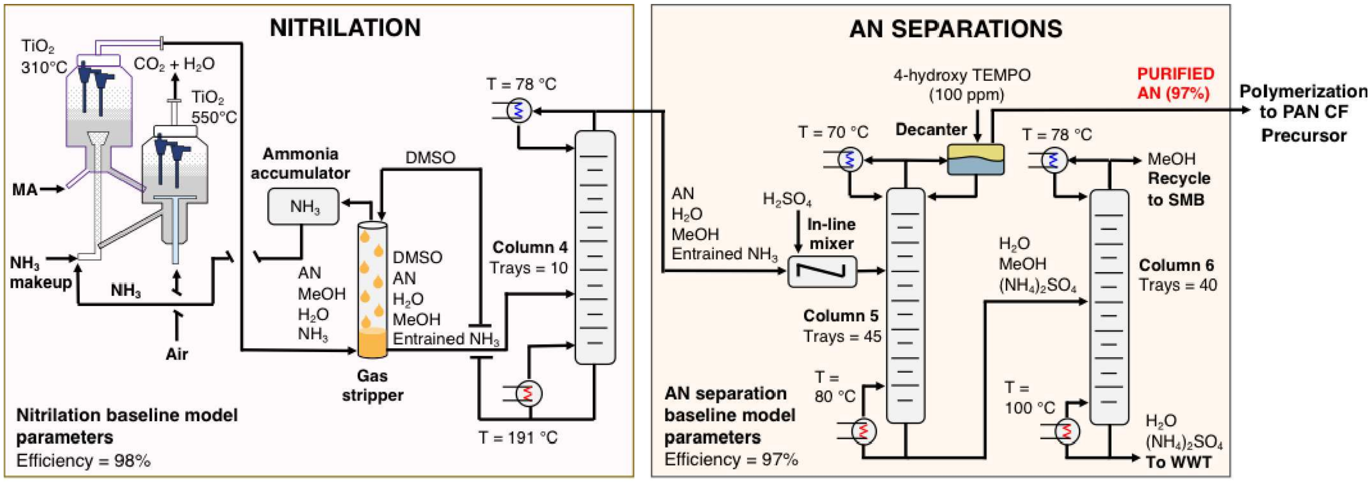
As shown in the polymerization summary in **Table 1**, the yield was somewhat reduced for all of the samples employing MeOH as the CTA, with these experimental yields ranging from 21.0 wt% to 79.7 wt% relative to experimental yields ranging from 88.6 wt% to 94.3 wt% for the samples employing DDM as the CTA. However, when MeOH is used as the CTA, separation of AN is not required; to further separate pure AN from the ternary mixture would require azeotropic distillation, employing an entrainer. Preliminary results described in the SI utilizing methyl acetate as an entrainer resulted in low yield (~54%) of relatively high purity (>95 wt%) AN, by spinning band distillation at atmospheric pressure (^{1}H NMR spectrum shown in **Figure S1**). Although yield would arguably be higher in a continuous column at the industrial scale, at the laboratory scale this translates to a reduction in overall yield for Samples 7-10 by approximately a factor of two, making overall yields for Samples 2-4 more favorable.

A process analysis also predicts substantial energy savings when the process operations to recover and purify the bio-derived AN product are removed. As outlined by Karp *et al.*[15], the proposed AN production scheme includes a 2-stage separation and purification process which first recovers the AN from residual solvents from the process at a purity of greater than 97%. The process also recovers the residual alcohol at high purity (>99.9%) and returns it to the process for further conversion. Since the AN and residual solvents (namely, water and alcohol) form a ternary azeotrope, the heat duty required for separation is very large. Removal of this separation step reduces the heat demand in the entire process by 35%. Of this reduction, 80% is due to the removal of the reboiler duty required for the AN purification, while the remaining reduction is due to the removal of the alcohol recovery unit. Because of the reduction of heat demand, there is additional steam in the process to generate electricity. This reduction in heat/steam demand results in reduction of electricity imported to the process by nearly 40%. Other utilities in the process are also affected by this design change, but the impact is relatively minimal. Specifically, cooling and chilled water demands are reduced by 3% and 1.7%, respectively. A graphical depiction of the process flow diagram and the green chemistry benefits of the proposed process is shown in **Figure 7**.

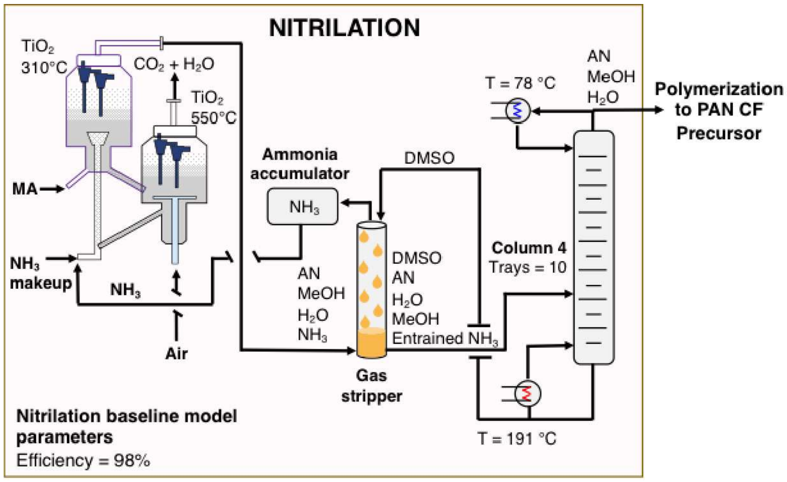
Experimental product flowrates of MA nitrilation are shown in **Figure 2**. Gas phase products are quantified using an FTIR continuous gas analyzer, to reveal near stoichiometric amounts of AN (0.52 mol), MeOH (0.56 mol), and water (0.48 mol). Trace water in the FTIR nitrogen purge gas (50-60 ppm) makes accurate quantification of water challenging, which explains the less-than-stoichiometric amount of water in the product stream. Ongoing studies consistently find MeOH/AN ratios greater than one, which is a phenomenon currently attributed to catalyst deactivation. Carbon laydown of a reactive intermediate leads to catalyst deactivation, where the intermediate is formed after release of the alcohol group.

In addition to stabilization in temperatures up to 400°C and carbonization in temperatures up to 1,600°C, CF precursor must be able to withstand graphitization in temperatures up to 3,000°C.[5] Typically, efforts to enhance CF tensile strength have concentrated on the stabilization and carbonization reaction, emphasizing the importance of the thermal properties of the precursor. In this study, minor differences were observed in the DSC and TGA thermograms, according to how the copolymer was prepared. Typical carbon yields for CF precursors are ~50%, which was closely matched by Sample 3, at 48 wt% recovery.[1, 35, 45-46] Ultimately, mass yields at 900°C were comparable for PAN copolymers prepared in aqueous MeOH relative to water, and minimal weight loss is expected after 900°C, suggesting that the PAN copolymers would have suitable thermal properties for acting as CF precursor.

Original Separations Approach:



Proposed Direct Polymerization Approach:



GREEN CHEMISTRY BENEFITS OF REMOVING SEPARATIONS

- **Heat demand reduced by 35%**
- **Imported electricity reduced by ~40%**
- **Reduction of cooling water demand**
- **Coproducts utilized for polymerization**
- **MeOH substituted for toxic DDM**

Figure 7. Graphical representation of the process flow diagram for including separations after nitrilation or circumventing separations after nitrilation to directly polymerize AN in MeOH and water coproducts. Process diagram adapted from the supporting information of ref. 15.

Conclusions

To contribute to the overall goal of developing bio-based CF, the emulsion polymerization of CF precursors, PAN-*r*-PMA copolymers, was studied in excess MeOH and compared to conventional emulsion polymerization. This new synthetic approach is complementary to a new process recently developed to produce bio-based AN *via* methyl acrylate nitrilation with a MeOH coproduct. Most notably, this method of polymerizing AN in the presence of the aqueous MeOH byproducts precludes the need for isolating pure AN from the product mixture *via* additional energy- and capital-intensive distillation steps. Avoiding the conventional separation steps will ultimately benefit the economics of the overall process by reducing the number of unit operations and energy requirements. According to preliminary analysis, removal of the process operations to recover and purify the bio-derived AN product shows a substantial reduction of the heat demand in the entire process by 35% and a reduction of electricity that must be imported to the process by nearly 40%. Alongside designing for energy efficiency, additional green chemistry principles are addressed by utilizing MeOH and water byproducts within the polymerization reaction, and substituting the relatively benign MeOH for dodecyl mercaptan, a corrosive liquid considered highly hazardous to water. Characterization results (^{1}H NMR, FTIR, GPC, TGA, DSC) demonstrate that this new procedure yields high purity PAN copolymers of target composition and controlled molecular weight, meeting the criteria for high-quality CF-precursor. Aqueous MeOH as the solvent basis allowed access to a higher molecular weight region than that which was easily accessible under the same conditions with aqueous solvent and DDM, and provided better control over molecular weight (i.e., lower PDI). Overall, the successful synthesis of PAN copolymers in MeOH is highly attractive for the CF industry from an economic and green chemistry perspective.

Materials and Methods

Acrylonitrile (≥99%, contains 35-45 ppm monomethyl ether hydroquinone as inhibitor) and methyl acrylate (99%, contains ≤100 ppm monomethyl ether hydroquinone as inhibitor) were obtained from Sigma-Aldrich and passed through inhibitor removal columns packed with Al_2O_3. Methanol, ammonium persulfate, dodecyl mercaptan, and magnesium sulfate were used as received from Sigma-Aldrich. DOWFAX 8390 surfactant was obtained from The Dow Chemical Company. Deionized (DI) water was used as appropriate.

Polymer Synthesis

Synthesis of copolymer PAN-*r*-PMA was performed by emulsion polymerization of commercially available acrylonitrile. Results of a typical polymerization using no chain-transfer agent (CTA) are listed in Table 1, Sample 1. The reaction mixture contained 175 mL water, 5.15 g surfactant (DOWFAX 8390), 51.25 g AN, 2.60 g MA, 34 mg initiator (ammonium persulfate). All materials were stirred in a round bottom flask and purged with nitrogen for 0.5 h, then reacted under nitrogen balloon at 65 ˚C for 24 h. The resultant emulsion was added to 700 mL of a 1 wt% aqueous $MgSO_4$ solution at 70 ˚C and stirred briefly to break the emulsion, then the solid polymer was filtered. The solid powder was washed by stirring in 500 mL of DI water, filtered, and dried at 70 ˚C under convection overnight. Yield 50.0 g of solid white powder (92.9%).

Results of typical emulsion polymerizations of PAN-*r*-PMA using MeOH as a CTA are listed in **Table 1**, Samples 2-6. In a typical reaction (Sample 3), the reaction mixture contained 130 mL water, 45 mL MeOH, 5.15 g surfactant (DOWFAX 8390), 51.25 g AN, 2.60 g MA, 34 mg initiator (ammonium persulfate). All materials were stirred in a round bottom flask and purged with nitrogen for 0.5 h, then reacted under nitrogen balloon at 65 ˚C for 24 h. The resultant emulsion was added to 700 mL of a 1 wt% aqueous $MgSO_4$ solution at 70 ˚C and stirred briefly to break the emulsion, then the solid polymer was filtered. The solid powder was washed by stirring in 500 mL of DI water, filtered, and dried at 70 ˚C under convection overnight. Yield 42.8 g of solid white powder (79.5%). Additional polymerizations following the same procedure were performed at various concentrations of MeOH to produce a range of molecular weights. MeOH volume was varied linearly, and water was added in corresponding volumes such that the total separate volumes of the MeOH and water totaled to 175 mL; note that because alcohol and water volumes are not additive, upon combining the solvents the volume decreased such that total solution volume across reactions varied slightly. Synthesis results are summarized in **Table 1**, Samples 2-6.

Results of typical emulsion polymerizations of PAN-*r*-PMA using DDM as a CTA are listed in Table 1, Samples 7-10. In a typical reaction (Sample 8), the reaction mixture contained 175 mL water, 5.15 g surfactant (DOWFAX 8390), 51.25 g AN, 2.60 g MA, 250 mg chain-transfer agent (dodecyl mercaptan (DDM)), 34 mg initiator (ammonium persulfate). All materials were stirred in a round bottom flask and purged with nitrogen for 0.5 h, then reacted under nitrogen balloon at 65 ˚C for 24 h. The resultant emulsion was added to 700 mL of a 1 wt% aqueous $MgSO_4$ solution at 70 ˚C and stirred briefly to break the emulsion, then the solid polymer was filtered. The solid powder was washed by stirring in 500 mL of DI water, filtered, and dried at 70 ˚C under convection overnight. Yield 48.9 g of solid white powder (90.8%). Additional polymerizations following the same procedure were performed at various concentrations of DDM to produce a range of molecular weights. Synthesis results are summarized in **Table 1**, Samples 7-10.

Molecular Weight Characterization

Molecular weight (M_N) and molecular weight distribution (polydispersity index, PDI) were determined in DMF (with 0.05 mol LiBr) *via* size exclusion chromatography (SEC) at 60 °C and a flowrate of 1 mL min^{-1}. The SEC system consisted of a Waters 1515 Isocratic HPLC pump equipped with 2414 Refractive Index (RI) detector. Polyethylene oxide/polyethylene glycol standards were used with Styragel HR 3 and HR 4 columns maintained in a column heater compartment. Integration was performed against standards using Empower software. Eluograms were baseline corrected to zero at 8 min elution time and normalized by peak intensity. SEC eluograms are shown in the Supporting Information, **Figure S2**. M_N and PDI of the copolymers are listed in Table 1, and M_N is plotted relative to CTA concentration in **Figure 3**.

Thermal Characterization

Thermal behavior of the copolymers was observed by differential scanning calorimetry (DSC; TA Instruments, Q2000) over a temperature range of 0 to 450 °C at a heating/cooling rate of 10°C/min under a N_2 environment using a heat/cool/heat method. Thermal degradation of the copolymers was measured by thermal gravimetric analysis (TGA; TA Instruments, Q500) using a temperature ramp to 900°C at a heating rate of 10°C/min under a N_2 environment. Intermediate cyclization products were also produced by TGA using a temperature ramp to 500°C at a heating rate of 10°C/min under a N_2 environment. Thermograms resulting from DSC and TGA analysis are shown in **Figure 5**.

Structural Characterization

Chemical structures and compositions of the copolymers and AN solution were characterized by ^1H NMR spectroscopy (**Figure 4** and **Figure S2**, respectively) using a Varian 500 MHz spectrometer at 23°C with DMSO-d_6 as the solvent. The chemical shifts were referenced to DMSO-d_6 at 2.50 ppm. Copolymer molar compositions were determined by comparing the integrals of the proton signals in the repeat units. The signal at 3.2 ppm (b; integrated from 3.28 ppm to 2.66 ppm) corresponds to the methine (CH) protons from PAN and PMA. The signal at 3.7 ppm (c; integrated from 3.80 ppm to 3.53 ppm) corresponds to the methyl (CH_3) protons of the PMA units. The molar content of MA in the copolymer was calculated from the integral values of the methyl protons relative to the methine protons (*i.e.*, (c/3)/b).

Chemical structures of the copolymers and intermediate cyclization products were investigated with infrared spectroscopy using a Fourier transform infrared (FTIR) spectrometer (PerkinElmer Frontier). All spectra were collected at 32 scans per spectrum. Before each experiment, a background spectrum was collected, and each subsequently collected spectra was subtracted from the background spectrum. **Figure 6** shows FTIR spectra for PAN-*r*-PMA and intermediate cyclization products. **Table 2** provides a summary of the characteristic FTIR peak frequencies and functional groups of the PAN copolymers before and after heat treatment.

Methyl Acrylate Nitrilation

Nitrilation experiments were performed in a vapor-phase flow reactor system with heated lines and a 0.75” ID x 8” long reactor (Parr Instrument Company). Gas was delivered with nitrogen and ammonia mass flow controllers (MKS instruments), and methyl acrylate was delivered with an NE-1000 (New Era Pump Systems Inc.) syringe pump, wherein methyl acrylate was injected into a heated nitrogen carrier stream. Ammonia was introduced just upstream of the reactor bed. The reactor bed was packed with catalyst held between two quartz plugs, with 1 mm, 2mm, and 3 mm glass beads packed upstream of the catalyst bed to mix gases and prevent channeling. The effluent gas is quantified with an online MKS MultiGas 2030 FTIR continuous gas analyzer with a 2-cm cell (MKS Instruments) calibrated with authentic standards to quantify all reactant and product gases simultaneously. For the nitrilation of methyl acrylate the reactor was packed with 45 g of TiO_2 (Johnson-Matthey, 0.5 mm particle size, roughly 45 mL bed volume), and heated to 315 ^{0}C under flowing nitrogen (1923 sccm). Once the reactor reached the set temperature, ammonia was introduced (128 sccm), then methyl acrylate was introduced (0.077 mL min^{-1}). For collection, the effluent gas from the FTIR flowed into a knock-out pot chilled to 5 to 10^{0}C, packed with 6 mm soda lime glass beads, and containing a solution of 100 ppm 4-hydroxy TEMPO in 400 mL DMF.

Conflicts of Interest

A patent application has been filed on this work.

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