Condensation of DAMN with Conjugated Aldehydes and Polymerizations of the Corresponding Imines

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ABSTRACT: The reaction of diaminomaleonitrile (DAMN) with aldehydes such as acrolein, methacrolein, and crotonaldehyde in the presence of acid catalyst at low temperature yielded exclusively monoimine derivatives of DAMN. These compounds have very low loss of volatiles up to 1000 °C and form high char yields. The residual mass at 800 °C for the acrolein derivative was found to equal 70% of the starting material. Thermally induced step growth 1,4-conjugate addition polymerization on these compounds yields moderate molecular weight oligomeric materials ($M_n = 1376$, $M_w = 2050$). *N*-EthylDAMN was synthesized by reaction of DAMN with acetaldehyde followed by reduction with $NaBH_4$. *N*-EthylDAMN reacted with acrolein, methacrolein, and crotonaldehyde to form *N*-ethyl-monoimine derivatives of DAMN. These analogues also undergo 1,4-conjugate addition polymerization to yield linear polymers. The dimethylamino derivative was found to undergo polymerization by a different mechanism, strengthening the proposed 1,4-conjugate addition mechanism.

Introduction

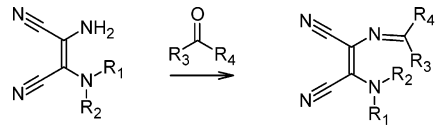
Diaminomaleonitrile (DAMN) (**1**) is synthesized in high yield by direct oligomerization of hydrogen cyanide[1] (Scheme 1). This is a remarkable reaction in that it provides a nearly singular outcome from conditions that might have been expected to yield numerous products. Three carbon−carbon connections are formed in the condensation, and therefore the product does not readily revert to hydrogen cyanide.

DAMN is a weakly basic diamine which can react with a number of electrophiles. Reaction between DAMN and aldehydes or ketones can result in Schiff base formation[2] (Scheme 1). In contrast to methylation, where the first substitution activates additional substitution, Schiff base formation at one nitrogen deactivates the second nitrogen, and only the monoimines form under mild conditions.[3,4] DAMN has also been used to prepare 5,6-dicyanopyrazines,[5−12] purines,[13] and amides.[14,15]

The conjugated aldehyde and vinyl group in acrolein lead to reactions that are facile, and often different, from those of other aldehydes. The products, which arise from attack by nucleophiles, can be based on 1,4-conjugate addition, Schiff base formation, or both; many known examples of acrolein derivatives lead to cyclic and heterocyclic compounds.[16]

The formation of the Schiff base from DAMN and acrolein yields a material which, due to its vinyl function, may be polymerizable and thus is of interest for the study of high-nitrogen-content materials. The initial report[2] of the synthesis of this compound, (2*Z*)-2-amino-3-[(1*E*)-prop-2-en-1-ylideneamino]but-2-enedinitrile (**2**), involved boiling DAMN in acrolein and resulted in a modest (60%) yield. Little else was reported about the chemistry of this novel and highly reactive compound, which we call acrodamn (**2**). The present reports detail our syntheses of analogues of acrodamn[17] as well as the investigation of the rich chemistry of acrodamn and its derivatives.

Scheme 1. Imines Formed from DAMN and AlkylDAMNs



(1) R_1=R_2=H
(5) R_1=H R_2=Ethyl
(6) R_1=R_2=Me

(2) R_1=R_2=R_3=H R_4=vinyl
(3) R_1=R_2=R_3=H R_4=2-methylvinyl
(4) R_1=R_2=R_3=H R_4=1-methylvinyl
(7) R_1=R_2=methyl R_3=H R_4=vinyl
(8) R_1=R_2=R_3=H R_4=4-hydroxyphenyl
(9) R_1=R_2=methyl R_3=H R_4=4-hydroxyphenyl

Experimental Section

Methods. ^{1}H NMR spectra were collected with Varian 300, 400, or 500 MHz field instruments. NMR spectra were recorded using the Bruker AM-360 (^{1}H NMR (360 MHz), ^{13}C NMR (90.6 MHz)), AM-300 (^{1}H NMR (300 MHz), ^{13}C NMR (75.5 MHz)), AM-200 (^{1}H NMR (200 MHz), ^{13}C NMR (50.3 MHz)), a Varian AM-300 (^{1}H NMR (300 MHz), ^{13}C NMR (75.5 MHz)), or a Varian INOVA-500 (^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz)). ^{13}C NMR spectra were taken using broadband proton decoupling. IR spectra were collected with a Nicolett 60 SX or a Perkin-Elmer Spectrum BX FT-IR system. Mass spectra were collected with Micromass V6 70-250-5 magnetic sector mass spectrometer, using electron impact (70 eV), fast atom bombardment, or chemical ionization (ammonia) for ionization or a Finnegan Polaris GC-MS. UV spectra were collected with a Shimadzu UV160U spectrometer. Melting

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points were determined with a Mel-temp and are uncorrected. TLC were performed on Whatman silica gel plates 250 μm layer with fluorescent indicator. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer at the University of Michigan Microanalysis Laboratory. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were done on a Perkin-Elmer 7/DX thermal analysis system with heating rates of 10 °C/min for TGA and 10 °C/min for DSC. DSC for kinetics was performed on a Shimadzu DSC-60 with variable heating rates. Molecular weights for polymer samples were performed using gel permeation chromatography at 25 °C using a Waters 510 GPC system. Molecular weights were calibrated using polystyrene standards; $M_n = 123\ 000$ and PDI = 1.08; Alfa Aesar Stock # 43152, lot #D02M03. Viscometry data were collected using dimethyl sulfoxide as a solvent with a 75 μm Ubbelohde viscometer in a 25 °C constant temperature water bath. Conductivity measurements were obtained by a method described by Kolowich,[18] using a powder conductivity press. ^{60}Co irradiation studies were performed at the Phoenix Memorial Laboratory on the University of Michigan North Campus, and dose rates were measured with a Reuter-Stokes ion chamber model RS-C4-1606-207. Crystal structure analysis was done by Crystalytics Co. using a four-circle Nicolett autodiffractometer and Siemens SHELXTL-PC software. Wide-angle X-ray scattering was performed using a Rigaku Geigerflex X-ray diffractometer set at 30 kV and 25 mA in the theta−theta mode and was scanned from 0 to 50 theta.

Tetrahydrofuran (THF) was dried with sodium/benzophenone ketyl before use. Acetonitrile was distilled from calcium hydride before use. DMSO-d_6 and DMSO were normally used with residual water present; if dryness was required, the DMSO was frozen, and the unfrozen residual water was decanted. DAMN was purchased from Nippon Soda Co. Ltd., Chiyoda-ku, Tokyo, Japan, from whom it is available in kilogram quantities. All other reagents and solvents were purchased from Aldrich Chemical Co., Milwaukee, WI.

Polymerizations of the imines were conducted by mixing in various proportions with base under nitrogen, heating both solutions and neat imine, exposing to ^{60}Co γ radiation, and radical initiation of a degassed solution.

Syntheses. *(2Z)-2-Amino-3-[(1E,2E)-but-2-en-1-ylideneamino]but-2-enedinitrile (crotodamn)*[19] (**3**). A solution of DAMN (4.015 g, 37.1 mmol) in THF (100 mL) at 0 °C was added slowly to a stirred solution of predominantly *trans*-crotonaldehyde (3.3 mL, 40.0 mmol) and 10 drops of 1 M HCl (10 drops) in THF (40 mL) at 0 °C. After 5 min the solution was poured over 500 mL of cold hexane. The resulting precipitate was collected and dried to give a white, fluffy powder (3.9 g). The mother liquor was stripped down to give an additional crop of light yellow powder (1.9 g, total yield 97%). The powder was recrystallized from ether/hexane to give white/light yellow powdery crystals. Upon sublimation at reduced pressure, clear yellow needle-shaped crystals were formed; mp 109−112 °C. IR: 3457, 3349 (−NH_2), 2950 (alkyl), 2239, 2206 (−CN), 1638, 1620, 1606, 1587, 1563, 1370, and 985 cm^{-1}. ^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm) 1.9 (d, 3H), 6.3 (m, 1H), 6.6 (m, 1H), 7.6 (s, 2H), and 7.9 (d, 1H). Anal. Calcd for $C_8H_8N_4$: C, 60.0; H, 5.0; N, 35.0. Found: C, 60.4; H, 5.1; N, 33.9.

(2Z)-2-Amino-3-{[(1E)-2-methylprop-2-en-1-ylidene]amino}but-2-enedinitrile (Methacrodamn)[19] (**4**). **4** was prepared analogously to **3**, using methacrolein in place of crotonaldehyde. The resulting precipitate was collected, and mother liquors were concentrated to yield 4.9 g (83%) of light brown fluffy power; mp 118−120 °C. IR: 3451, 3418, 3306 (−NH_2), 2959 (−alkyl), 2244, 2207 (−CN), 1614, 1595, 1389, 1350, 909 cm^{-1}. ^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm) 1.9 (s, 3H), 5.76 (s, 1H), 5.80 (s, 1H), 7.7 (s, 2H), 7.9 (s, 1H). Anal. Calcd for $C_8H_8N_4$: C, 60.0; H, 5.0; N, 35.0. Found: C, 60.3; H, 5.2; N, 34.3.

N-EthylDAMN[20] (**5**). *N*-Ethyl DAMN has been previously synthesized in low yield.[20] The following is an improved synthesis of this compound:

DAMN (20.004 g, 185 mmol) was added to THF (400 mL) in a round-bottom flask under nitrogen. The solution was cooled to 0 °C with an ice/water bath. Acetaldehyde (10.24 g, 227 mmol) was added via syringe to the reaction mixture. 1 M HCl (90 drops) was added to the reaction mixture while stirring. After the DAMN had disappeared (monitored by TLC, 1:1 EtOAc/hexane), methanol (100 mL) was added to the reaction mixture. Sodium borohydride (7.002 g, 185 mmol) was then added in portions. The reaction mixture was allowed to stir for 45 min and was then poured into ice water (1200 mL). The water solution was neutralized with 200 mL of 10% HCl. The organics were extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried with magnesium sulfate. Solvent removal under reduced pressure yielded a light brown oil. This oil was triturated with hexane, yielding a light brown precipitate. The precipitate was filtered and dried, yielding 18.42 g (73% yield) of a light brown powder. This powder was recrystallized with THF/hexane; mp 96−98 °C (lit. mp 105 °C). IR: 3435, 3346 (−NH_2), 2981, 2882 (−CH), 2216, 2207 (−CN), 1625, 1607, 1370. ^{1}H NMR (DMSO-d_6, 300 MHz): δ (ppm) 51.1 (t, 3H), 3.1 (q, 2H), 5.1 (t, IH), 5.5 (s, 2H).

(2Z)-2-(Dimethylamino)-3-[(1E)-prop-2-en-1-ylideneamino]-but-2-enedinitrile (Dimethylacrodamn) (**7**). *N*,*N*-Dimethyl-DAMN (**6**) was prepared by the method of De Vries.[21] Crude *N*,*N*-dimethylDAMN (620 mg, 4.5 mmol) was dissolved in THF (10 mL) containing acrolein (0.31 mL, 4.6 mmol, Aldrich, 90%) added. This mixture was cooled in an ice/water bath for 5 min, and then 5 drops of trifluoroacetic acid was added. After 2 h stirring, the reaction was not complete as indicated by TLC. Additional acrolein (0.4 mL, 6.0 mmol) was added, and the reaction was allowed to stir an additional hour. TLC indicated the reaction was complete. The mixture was poured into water (30 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The organic layers were dried with sodium sulfate and concentrated under reduced pressure to yield 0.29 g (37% yield) of oil which solidified upon standing. The material was purified by column chromatography on silica gel using gradient elution starting at 100% hexane and gradually increasing to 100% ethyl acetate. The purified product was initially bright yellow in color but darkened upon standing while attached to a vacuum pump. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.9 (d, 1H, J = 8.8 Hz), 6.5 (ddd, 1H, J = 17.6 Hz, 10.3 Hz, 8.8 Hz), 5.8 (2 overlapping, d, 2H, J = 10.3 Hz, J' = 17.1 Hz), 3.4 (s, 6H). LRMS (EI/70 eV): *m/z* peak, 174 (100, M^+), 173 (53, M^+−H), 146 (27), 119 (21), 77 (22), 67 (49), 54 (20).

(2Z)-2-Amino-3-{[(1E)−(4-hydroxyphenyl)methylene]amino}-but-2-enedinitrile[2] (**8**). To a mixture of DAMN (5.2486 g, 48.6 mmol) in THF (75 mL) and 4-hydroxybenzaldehyde (5.93 g, 48.6 mmol) was added trifluoroacetic acid (0.7 mL), and the solution was allowed to stir overnight. The mixture was concentrated under reduced pressure. The beige-green residue was recrystallized from methanol/water, yielding 9.27 g (90% yield). ^{1}H NMR (DMSO-d_6, 500 MHz): δ (ppm) 10.24 (s, 1H), 8.17 (d, 2H), 7.89 (d, J = 8.8 Hz, 2H), 7.70 (br s, 2H), 6.85 (d, J = 8.8 Hz, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz): 161.0, 155.1, 131.3, 126.97, 125.50, 115.75, 114.79, 114.03.

2-(Dimethylamino)-3-{[(4-methoxyphenyl)methylene]amino}-but-2-enedinitrile (**9**). To a flask charged with **8** (1.77 g, 8.3 mmol) was added THF (20 mL) and dimethyl sulfate (4.4 mL, 29.2 mmol). In a separate flask, sodium hydride (1.14 g, 28.5 mmol, 60% dispersion in mineral oil) was mixed with THF (10 mL). The imine solution was added to the sodium hydride solution via cannula, with rinse of 15 mL of THF. After stirring overnight, the mixture was concentrated under reduced pressure. The residue was dissolved in ethyl acetate (50 mL) and washed with 10% aqueous sodium hydroxide (3 × 20 mL), dried with magnesium sulfate, and concentrated under reduced pressure. The crude mixture was purified via recrystallization with methanol/water, yielding beige powder 1.86 g (88% yield) in two crops. The purified material proved to be a 1.5:1 mixture of isomers, as evidenced by a doubling of peaks in the NMR and spectrum. Literature precedent suggests these are *E*/*Z* isomers.[3,22] ^{1}H NMR (DMSO-d_6, 500 MHz): δ (ppm) (peak doublings are *E*/*Z* pairs) 8.292/8.216 (s, 1H), 7.79/7.67 (d, 2H) 6.956/6.938 (d, 2H), 3.861 (s, 3H), 3.427/3.355 (s, 6 H). ^{13}C NMR ($CHCl_3$-*d*, 125 MHz): δ (ppm) (peak doublings cannot be readily assigned from *E*/*Z* pairs) 155.08, 153.67, 130.35, 130.27, 128.67, 114.39, 114.24, 94.75, 59.84, 55.40, 44.10,

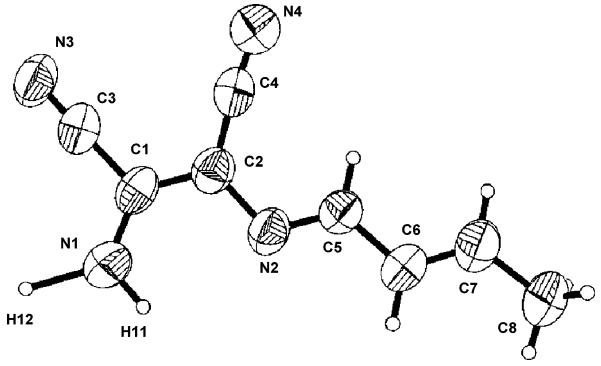


Figure 1. ORTEP structure of crotodamn.

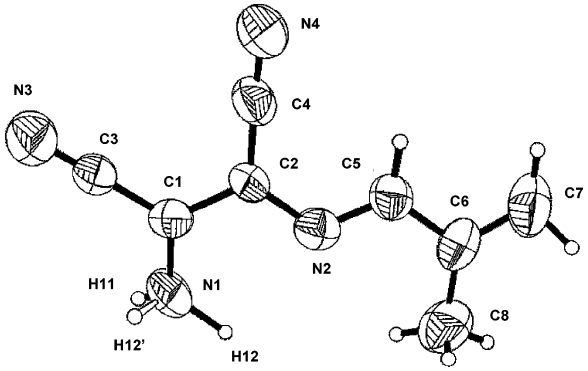


Figure 2. ORTEP structure of methacrodamn.

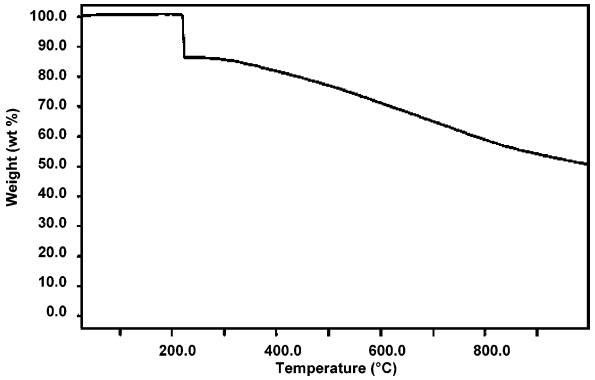


Figure 3. TGA data for acrodamn.

43.88, 29.68. LRMS (EI/70 eV): *m/z* 255 (18), 254 (100), 253 (22), 213 (49), 210 (24), 196 (18), 195 (17), 135 (16), 134 (67), 119 (22).

Results and Discussion

Condensation of DAMN with Aldehydes. The typical conditions for Schiff base condensations, of high temperatures and dehydrating conditions, lead to deeply colored tars and oils when applied to DAMN and acrolein. However, at 0 °C with dilute acid catalyst in THF, the reaction of DAMN with acrolein forms exclusively the monoimine. The reaction is almost instantaneous upon addition of the acid catalyst, and there is no evidence for a second condensation.

The double bond, which lies in conjugation to the DAMN end of the molecule, is now highly activated toward nucleophilic addition. During synthesis, this leads to a competition between condensation with acrolein and oligomeric initiation of the acrodamn by residual DAMN present in solution. As a result, a variable yield of oligomers occurs along with the synthesis of monomeric product. These oligomers are characterized by their extremely broad peaks in proton NMR and their insolubility in ether, which is useful in separating the monomeric product from the mixture. The oligomers also tend to be somewhat darker than the bright yellow monomer.

To avoid formation of oligomers, we adjusted the solvent conditions; switching from THF, in which both DAMN and acrodamn are soluble, to diethyl ether in which acrodamn is sparingly soluble, but DAMN is quite insoluble. This change in solvent resulted in a two-phase reaction that keeps the DAMN isolated from the growing concentration of acrodamn, preventing oligomerization. This improvement leads to more efficient purification of material, as any oligomers formed are easily filtered from the ether solution. Additionally, we observed higher yields than those found previously.[23]

Although the parent member of this family is the Schiff base formed from acrolein and DAMN, identical experiments carried out using crotonaldehyde, and methacrolein, gave similar results in both THF and ether solutions. We call these adducts methacrodamn and crotodamn by extension to acrodamn. In all cases, the yields for the condensation products are high, from 80 to 97%, in both solution and two-phase syntheses.

Derivatives of DAMN are known to undergo *E*/*Z* isomerization if the nitrogen substituents are sufficiently bulky. However, we were able to obtain X-ray crystal structures of both crotodamn and methacrodamn because their sublimation without polymerization under reduced pressure affords long needles. The molecular ORTEP views (Figure 1 and Figure 2) confirm the composition of these compounds and show that at least in the solid state the DAMN remains *Z*, the imine nitrogen is *anti*, and the crotonaldehyde vinyl group remains *E*.[24] Similarly, **8** appears to be a single isomer. However, when methyl groups are added to the amine in **9**, the ^{1}H NMR clearly shows a doubling of peaks, strongly suggesting *E*/*Z* isomerization of the dicyanoalkene.

While the imines between DAMN and the conjugated aldehydes appears to form both readily and irreversibly, formation of imines from nonconjugated aliphatic aldehydes, including formaldehyde, acetaldehyde, propionaldehyde, and isobutryaldehyde, appears to be reversible, making isolation of pure products difficult.

Thermal Characterization of Synthesized Imines. Thermal gravimetric analysis (TGA) of the imines revealed that these compounds have very low loss of volatiles up to 100 °C and form high char yields. Figure 3 shows TGA data (carried out under nitrogen) for acrodamn, a representative for all members of this series. These TGA data are quite remarkable for organic compounds. The remaining mass at 800 °C for acrodamn is almost 60% of the starting material. Even with an additional methyl group in both crotodamn and methacrodamn, the remaining mass is approximately 50%.

To elucidate this thermal behavior further, a series of isothermal thermolysis were carried out on larger samples. Samples of the compounds were held at a varying test temperature for 24 h in a tube furnace under nitrogen flow. Following this curing procedure, the samples were analyzed for C, H, and N. The conductivity of the samples was also measured using a two-point probe method.[18]

As seen in Figure 4, the electrical conductivity goes through a large increase between 600 and 800 °C. Although it was clear that the low weight loss could only

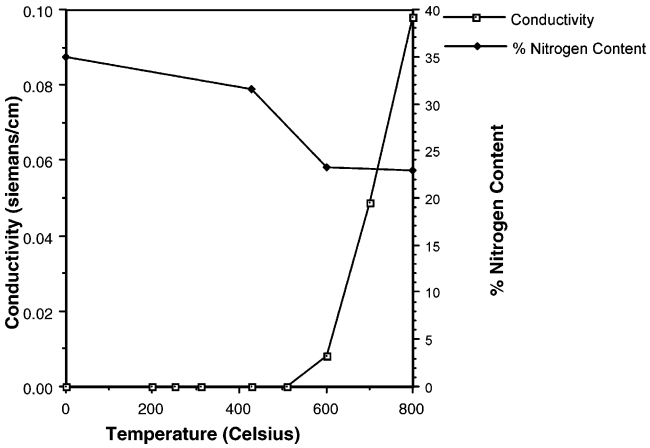


Figure 4. Percent nitrogen content and conductivity vs temperature for crotodamn.

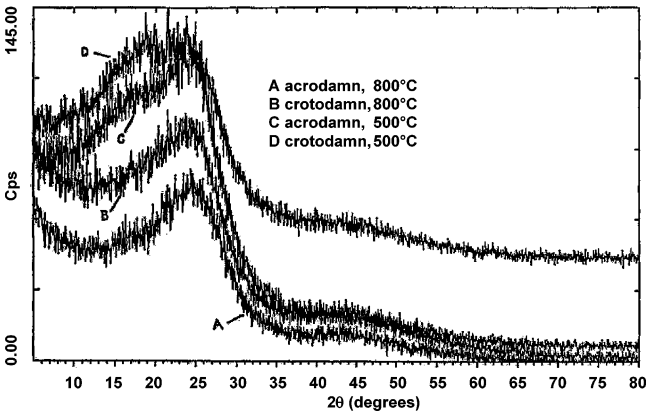


Figure 5. Wide-angle X-ray scattering for crotodamn thermolysis samples.

imply retention of considerable nitrogen (the starting nitrogen content was 35% for example for crotodamn), it is surprising to find that after partial graphitization at 800 °C the nitrogen content is still 23%. This implies the formation of a novel structure with a ratio of C/N similar to that of pyridine. Eventually as the temperature is raised, further graphitization takes place. The crystallinity of the thermolysis products was examined by wide-angle X-ray scattering (WAXS). These results are shown in Figure 5. All samples show a very low order of crystallinity; however, slight differences are observed between the pre-transition samples and the post-transition samples. In Figure 5, curves A and B are 800 °C samples whereas C and D are 500 °C samples. The X-ray diffraction pattern of graphite has an extremely strong peak at $2\theta = 26.2°$. It is clear that while A and B, the 800 °C samples, have 2θ peaks shifted toward the graphite direction, compared to C and D, the degree of graphitization and crystallinity overall is low.

To further elucidate and characterize the thermal behavior of these monoimine derivatives, differential scanning calorimetry (DSC) was also carried out on these compounds. The example of acrodamn is shown in Figure 6 and is typical of other members of the series, in showing a strong exotherm above 100 °C.

Whereas acrodamn undergoes an exotherm upon heating with only a brief passage through the liquid phase, crotodamn melts and then has an exotherm somewhat less suddenly than acrodamn, at a temperature 42 °C above the melting point. This result shows

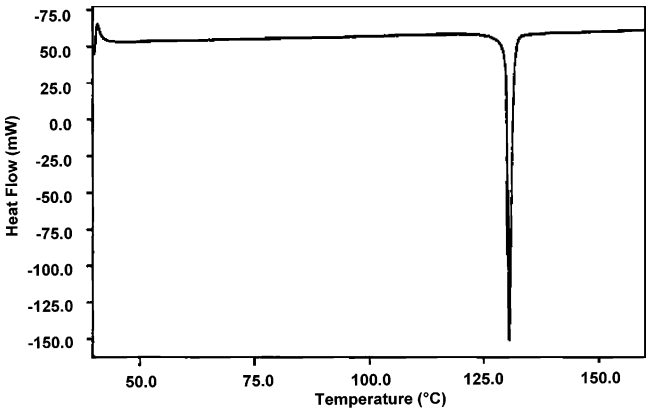


Figure 6. DSC for acrodamn.

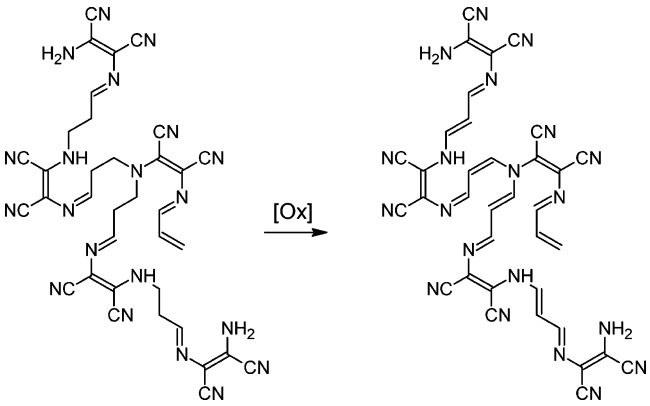


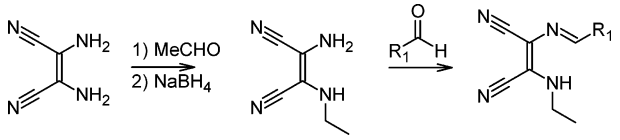
Figure 7. Acrodamn oligomer and its oxidized derivative.

the steric influence of the terminal methyl group very clearly. These data indicate that, upon heating, solid samples of these three compounds, an exothermic reaction occurs at the conjugated double bond. Such a reaction is not surprising as the strongly electron-withdrawing cyano groups in conjugation with the double bond make the double bond highly activated.

From the DSC results and observations on the properties of the products formed under mild heating, we propose that these compounds undergo a step growth 1,4-conjugate addition polymerization between the free amine and the highly activated terminal double bond. The fraction of amines that react twice (an A_2B polymerization leading to a hyperbranched architecture) compared to the amines that only react once (an AB polymerization leading to a linear polymer) is difficult to estimate by NMR, but the solubility is consistent with a highly branched structure (Figure 7). Visually, one observes a rapid darkening in color during this relatively low-temperature transition, which also suggests that the oligomer undergoes self-oxidation or oxidation by adventitious oxygen to increase conjugation.

To better establish this reaction pathway, it is was desirable to have an *N,N*-alkyl derivative of acrodamn. With this derivative, it would be possible to test the potential for the vinyl group to undergo addition polymerization in the absence of the free amine. The synthesis of *N,N*-dimethylDAMN has been reported previously through a relatively cumbersome procedure.[21] This product also condenses with acrolein, in a fashion similar to acrodamn, yielding the corresponding analogue in low yield. This material is brilliant yellow but decomposes slowly under vacuum, presumably through a photochemical process. Nonetheless, this

Scheme 2. Synthesis of *N*-Ethylacrodamn and Analogues



decomposition is slow enough to permit analysis of the fresh material.

Contrary to our hypothesis, dimethylacrodamn does in fact polymerize. However, analysis of the kinetics using the Ozawa method[25] shows activations energies of 147.95 and 99.86 kJ/mol and preexponential factors of 9.35×10^{18} and 2.14×10^{12} min^{-1} for acrodamn and dimethylacrodamn, respectively. The large difference in the values for these data strongly suggests the two polymerizations are operating by different mechanisms and that acrodamn may be polymerizing by a 1,4-conjugate addition mechanism.

While acrodamn should lead to a hyperbranched polymer, a singly alkylated acrodamn should lead to linear polymers. To get around the difficulties associated with direct alkylation of DAMN, as described above, we devised a procedure to get a monoalkylated derivative of DAMN by reducing its Schiff bases. We first form the monoimine derivative of DAMN with acetaldehyde and then reduce this compound using sodium borohydride (Scheme 2). This one-pot procedure gives *N*-ethyl-DAMN[20] in 73% yield. The *N*-ethylDAMN can be subsequently reacted with acrolein, methacrolein, and crotonaldehyde to give an *N*-ethyl-monoimine derivative of DAMN. In all of these cases, oligomers are formed in conjunction with the monomeric product. The oligomers are evidenced by the formation of ether-insoluble materials. The oligomers have substantially broadened peaks in the ^{1}H NMR, making characterization difficult.

Polymerization of Imines. Attempts to polymerize acrodamn thermally result in materials with $M_n = 1400$ and polydispersity (PDI) of 1.49. Thermal polymerization in THF yields similarly narrow PDI of 1.41 but lower M_n's of 591. Melt polymerization gives PDI of 1.45 and a M_n of 522. In all cases with solvent the polymers remained in solution, seeming to indicate a subtle solvent effect on the polymerization. Further evidence for this effect on polymerization is the formation of oligomers in the THF-solvated synthesis of acrodamn, while the ether-solvated synthesis of acrodamn forms no such oligomers.[23] Base-catalyzed polymerizations yield materials with a wider range of polydispersities, from 2 to 4 and wider ranges of M_n's from 1700 to 4000. Interestingly, the amount of base present does not appear to correlate with the molecular weights observed, suggesting a catalytic role in the polymerization process instead of an initiating role. Attempts to polymerize acrodamn using radical initiators such as AIBN resulted in polymers that could not be distinguished from thermal polymers. This is not surprising since imines are known to readily participate in radical addition reactions.[26]

The various polymerization reactions of acrodamn typically yield brittle black solids that are soluble in solvents such as THF and acetone. The low molecular weights and solubility of these materials indicate that polymerization stopped at the oligomer stage or that the polymeric materials were hyperbranched. Evidence for hyperbranching is also seen in the MALDI-TOF-MS[27] for the acrodamn polymers (Figure 8), which shows

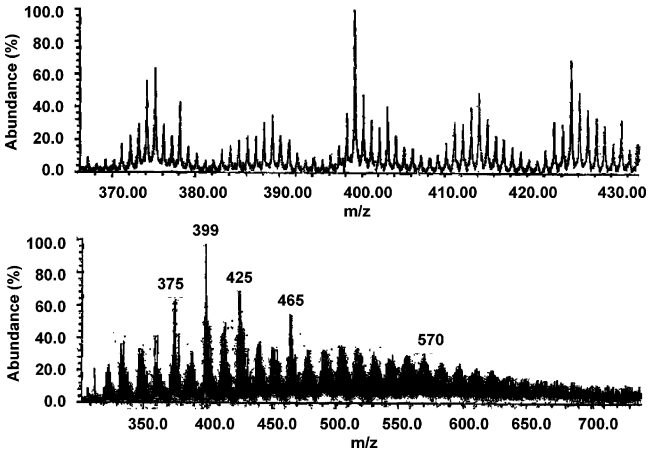


Figure 8. MALDI-TOF-MS for acrodamn polymer.

considerable fragmentation. The isolation of only low molecular weight materials may be due to the nature of molecular weight evolution in step growth polymerization.[28]

The TGA properties of these compounds are similar to the unalkylated compounds in that they have very low weight loss up to very high temperatures. The *N*-ethylacrodamn product behaves very differently in the DSC from the unalkylated monoimines with a melting point at 84 °C followed by a broad and less pronounced exotherm. The 1,4-conjugate addition reaction is expected to be slowed because of the steric hindrance at the alkylated nitrogen. The DSC data for the *N*-ethylmethacrodamn and *N*-ethylcrotodamn are similar. As noted above, the terminal double bond in acrodamn and the closely related imines is highly activated. Even the weakly nucleophilic character of the amine of the acrodamn adduct can participate in 1,4-conjugate addition to this double bond.

A subtle and somewhat puzzling aspect of the chemistry of the unsaturated monoimines of DAMN is the formation of acyclic derivatives rather than the seven-membered rings which can result from Michael addition. This subtlety is evident when one considers that in the reaction of methyl vinyl ketone with DAMN only the diazepine product is observed. In the original synthesis, reported by the DuPont group, refluxing conditions without added acid led to a 31% yield.[3] We have rerun this reaction at much lower temperatures with acidic catalysis, in a manner typical of the procedures reported here for condensation with aldehydes, and have not been able to isolate any of the presumed acyclic intermediate but do observe a 80% yield of the same cyclic product. Furthermore, when our monoimines described above are thermolyzed, we find no evidence from NMR or mass spectroscopy that the diazepines have formed. The cause of this effect is unclear.

Attempted Radiation-Induced Polymerization. Crystals of monomers with reactive double bonds which lie less than 4 Å apart can often undergo a solid-state radiation-induced polymerization,[29] giving rise to a single polymer crystal. The crystal structure analysis for crotodamn (Figure 1) shows that the geometry of the crystal lattice is such that the vinylic C=C bonds of crotodamn lie directly above one another and are only 3.95 Å apart. A ^{60}Co γ irradiation study was carried out to determine whether crystals of crotodamn would undergo a solid-state polymerization. Samples of needle-shaped crotodamn crystals (formed by sublimation) were

irradiated for 0.0011−0.4147 h at a series of intensities (15 000−2 000 000 rad). Subsequent analysis of the samples, however, showed no signs of radiation-induced polymerization.

Monoimine Selectivity. It is somewhat unusual to see the exclusive selectivity for the formation of monoimines with DAMN in the context of what appears to be two equivalent amine groups. The reason for this selectivity lies in the highly conjugated nature of DAMN and its imines. The lone pairs on the nitrogen amines are in conjugation with the nitriles, leading to delocalization of electron density. However, both lone pairs are interacting, and there is a cross-conjugation effect, hindering the reduction of electron density at either amine. Additionally, the amines are directly conjugated with each other, slightly increasing the electron density, vinylogous to hydrazine. Combined with the cross-conjugation effect, this renders DAMN as reactive as a weak amine rather than unreactive like cyanamide.

When DAMN condenses with an unsaturated aldehyde, crystal structures suggest a geometric reorientation. The result is that α,β-unsaturated imine π-system comes into conjugation with the nitriles and alkene bond of DAMN. This reorientation would also take the lone pair of electrons on the imine out of conjugation with the free amine. Thus, the reorientation prevents the nonbonded electro pair at the imine nitrogen from participating in the conjugation and cross-conjugations effects that increase DAMN's nucleophilicity. As such, the nucleophilicity declines dramatically, and the second Schiff base does not form.

Molecular orbital plots suggest that while the lone pairs on the amine nitrogens play a significant role in the HOMO of DAMN, there is no contribution from the nonbonded electron pair on the imine nitrogen to the HOMO of acrodamn. Predictions made at the HF/6-31G* level of theory suggest that imine's lone pair are lowered in energy and contribute to the HOMO-2. The same prediction also shows no contribution from the amine lone-pair to the HOMO-2. Electrostatic plots also subtly suggest a slight decrease in electron density at the amine nitrogen of acrodamn as compared to DAMN.[30]

To test this idea, we examined the methylation of *N*-benzylideneDAMN. The use of *N*-benzylideneDAMN[3] as a model for acrodamn has utility in that the stabilization from conjugation of the phenyl ring is expected to have a similar, but perhaps larger, stabilizing effect on imine formation, while lacking the vinyl group that might react via polymerization. Several conditions for methylation were attempted, using a variety of bases such as sodium hydride, triethylamine, and pyridine, and methylating agents, including methyl iodide and dimethyl sulfate. In the most strenuous case attempted, with sodium hydride serving as a base, dimethyl sulfate alkylation in boiling THF led to recovery of starting material. This demonstrates a lack of nucleophilicity at the free amine in *N*-benzylideneDAMN.

However, applying similar reaction conditions to the Schiff base of 4-hydroxybenzaldehyde and DAMN leads to the formation of a mixture of products, corresponding to the permethylated material, and its *E* isomer (**9**). The formation of the *E* isomer is not entirely unexpected, as *N,N,N′,N′*-tetramethylDAMN has been shown to undergo *E*/*Z* isomerization under relatively mild heating.[3] The hydroxy group was also methylated; we did not determine whether alkylation first occurs at the nitrogen or oxygen. In this case, the lone pairs of electrons in the hydroxy/methoxy group were in conjugation and cross-conjugation with the free amine, leading to an increase in its reactivity. Thus, the increase in electron density in the DAMN Schiff base via conjugation has a dramatic impact on its reactivity, confirming our hypothesis regarding the exclusive formation of the monoimine.

Conclusions

We have presented an improved synthesis of the imines formed between DAMN and acrolein and some of its simple analogues. These materials undergo thermal polymerization via 1,4-conjugate addition to yield hyperbranched polymers. The polymerization may also be catalyzed by acid or base. We have synthesized the *N*-ethyl derivatives of the Schiff bases and observed that polymerization takes place in a manner similar to that of the parent compounds, but without forming hyperbranched materials.

Supporting Information Available: HOMO plots for acrodamn and DAMN, HOMO-2 plot for acrodamn, and electrostatic plots for acrodamn and DAMN. This material is available free of charge via the Internet at http://pubs.acs.org.

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