An Improved Synthesis of 2-Vinyl-4,5-dicyanoimidazole and Characterization of Its Polymers

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ABSTRACT: An efficient synthesis of (1*Z*)-1-amino-1,2-dicyano-3-aza-1,3,5-hexatriene (acrodamn), via condensation of acrolein and diaminomaleonitrile (DAMN), is described. A larger laboratory-scale synthesis of 4,5-dicyano-2-vinylimidazole (vinazene) is described in detail. The alkylation of vinazene proceeds with strong electrophiles. The compound, 4,5-dicyano-1-methyl-2-vinylimidazole (1-methylvinazene), undergoes Michael addition with pyrrolidine, morpholine, and thiophenol and at higher temperatures with itself, resulting in step-growth oligomerization. Direct measurements of kinetic rates for vinylic radical addition polymerization of vinazene yielded $k_{app} = k_p/2\sqrt{k_t f k_d}$ values of $(7.2 \pm 0.25) \times 10^{-3}$ and $(6.6 \pm 0.27) \times 10^{-3}$. Direct measurements of kinetic rates for 1-methylvinazene yielded $k_{app} = k_p/2\sqrt{k_t f k_d}$ values of $(4.3 \pm 0.31) \times 10^{-3}$ and $(3.7 \pm 0.06) \times 10^{-3}$. Indirect measurements show the polymerization obeys first-order kinetics. The poly(vinazene) is an acidic material with molecular weights ranging from 100 000 to 200 000 and polydispersities between 2.0 and 2.9. The Mark−Houwink constants for poly(vinazene) in 0.05 M LiBr in *N*-methylpyrrolidinone were $K = 3.35 \times 10^{-5}$ and $a = 0.889$. The titration behavior is similar to poly(methacrylic acid).

Introduction

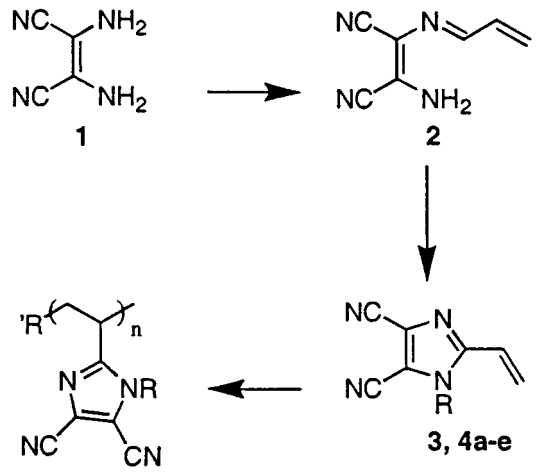
Dicyanoimidazole compounds, synthesized from the well-known HCN tetramer diaminomaleonitrile (DAMN), were first reported by D. W. Woodward in a patent assigned to Dupont.[1] An early paper by Bredereck and Schmötzer[2] described a number of Schiff base forming reactions of DAMN. Later, the chemistry of DAMN was explored in depth at Dupont in the 1970s and was reviewed by Donald and Webster.[3] Extensive use has been made of this convenient reagent for the preparation of heterocyclic molecules, but surprisingly, little or no work leading to vinylic polymers has been described. We now report our findings that simple derivatives of DAMN can lead to vinylic monomers that form high polymers with desirable properties.

The synthesis begins by the formation of the Schiff base between acrolein and DAMN. Although this simple, but highly conjugated and reactive, monomer polymerizes upon heating above 120 °C, it is stable enough to be isolated and crystallized. We have described the polymers formed from acrodamn and closely related anils elsewhere.[4]

An oxidative method of preparing dicyanoimidazoles from Schiff bases of DAMN was reported by Patel.[5] This method was used by Hosogai[6] to prepare 2-vinyl-4,5-dicyanoimidazole; however, no polymerizations, or other reactions, were reported. We have found that, when purified, 2-vinyl-4,5-dicyanoimidazole, which we call vinazene, polymerizes readily.

Poly(2-vinyl-4,5-dicyanoimidazole) or poly(vinazene) is acidic, with $pK_a = 5.5$. This acidity leads to solubility in aqueous bases; the polymer is also sparingly soluble in very polar organic solvents. The monomer can be alkylated in good yield at the 1-position of nitrogen, to afford a family of derivative monomers. Dicyanoimidazoles have found applications in promoting various reactions, most notably the phosphitylation step in DNA synthesis, and a polymer bound form of this reagent has particular advantages.[7] In this paper we describe improvements in the synthesis of the key intermediate and monomer and our results on the characterization of the polymers. In future reports we will describe controlled radical polymerizations and copolymerizations.

Scheme 1. Outline of Present Work



Results and Discussion

Monomer Synthesis. The synthesis of acrodamn was originally reported by Vaughan and Robertson,[4] by boiling DAMN in acrolein and collecting the precipitate that results upon cooling, in approximately 60% yield; no details of its reactivity were given. Hosogai's synthesis of vinazene used lead tetraacetate to oxidize acrodamn in toluene and achieved a 67% yield, 40% over two steps from DAMN. Hosogai did not report any details about the chemistry of this compound nor did he report any polymerizations. Our discovery that, when carefully purified, vinazene polymerizes readily led us to examine and improve Hosogai's synthesis of this new monomer.

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More recent efforts by Reybuck et al. led to an improved synthesis of acrodamn via acid catalysis of the Schiff base condensation with aqueous HCl, using THF as a solvent.[3] Reybuck's method results in a 92% yield of product, but up to one-third of the material was oligomeric. When acrodamn is present in an acidic environment with a nucleophile, such as unreacted DAMN, oligomerization can result. Additionally, we found that minor variations in the precipitation time seriously affected the oligomer content. However, this method was a significant improvement over Vaughan and Robertson's synthesis in that only a stoichiometric equivalent of the highly volatile and strongly lachrymatory acrolein was required. This result is an important advantage when operating at a larger scale.

We hypothesized that if the unreacted DAMN could be kept isolated from the acrodamn, there would be fewer problems with oligomerization. To do this, we used ether as a solvent for the condensation. The insolubility of DAMN in ether results in a two-phase suspension, whereas the sparing solubility of acrodamn leads to partitioning of acrodamn into the liquid phase, away from DAMN, upon formation. Additionally, the precipitation of acrodamn into a second solid phase also isolates the DAMN and acrodamn from each other. A second improvement was the substitution of anhydrous trifluoroacetic acid for aqueous HCl. The volatility of trifluoroacetic acid makes isolation of the product quite facile. These improvements made the synthesis highly efficient and afforded nearly quantitative yields, free from oligomers.

We also improved upon Hosogai's method by switching to acetonitrile as solvent. Hosogai's use of toluene is not ideal, since neither acrodamn nor lead tetraacetate is significantly soluble in it, and the reaction time is overnight. When we switched the solvent to acetonitrile, yields improved to 85%, and reaction times were much shorter, on the order of 5 min. Together with the improved preparation of acrodamn, our synthesis results in up to 80% overall yield of vinazene from DAMN, a significant improvement over previous methods.

When vinazene is synthesized in this fashion, it typically has a reddish color from a minor impurity, formed in situ. This impurity does not appear to affect the chemistry of vinazene, except polymerization, which is almost totally inhibited. The impurity was readily removed by filtration through an alumina plug with ether as eluent. The resulting product then polymerizes readily via free-radical initiation (vide infra).

The vinazene anion proved to be a weak nucleophile, which makes alkylation difficult with all but very strong electrophiles. For example, use of methyl iodide as an alkylating agent resulted in no reaction. Dodecyl bromide resulted in only an 18% yield of 1-dodecylvinazene after 13 days at room temperature. The use of benzyl chloride with catalytic amounts of potassium bromide yielded 64% 1-benzylvinazene, with a similarly long reaction time. The more potent electrophiles, dimethyl or diethyl sulfate, resulted in good yields (75−80%) of alkylated product following reasonable reaction times (2−5 days) at room temperature. These procedures led to acceptable quantities of the readily polymerized (vide infra) 1-methyl- and 1-ethylvinazene.

Michael-Type Addition and Diels−Alder Reactions of Vinazene. A typical procedure to decrease long reaction times, such as those required for the alkylation of vinazene, is to heat the reaction. We have found that refluxing vinazene does not result in alkylation but causes a thermal oligomerization. When we recorded the differential scanning calorimogram (DSC) of vinazene, a large exotherm was observed immediately after the melting endotherm. In the thermogravimetric analysis (TGA), up to 900 °C under nitrogen, we observed significant retention of mass. These data also supported the hypothesis of an oligomerization. We presumed this proceeds via a Michael addition mechanism since 1-methylvinazene did not exhibit an exotherm following melting, nor did it appear to oligomerize at temperatures where reaction occurs for unsubstituted vinazene.

To verify the Michael addition hypothesis, we heated vinazene in a high-boiling NMR solvent (DMSO-d_6) to 130 °C. Over the course of several days, new peaks appeared among the vinazene peaks in the spectrum. Some of the new peaks appear in the vinyl region and had shifts similar to alkylated vinazenes, such as 1-ethylvinazene. Alkylated vinazenes typically have a ~0.2 ppm shift from corresponding peaks in the parent compound. Additionally, a new peak appeared at 4.2 ppm, very close in shift to that of the corresponding methylene of 1-ethylvinazene at 4.3 ppm and hence consistent with alkylation of the 1-position. The sum of these data gives strong support for the Michael addition pathway. The presence of vinylic end groups in the oligomers similarly confirms a step growth mechanism rather than an addition polymerization process.

We also demonstrated the reactivity of vinazene as a Michael acceptor by synthesizing several adducts of 1-methylvinazene. Vinazene was allowed to react with excess morpholine, excess pyrrolidine, or excess thiophenol with catalytic triethylamine.

To characterize the reactivity of vinazene further, we examined its Diels−Alder reaction with cyclopentadiene. When vinazene, 1-methylvinazene, or 1-ethylvinazene is stirred with excess cyclopentadiene in ether, there was no reaction at room temperature. However, upon addition of LiCl, Diels−Alder adducts started forming immediately. After stirring overnight, these reactions yielded mixtures, which could be analyzed by NMR. We found *endo:exo* ratios of 3:1 for the case of 1-H- and 1-methylvinazene and 19:1 for the case of 1-ethylvinazene. This was determined by the similarity of the chemical shifts for the major products' alkene protons and by COSY analysis, which indicates the major product is *endo*. The isolated adducts were likely not in thermodynamic equilibrium during the reaction, since the reverse Diels−Alder reaction is unlikely at lower temperatures. Hence, the selectivities observed were kinetic effects, presumably from the steric bulk of the 1-ethyl group.

Free-Radical Addition Polymer Properties. Vinazene homopolymerizes in solution via a free-radical addition pathway to form moderately high molecular weight polymer, which, when cast as film, was hard and somewhat brittle. Poly(vinazene) color ranges from pale yellow in thin films to dark brown as a solid mass. Solvent was difficult to remove by reduced pressure evaporation, but when solvent is present, the material is somewhat plasticized. Films can be cast from concentrated solutions of poly(vinazene) in DMF, acetonitrile, or aqueous ammonia. When the solvent was thoroughly removed by use of a vacuum oven at high temperature, the polymer has a tendency to absorb humidity from the atmosphere. The water content varies but is typically 10%. The polymer darkens and

softens somewhat upon heating but decomposes before melting. When the bulk material is ignited in air with a propane torch, it burns, but when the torch is removed, the material is self-extinguishing. Because of the acidity of the 1-H, the polymer can be dissolved in dilute aqueous bases such as 10% sodium bicarbonate solution or aqueous ammonia. It is also soluble in DMF, DMSO, NMP, and, to a lesser degree, acetonitrile. The polymer is insoluble in other common organic solvents, such as chloroform, acetone, ethyl acetate, hexafluoroisopropyl alcohol, or ethanol. Under UV light, the material fluoresced brightly.

It is important to note that the structure of this polymer formed by the addition polymerization is different from the Michael-type addition oligomer. Additionally, because the thermal initiation temperature necessary to effect the Michael-type addition (vide supra) is substantially above the typical AIBN free radical polymerization temperature, we can control which of the two polymers is formed. For clarity, all subsequent references to poly(vinazene) refer to the addition polymer formed by radical initiation.

Free-Radical Polymerization Kinetics. We measured polymerization kinetics directly and also indirectly kinetic chain length. The kinetic chain length, ν, is approximately equal to the number of monomer repeat units per initiator fragment:

$$\nu = \frac{\text{no. of monomers propagating}}{\text{no. of initiators initiating}} \qquad (1)$$

This expression can be written with the variables of a typical polymerization experiment as[8]

$$\nu = \frac{k_p[\mathrm{M}]}{(2k_t f k_d[\mathrm{I}])^{1/2}} \qquad (2)$$

To test the validity of this expression for vinazene, two series of experiments were carried out. In the first series, the concentration of initiator was varied while the concentration of monomer remained constant. In the second, the concentration of monomer was varied while the concentration of initiator was held constant. All samples were degassed and allowed to polymerize to completion. The solvents were removed, and the number-average molecular weight was determined by GPC. The linear relations were quite good as evidenced by a Pearson-squared correlation coefficients of 0.98 for the first series and 0.97 for the second. These data verified the assignment of typical free-radical addition kinetics for this system.

The polymerization rates were measured directly by an NMR experiment. The line heights[9] of the various peaks measured as a variable of time. The peak heights were compared to the peak heights at time zero, and an average of the eight peak heights resulting from *cis/trans* coupling was used as the measure of concentration. Figure 5 shows a typical kinetic experiment using this method. The curvature of the data from the regression line beginning at about 120 s is probably caused by the onset of higher viscosity. At this point in the polymerization, approximately 20% conversion, the high molecular weight species being generated are of sufficient concentration to noticeably increase the viscosity. The use of DMSO-d_6 as a solvent further exacerbates this problem due to its own viscosity. This change in viscosity in turn affects the NMR shim values, which introduces some error in peak shape. There appeared to be no practical way around this problem. However, the deviation from linearity is moderate and does not appear to distort the data or prevent kinetic analysis. At conversions higher than 90% the apparent rate of polymerization drops substantially, presumably because the lower concentration of monomer leads to initiator efficiency effects, where it becomes more difficult for the initiator to initiate a new chain at low monomer concentration. To avoid the influence of these effects upon our data, we have omitted data points beyond 90% conversion in the calculations.

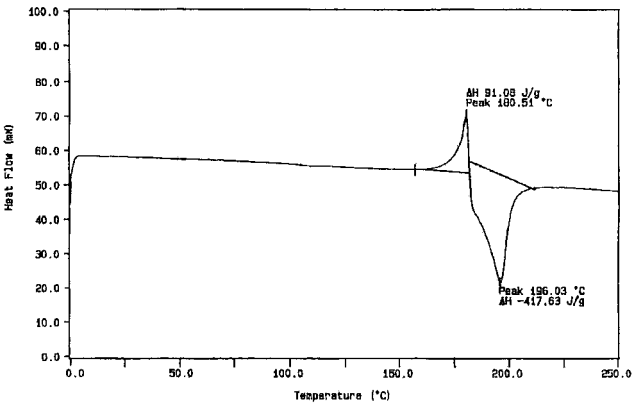

Figure 1. DSC trace of vinazene.

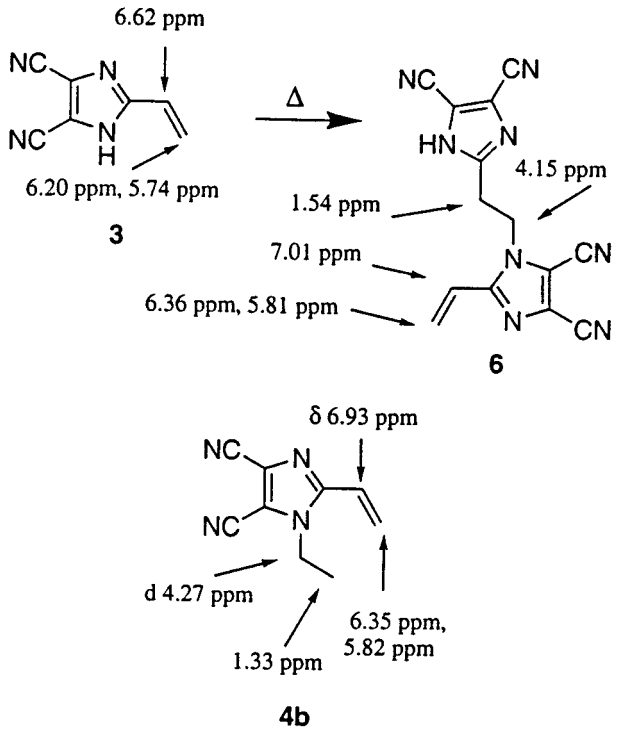

Figure 2. Summary of NMR assignments of thermal vinazene oligomer.

The equations shown in Figure 5 and in subsequent similar graphs show the linear regression of the monomer concentration (y-axis) versus time (x-axis). The slopes of these lines are equal to the apparent rate of reaction, $k_{app} = k_p^* \sqrt{(2k_d f[\mathrm{I}])}/\sqrt{k_t}$, where k_p represents the rate constant of propagation, k_t represents the rate constant of termination, and k_d represents the rate constant of decomposition of the azo-initiator, assuming no chain-transfer processes. These data are shown with their Pearson-squared correlation coefficient of 0.98,

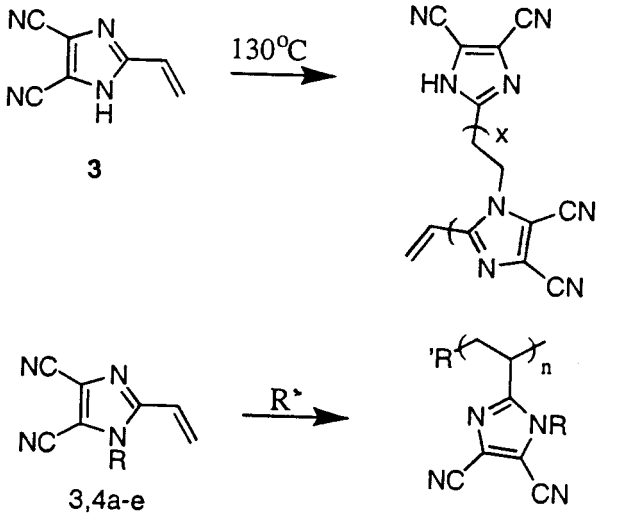

Figure 3. Both polymers from vinazene.

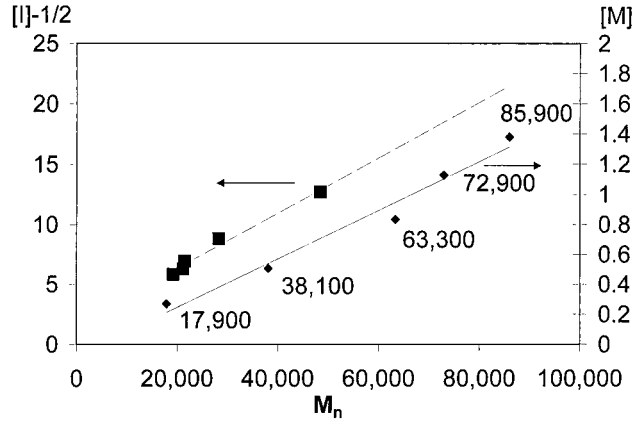

Figure 4. Kinetic chain length studies.

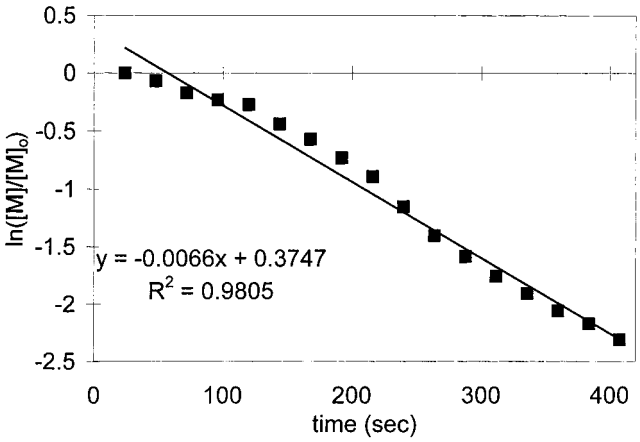

Figure 5. Kinetics of vinazene polymerization.

indicating a linear relation with the $\ln([M]/[M]_0)$, as expected. It is notable that the rate is rapid, giving 90% conversion of monomer, after only 8 min at these concentrations. Although this experiment is readily reproducible, at high concentrations, occasionally Tromsdorff-type autoacceleration appears. At concentrations below 1 M, this did not occur, but above 2 M this effect was routine.

When vinazene is dissolved in an aqueous base, it polymerizes upon addition of water-soluble initiators. In addition, vinazene polymerizes free radically in organic solvents in the presence of bases, such as pyridine or triethylamine. These polymerizations seemed somewhat sluggish compared to those run without added base, but no quantitative kinetics experiments were done to measure these rates.

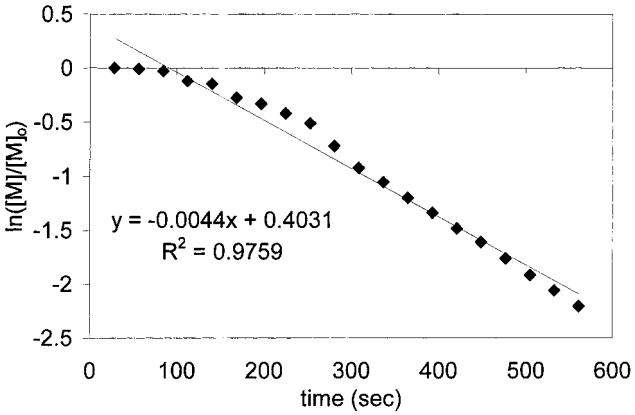

Figure 6. Kinetics of 1-methylvinazene polymerization.

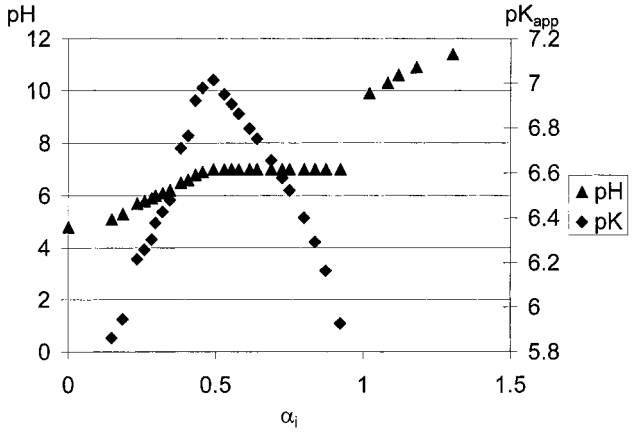

Figure 7. pH and pK_{app} vs α_1 in the titration of poly(vinazene).

The free-radical polymerization kinetics of 1-methylvinazene were measured in a similar fashion as the 1*H*-vinazene. The kinetics proved similar, with 1-methylvinazene being roughly 25% slower than 1*H*-vinazene. This might be caused by a small steric effect or be due to differences in solvation. Again, good reproducibility among replicate kinetic experiments was observed.

A few other derivatives of vinazene were qualitatively assessed for their ease of polymerization. The 1-methylvinazene and 1-ethylvinazene behaved very similarly, and 1-benzylvinazene also polymerized readily. The short-chain alkylvinazenes formed polymers that were insoluble in THF, whereas the product of the reaction of 1-dodecylvinazene with AIBN yielded a THF-soluble material. However, this material also had a very low degree of polymerization.

Polymer Chemistry and Properties. Conversion of poly(1-methylvinazene) to poly(vinazene) can be accomplished by a demethylation reaction. The polymer is boiled in NMP and lithium chloride. Methyl chloride is eliminated, leaving the poly(lithium vinazene), which can be converted to poly(vinazene) by precipitation into acid. This technique proves to be useful for synthesis of poly(vinazene) in polymerizations that would lead to thermal oligomerization of vinazene at higher temperatures (vide supra). The protected 1-methylvinazene is not subject to these side reactions and thus can cleanly

polymerize under these conditions; subsequent deprotection then yields the poly(vinazene).

Solution polymerization yields polymers with weight-average molecular weights ranging from 100 000 to 200 000 g/mol. Polydispersities from these samples range between 2.0 and 2.9. These polydispersities were somewhat broader than what would be expected for an typical bimolecular terminated free-radical polymerization with low chain transfer. We tentatively assume that chain transfer processes affects the polymerization, particularly those run to high conversion.

The presence of the N−H protons leads to extensive hydrogen-bonding interactions between the polymer repeat units, an effect we have previously noted in other 2-substituted imidazoles.[10] It is likely that this hydrogen bonding between repeat units would affect the stiffness of the polymer chain in solution. From light-scattering gel permeation chromatography (GPC) in [NMP/0.5 M LiBr][11] data, we found Mark−Houwink coefficients for poly(vinazene) of $a = 0.89$ and $K = 3.3 \times 10^{-5}$. Similar values for poly(styrene) in toluene are $a = 0.69$ and $K = 1.7 \times 10^{-4}$. From these data we concluded that poly(vinazene) had somewhat less flexible chains than poly(styrene), most likely due to the hydrogen bonding and polarity of the dicyanoimidazole pendant groups.

The titration behavior of poly(vinazene) is somewhat complex. When a solution of polymer is dissolved in 0.025 M LiBr in 50% NMP in H_2O and titrated by the addition of aqueous base, one can compare the pH to the expected degree of ionization, α_i. During the initial addition of base the pH rose steadily, until approximately half of the repeat units were deprotonated ($\alpha_i = 0.5$). After this point the pH remained at 7, despite addition of base. When the stoichiometry of addition indicated all of the repeat units should be deprotonated ($\alpha_i = 1$), the pH again rose with the addition of base. Morawetz has suggested that such data are better analyzed by following the variation of apparent pK with degree of ionization.[12] This can be done in the form

$$\mathrm{pH} = \mathrm{p}K + n' \log[\alpha_i/(1 - \alpha_i)] \qquad (4)$$

where n' is an arbitrary constant.

Plotting the data in this form reveals an apparent change in behavior when the degree of ionization approaches $\alpha_i = 0.5$. Initially, there is a general increase in pK_{app}, as one would expect with a polyprotic acid, such as poly(acrylic acid). Similar observations have been cited as evidence for change in chain conformation in poly(methacrylic acid).[6] During the early stage of the titration the hydrogen bonding apparently keeps the polymer in a somewhat folded conformation. At present, it is unclear whether the hydrogen bonding is primarily imidazole to imidazole−anion interactions or interactions between imidazoles that are protonated since both types of hydrogen bonds could contribute to the conformational restriction. However, electrostatic shielding of a base during titration by the imidazole anion would result in the initial increase in pK_{app}. When the degree of ionization approaches $\alpha_i = 0.5$, charge repulsion begins to cause the chain to extend and makes formation of these hydrogen bonds more difficult. Additionally, this charge repulsion would begin to break up the imidazole to imidazole−anion hydrogen bonds, leading to greater accessibility of the remaining acidic protons, and the pK_{app} would decrease.

Conclusions

A new family of vinylic monomers have been synthesized in high yields from commercially available materials in 2−3 steps. Purity issues, which have previously inhibited study of this monomer, have been resolved. The parent monomer exhibits two modes of polymerization: a step-growth Michael-type addition pathway and an addition radical initiated pathway. Model Michael-type additions to a substituted vinazene demonstrate the ability of the vinazene nucleus to accept nucleophilic attack.

Both direct kinetic measurements and indirect kinetic chain length measurements indicate that vinazene and 1-methylvinazene behave as typical, but rapidly propagating, vinylic monomers. Polymers with weight-average molecular weights up to 200 000 g/mol have been synthesized. Mark−Houwink constants of $a = 0.89$ and $K = 3.3 \times 10^{-5}$ were determined and suggest a relatively stiff polymer backbone. Titration data for poly(vinazene) suggests behavior similar to poly(methacrylic acid).

Experimental Section

Methods. ^{1}H NMR spectra were collected with Varian 300, 400, or 500 MHz field instruments. ^{13}C NMR were collected at 75 or 100 MHz. Temperature was monitored in the NMR cavity by thermocouple where necessary. IR spectra were collected with a Nicolett 60 SX or a Perkin-Elmer Spectrum BX FT-IR system. Mass spectra were collected with a Micromass V6 70-250-5 magnetic sector mass spectrometer, using electron impact (70 eV), fast atom bombardment, or chemical ionization (ammonia) for ionization. UV spectra were collected with a Shimadzu UV160U spectrometer. Melting points were collected with a Mel-temp and are uncorrected. Elemental analyses were determined with a Perkin-Elmer CHN 2400. TLC were performed on Whatman silica gel plates 250 μm layer with fluorescent indicator. TGA data were collected with a Perkin-Elmer TGA 7. DSC data were collected with a Perkin-Elmer DSC-7.

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. All other reagents and solvents were purchased from Aldrich or Fischer Scientific.

Characterization. (1*Z*)-1-Amino-1,2-dicyano-3-aza-1,3,5-hexatriene [Acrodamn] (2). To a 500 mL Erlenmeyer flask, fitted with magnetic stirbar and an ice/water cooling bath, were added DAMN (20 g, 190 mmol) and ether (250 mL). The suspension was allowed to cool for 15 min. The mixture appeared as a dark brown powder suspended in a colorless liquid. To this mixture, 15 mL of 90% acrolein (210 mmol) was added with stirring, and the mixture was allowed to cool for 15 min. Upon addition of five drops of TFA the mixture took on a brief reddish color, and the brown powder appeared to dissolve. After approximately 2 min, a beige precipitate (acrodamn) began to form. The reaction was allowed to stir for 30 min total. The reaction mixture was poured into 1.5 L of precooled hexane with rapid stirring. The reaction mixture was filtered, leaving 27 g (97%) of acrodamn as a yellow precipitate. The acrodamn was allowed to air-dry overnight. Acrodamn prepared this way can be used without subsequent purification and matches previously reported spectral data.[5,13]

4,5-Dicyano-2-vinylimidazole [Vinazene] (3).[14] A 1000 mL flask fitted with a magnetic stirbar and an ice/water cooling bath was charged with 95% lead tetraacetate (85 g, 190 mmol). The lead tetraacetate was dissolved by addition of 400 mL of acetonitrile from a factory-sealed container. Crude acrodamn (27 g, 180 mmol) was dissolved in 600 mL of acetonitrile and poured into the lead tetraacetate solution over approximately 1 min. The lead tetraacetate solution was initially colorless with small amounts of a white precipitate,

and the acrodamn solution was initially dark. Upon addition of acrodamn, the lead solution turned dark cherry red, with formation of a volumous white precipitate bearing a slight metallic sheen. The solution was allowed to stir for an additional 50 min and then was filtered. The residual precipitate was washed with ethyl acetate until color was no longer evident in the extract. The combined organic filtrates were evaporated under reduced pressure. The residue was extracted with several portions of ether, until the extracts no longer appeared colored. The ether was removed by evaporation under reduced pressure, yielding 20.2 g (75%) of vinazene as an orange clumpy solid.

The product prepared in this way contains a trace of acetic acid present and is pure enough for most purposes, except polymerization. To purify the material for polymerization, it is necessary to filter the monomer through an alumina plug with extensive ether washings, until the color of the filtrate is indiscernible. The ether is evaporated under reduced pressure, to yield polymerizable material that is slightly yellow to white. Note: this material may oligomerize with excessive heating.

FW (calcd) 144.14; mp 176−180 °C (material begins to oligomerize at this temperature broadening the melting point); dec 200 °C (oligomerization was completed and material solidified by this point); TLC R_f 0.10 (50/50 hexanes/ethyl acetate), 0.38 (10% ethanol in ethyl acetate). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 6.62 (dd, 1H, α, J = 18.0 Hz, 11.2 Hz), 6.20 (dd, 1H, β-trans, J = 18.0 Hz, 0.8 Hz), 5.74 (dd, 1H, β-cis, J = 11.2 Hz, 0.8 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 149.95 (2), 124.03 (α), 123.33 (β), 111.08 (CN). IR (KBr Pellet, cm^{-1}): 3149−2488 (multiple peaks, indicative of 1,3-hydrogen bonding), 2242, 1911, 1728, 1644, 1574, 1510, 1433, 1405, 1370, 1300. LRMS (EI/70 eV): m/z 144 (60, M$^+$), 143 (60, M$^+$−H), 118 (11, M$^+$−CN), 84 (33), 60 (58), 59 (16), 45 (66), 44 (34), 43 (100), 42 (17). UV/vis (CH_3CN): λ_{max} (ϵ) (nm, M^{-1} cm^{-1}) 261 (16 900). Anal. Calcd for $C_7H_4N_4$: C, 58.3; H, 2.8; N, 38.9. Found: C, 58.6; H, 2.90; N, 39.0.

4,5-Dicyano-1-methyl-2-vinylimidazole [1-Methylvinazene] (4a).[1] In a 100 mL round-bottomed flask, vinazene (2.1 g, 15 mmol) was dissolved in 18 mL of THF by stirring. Upon addition of 2.1 g (15 mmol) of triethylamine, the brownish-orange solution darkened slightly. After 2 min, 1.6 mL (17 mmol) of dimethyl sulfate was added. This reaction was allowed to stir at room temperature for 2 days, sealed under a nitrogen blanket. The residue was diluted with 50 mL of ethyl acetate. The ethyl acetate was washed with three 50 mL portions of 10% aqueous NaOH, and the aqueous solution was back extracted with 2−20 mL portions of ethyl acetate. The combined organic layers were dried with magnesium sulfate and evaporated under reduced pressure. The remaining residue was dissolved in ether and passed through a 1 in. basic alumina plug, with generous ether elution. The ether was evaporated under reduced pressure, and the residue was recrystallized from ether hexanes to yield 1.7 g (75%) of product as yellow plates in two crops. Note: both the addition of the triethylamine and the dimethyl sulfate can be quite exothermic at large scales. An ice/water may be needed bath during addition of reagents if reaction quantities are above 10 g.

FW (calcd) 158.16; mp 98−100 °C (from ether/hexanes); TLC R_f 0.39 (50/50 hexanes/ethyl acetate). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 6.90 (dd, 1H, α, J = 17.2 Hz, 11.0 Hz), 6.33 (dd, 1H, β-trans, J = 17.2 Hz, 1.5 Hz), 5.81 (dd, 1H, β-cis, J = 11.0 Hz, 1.5 Hz), 3.82 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 149.63 (2), 124.90 (α), 121.50 (β), 112.39 (CN), 108.79 (5), 33.05 (Me). IR (KBr pellet, cm^{-1}): 2235, 1897, 1525, 1489, 1461, 1419, 1377, 1328, 1307. LRMS (EI/70 eV): m/z 158 (76, M$^+$), 157 (100, M$^+$−H), 132 (16, M$^+$−CN). LRMS (CI/NH_4^+): m/z 159 (100, M$^+$ + H), 176.0 (22, M$^+$ + NH_4^+). UV/vis (CH_3CN): λ_{max} (ϵ) (nm, M^{-1} cm^{-1}) 264 (11 600). Anal. Calcd for $C_8H_6N_4$: C, 60.8; H, 3.8; N, 35.4. Found: C, 61.0; H, 4.0; N, 35.2.

4,5-Dicyano-1-methyl-2-(2-morpholinylethyl)imidazole (5a).[5] In a test tube, 1-methylvinazene (200 mg, 1.3 mmol) was dissolved in 1 mL of DMSO with stirring, and morpholine (1 mL, 11 mmol) was added. The reagents were allowed to stir for 1 h. The solution was diluted with 50 mL of water and extracted with three 15 mL portions of ethyl acetate. The combined organics were evaporated in a test tube. The remaining residue was dissolved in 2 mL of acetone, and 14 mL of ether was added. The solution was allowed to partially evaporate. Crystals grew on the side of the test tube. The crystals were scraped off and rinsed with room-temperature ether. The crystals were collected to yield 22 mg (7%) and used for characterization. The crude product totaled 260 mg (84%) from the evaporated mother liquor.

FW (calcd) 245.28; mp 88−92 °C (from ether); TLC R_f 0.1 (50/50 hexanes/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.76 (s, 3H, Me), 3.56 (m, 4H, morpholine-3), 2.92 (m, 2H, β), 2.66 (m, 2H, α), 2.42 (m, 4H, morpholine-2). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 153.50 (2), 119.18 (CN), 111.88 (CN), 112.51 (5), 108.82 (4), 66.06 (morpholine-2), 55.04 (β), 53.03 (morpholine-3), 33.02 (Me), 24.07 (α). IR (KBr pellet, cm^{-1}): 2987, 2959, 2931, 2903, 2853, 2811, 2776, 2235, 1510, 1468, 1447, 1419, 1307. LRMS (EI/70 eV): m/z 245 (1, M$^+$), 227 (6), 214 (3), 202 (5), 160 (7), 159 (11, M$^+$ − morpholine), 100 (100, morpholine − CH_2^+). HRMS: 245.1280 (calcd for $C_{12}H_{15}N_5O$: 245.1276).

Typical Polymerization of Vinazene.[15] To a flask fitted with a stirbar were added 10 g of vinazene, 50 mg of AIBN, and 50 mL of DMF. The solution was degassed and placed in an oil bath at 70 °C for 3 h. The material was removed and the solvent removed by evacuation to yield the product polymer; an accurate yield cannot be computed because it is very difficult to remove all traces of solvent. Material polymerized in this way has a viscosity-average molecular weight of approximately 230 000 g/mol, η_{inh} = 1.9, in DMSO at 30 °C.

Deprotection of Poly(methylvinazene).[3] In a flask fitted with a stirbar and reflux condenser, 270 mg of polymethylvinazene was dissolved in 20 mL of NMP and 730 mg of LiCl. This solution was allowed to reflux overnight. The solution was precipitated into 10% aqueous HCl. NMR of the resulting material clearly shows the absence of a methyl peak present in the original compound.

The Free Radical Polymerization Kinetics of Vinazene by NMR. 1. Data Collection. A sample solution was prepared that was ∼0.5 M in monomer and ∼0.06 M in AIBN. NMR samples were taken from this solution. The NMR sample was appropriately shimmed, and the preliminary spectrum was recorded at room temperature. The sample was removed from the cavity, and the variable temperature device on the NMR spectrometer was raised to 60 °C, a process that took about 10 min. When the temperature had reached 60 °C, the sample was reinserted and quickly reshimmed. Then 40 data points were collected with a 30 s delay and a 41 s acquisition time, for a total of 71 s between each data point. A replicate experiment was performed by inserting the second sample into the NMR, while hot, quickly shimming, and collecting an identical set of data.

2. Data Analysis. The NMR measures intensities for kinetics experiments as a function of line height. In this case, the coupling of the vinyl peaks becomes a significant factor in interpreting the spectra. The α proton showed the cis and trans coupling, yielding four lines. The β protons each have their respective cis or trans coupling, and in addition each has a geminal coupling constant with each other. The geminal coupling is very small and difficult to resolve. Consequently, each peak for a β proton yielded two lines. These eight lines were used as a measure of concentration of the monomer. In each data set the first scan was carefully integrated and compared to the preliminary scan. Using this ratio, each line height was corrected to yield a direct measure of concentration and determine the loss of monomer during processing time. The average concentration indicated for all eight peaks was used for the timed-based logarithmic regression.

3. Results. The first data point showed approximately 10% conversion as compared to the preliminary spectrum. During the 10 min duration of heating from room temperature to 60 °C, there was some unavoidable initiation of polymerization. The replicate was inserted into the spectrometer cavity while

hot and consequently did not have the 10 min delay of heating from room temperature to 60 °C. Because of this, there was no conversion at the first data point in the replicate. At approximately 90% conversion, in both samples, 0.05 M in monomer, the rate appeared to slow considerably. This is thought to be a manifestation of initiator efficiency, an effect related to monomer concentration (vide supra). Consequently, for the purposes of data analysis, the data were analyzed between the first scan and the point of 90% conversion (approximately 400 s later). A deviation also occurs at approximately 60% conversion, where the data curves above the best line fit slightly. This is thought to be a manifestation of viscosity effects setting in; this occurs after approximately 2 min. No practical way around this problem was obvious.

Kinetic Chain Length Determination. 1. Experiment Detailing Dependence of M_n on Initiator Concentration. Test tubes containing five different amounts of AIBN, 5.1 mg, 10.6 mg, 17.1 mg, 20.7 mg, and 24.2 mg, were fitted with stir bars. To each sample was added 4 mL of 0.54 M monomer solution, and each sample was degassed. The samples were placed in an oil bath at 69−71 °C and allowed to stir overnight to ensure complete polymerization. After stirring overnight, excess solvent was removed with vacuum pumping. Light-scattering GPC provided M_n, M_v, and M_w (Figure 4).[11]

2. Experiment Detailing Dependence of M_n on Monomer Concentration. Test tubes containing five different amounts of vinazene, 0.80, 0.65, 0.48, 0.29, and 0.16 g, were fitted with stir bars. To each sample was added 4 mL of a 22 mM initiator solution, and each sample was degassed. The samples were placed in an oil bath at 65 °C and allowed to stir overnight. After stirring overnight, excess solvent was removed with vacuum pumping. Light-scattering GPC provided M_n, M_v, and M_w (Figure 4),[11] with samples that had been filtered through a 0.2 μm PTFE membrane filter (Whatman). The Mark−Houwink parameters were determined from this set of data.

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Supporting Information Available: Details on the synthesis of several derivatives of vinazene formed by Michael addition, Diels-Alder reactions, and alkylation. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) We are grateful to Larry Markowski, of the Beckmann Institute, University of Illinois, Urbana, IL, for obtaining light-scattering GPC data for our compounds in NMP.

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