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The Chemistry of 2-Alkenyl-5(4H)-oxazolones. IX. Acid-Catalyzed Oligomerization

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ABSTRACT

Results of the acid catalyzed oligomerization of 2-alkenyl-5(4H)-oxazolones are reported. Employing LC–MS and preparative LC methods, the oligomeric mixtures were characterized by NMR analyses and were discovered to consist of exclusively cyclic trimers to decamers, with tetramers and pentamers predominating. A nucleophilic oligomerization mechanism involving Michael addition and C-alkylation of a ketene-aminal to protonated monomer was proposed that resulted in irreversible cyclization at the trimer propagation stage. Subsequent oligomerization proceeded via enolization of α-hydrogens on 2-substituted 5(4H)-oxazolone products and continued Michael addition to protonated monomer. In the sense that when both enolizable hydrogens and protonated monomer are present, the oligomerization can be regarded as being "living."

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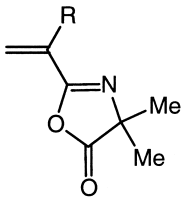
Key Words: Ketene-aminal; Nucleophilic oligomerization; Activated monomer mechanism; Azlactone.

INTRODUCTION

2-Alkenyl-5(4H)-oxazolones (azlactones) **1** are excellent monomers and comonomers in free radical chain-growth polymerizations.[1] Over the course of several years investigating the chemistry of these compounds, however, a tendency has been noted for them to thicken on standing, even in the refrigerator in the presence of oxygen and suitable free radical inhibiting additives. This thickening seemed to correlate most closely with the presence of adventitious acid and has prompted us to request our commercial supplier[2] of **1a** to add 0.1 wt.% triethylamine as well as 0.05 wt.% 2,6-di-t-butyl-4-methylphenol[3] as stabilizing agents to provide a non-acidic as well as a free radical stabilizing condition.



1a; R = H
1b; R = Me

The alkenyl group in **1** is clearly electron deficient based on determined polarity values[1b] (*e*, of +0.65 and +0.28) and chemical shifts of corresponding β-carbons ($\delta = 129.0$ and 123.7 ppm[4]) in the ^{13}C-NMR for **1a** and **1b**, respectively. In fact, monomer **1a** is quite analogous to methyl acrylate ($e = +0.64$[5] and $\delta = 130.6$ ppm[6]) in terms of the electronic nature of its carbon–carbon double bond. Participation of **1a** as a dienophile in a Diels-Alder reaction with electron rich cyclopentadiene[7] is also indicative of a relatively electron poor olefinic portion of the molecule. Therefore, acid-catalyzed oligomerization/polymerization was a surprising observation.[8]

Similar acid-catalyzed events have also been observed with analogous 2-alkenyl-2-oxazolines. Tomalia et al.,[9] reported "that a variety of unidentified polymers, gels, or oligomeric syrups were readily formed by merely allowing 2-alkenyl-2-oxazolines to come in contact with Brønsted acids at room temperature." The reaction product of equimolar quantities of 2-isopropenyl-2-oxazoline (IPO) and 2-isopropenyl-2-oxazolinium bisulfate (prepared by addition of IPO to an equimolar amount of sulfuric acid) consisted of oligomers with molecular weights from 900 to 2500 and was assigned the poly(Michael addition) structure **2** in which the oxazoline ring was intact and part of the oligomer main chain. In addition to other supporting evidences for structure **2**, the observation of terminal olefin CH resonances in the ^{1}H-NMR was especially compelling. An indication that oligomerization was controlled by rather subtle and unknown factors was obtained when IPO was reacted in the same manner with its trifluoromethanesulfonate salt; only cyclic dimers **3** and **4** were obtained in a ratio of 82 : 18.

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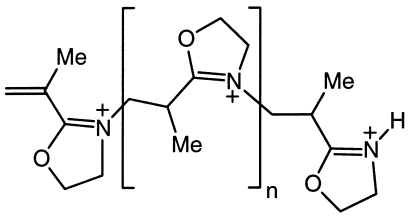

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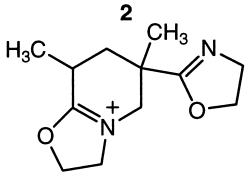

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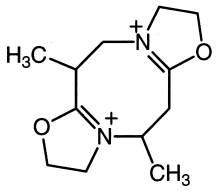

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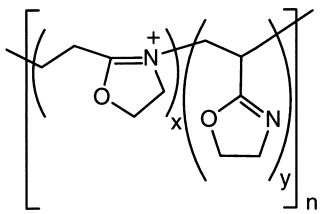
Saegusa et al.,[10] reported that both preparation of 2-vinyl-2-oxazolinium fluorosulfonate and "spontaneous" polymerization occurred upon addition of 2-vinyl-2-oxazoline to excess fluorosulfonic acid at 0°C, and the polymer could also be obtained when a small amount of pyridine was added to a solution of the 2-vinyl-2-oxazolinium salt. The low molecular weight polymer was assigned structure **5** based on its ^{1}H-NMR spectrum. Structure **5** represented a combination of poly(Michael addition) (x units, which predominated) and vinyl propagated structures (y units). The latter resulted from nucleophilic attack at the β-carbon of the vinyl group forming a ketene-aminal intermediate **6** (also proposed by Tomalia et al.[9]). This enamine-type nucleophile could subsequently participate in a Michael addition with protonated monomer as a carbon nucleophile resulting in restoration of the oxazoline side chain and formation of the y units. Miyamoto et al.,[11] later reported relevant results suggesting that steric factors may be important with an analogous system, 4,4-dimethyl-2-vinyl-2-oxazoline. Using catalytic quantities of trimethylsilyl triflate, only vinyl propagated polymers (y units; $M_N = 3200$–7600) were reported and no poly(Michael products) (x units) or cyclic products.



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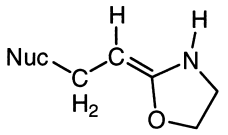

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The present work investigates a novel cyclooligomerization of **1** using catalytic quantities of strong Brønsted acids creating situations in which an excess of basic oxazolone nucleophiles exists and the acid can turn over in a catalytic sense. Predominantly, tetrameric and pentameric products are provided that result from initial Michael addition of the oxazolones themselves (or gegenions of certain Brønsted acids) to 2-alkenyl oxazolinium ion Michael acceptors. Resulting ketene-aminal adducts are then capable of further Michael addition propagation with 2-alkenyl oxazolinium ions. Cyclic oligomeric products are formed exclusively as evidenced by MS analyses and the absence of terminal carbon–carbon double bonds in NMR spectra. Although the distributions of oligomers obtained are not rigorously monodisperse, these nucleophilic oligomerizations have been shown to be "living" in the sense that propagation can continue as long as "enolizable" hydrogens on carbons adjacent to oxazolone rings and protonated **1** are present.

EXPERIMENTAL

Materials and Analyses

Unless otherwise indicated, polymerizations and oligomerizations were conducted in an Atlas Launderometer (available from Atlas Electric Devices Co., Chicago, IL). UV spectra were recorded using a Perkin-Elmer Model 330 Spectrophotometer. IR spectra were obtained using a Spectra Tech IRμs Microscope. Continuous IR monitoring was conducted using an ASI Applied Systems ReactIR 1000 fitted with a SiComp probe (silicon ATR sensor). Each spectrum recorded at various intervals was the average of 128 scans with 4 cm^{-1} resolution. All NMR spectra were acquired using either a Varian UNITY 400, UNITY 500, INOVA 500, or INOVA 600 MHz spectrometer. All spectrometers were equipped with *z*-axis pulse field gradients. Positive ion electrospray mass spectrometry was conducted using a Zabspec Magnetic Sector Mass Spectrometer (Micromass Inc.) equipped with an electrospray ionization source. The instrument scanned from m/z 100–1400 at a rate of 4 sec/decade, and the accelerating voltage was 4 kV. Both ammonium acetate and sodium acetate (0.1 mM solutions) were used as cationizing agents. Matrix-assisted laser desorption ionization (MALDI) mass spectrometry was obtained on a Voyager-Elite STR instrument (Perkin-Elmer, Perceptive Biosystems) equipped with a nitrogen laser emitting at 337 nm.[a] The instrument was operated in the linear delayed

[a]Sample preparation involved mixing a 0.1 mg/mL sample in acetonitrile-water with an equal volume of a saturated solution of 2,5-dihydroxybenzoic acid (used as matrix) in acetonitrile: 0.1% TFA (water) (70 : 30) solution. An aliquot (1 μL) of the resulting mixture was deposited onto a gold-plated MALDI sample plate for the actual analysis.

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extraction mode at an accelerating voltage of 20 kV. Fast Atom Bombardment (FAB) analyses were performed using a VG 7070E High Resolution Mass Spectrometer.[b] Gas chromatography (GC)–MS analyses were conducted using a Hewlett Packard 5995 instrument equipped with a 30 m DB-1 capillary column heated from 30 to 310°C at 15° min^{-1}; the separated components were subjected to electron bombardment, and full scan spectra were recorded from masses 29 to 600. Gas chromatographic analyses were conducted using either a thermal conductivity detection Hewlett Packard Model 5790A Gas Chromatograph or a flame ion detection Hewlett Packard Model 5890 Series II Gas Chromatograph equipped with an HP-5 High Performance Capillary Column. HPLC analyses were conducted using an Agilent Technologies Model 1100 HPLC System consisting of a quaternary pump, vacuum degreaser, autosampler, thermostatted column compartment and a diode array detector using a 150 × 3 mm Prontosil 120-3-C18-H column equilibrated with water and acetonitrile eluents containing 0.1% trifluoroacetic acid in both eluents. The column was equilibrated with 85/15 (v/v) water/acetonitrile at 0.50 mL min^{-1} and 40°C for at least 10 min prior to injection of 2.5 μL (or 50 μL for preparative separations) of a 0.11–0.12 g samples dissolved in 1 mL of 0.1% aqueous trifluoroacetic acid. Samples were also analyzed using HPLC with APCI MS detection using an Agilent Technologies HPLC/MSD system equipped with the previously described Model 1100 HPLC and a model G1047A mass selective detector operating in the APCI mode. Viscosities were obtained using a Brookfield Viscometer (available from Brookfield Engineering Labs. Inc., Stoughton, MA) at 22°C. Gel permeation chromatography (GPC) analyses were conducted using a Waters 717 autosampler and a Waters 590 pump equipped with an Erma ERC-7515A refractive index detector. Filtered tetrahydrofuran solutions were injected into a Polymer Labs PLgel-Mixed D column set for very low molecular weights and a Mixed B column set for high molecular weights operated at room temperature and flowing at 0.95 mL min^{-1}; this arrangement provided a capability of examining polymeric samples with molecular weights from 200 to 400,000. Molecular weight calculations were computed with Caliber software (Polymer Labs) and were based on calibrations made using narrow dispersity polystyrene standards ranging in molecular weight from 580 to 6,300,000.

Poly(4,4-dimethyl-2-vinyl-5(4H)-oxazolone) (**poly 1a**) was prepared according to a literature procedure[1a] employing free radical initiation and precipitated from solution into diethyl ether; the polymer possessed a weight-average molecular weight of 220,000. 4,4-Dimethyl-2-isopropenyl-5(4H)-oxazolone (**1b**) was prepared using a literature procedure[12] and was distilled prior to use. 4,4-Dimethyl-2-ethyl-5(4H)-oxazolone [**10**][13] and 2,2′-*m*-phenylenebis(4,4-dimethyl-5(4H)oxazolone)[14] were prepared using literature procedures.

[b]A portion of the sample was dissolved in a m-nitrobenzyl alcohol matrix and positioned at the end of the FAB probe. The probe was then introduced directly into the ion source of the mass spectrometer at ambient temperature and high vacuum. Ions were generated by exposure of the sample to a beam of neutral xenon atoms from the FAB gun at a voltage of 8 keV and an ion current of 1 mA. The mass spectrometer was operated at a mass resolution of approximately 4000 over a range of 50–1800 m/z, with a second analysis being performed over a mass range of 1400–3100 m/z.

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Preparation of 2,2′,2″-*cis*,*cis*-1,3,5-Cyclohexylenetris[4,4-Dimethyl-5(4H)-oxazolone] (11)

1,3,5-Cyclohexanetricarboxylic acid (Aldrich) was dried prior to use by heating at 65°C in a vacuum oven under reduced pressure (1 mmHg) for 15 h. The dried triacid (20.0 g, 92.5 mmol) was suspended in chloroform (100 mL), thionyl chloride (50.0 g, 0.42 mol) and *N*,*N*-dimethylformamide (0.5 mL), and the mixture was refluxed for 4 h. Chloroform and excess thionyl chloride were then removed at reduced pressure. The tris(acid chloride) was redissolved in chloroform (95 mL) and used directly in the next step without purification.

A mixture of 2-aminoisobutyric acid (57.8 g, 0.56 mol, Aldrich), sodium hydroxide (22.4 g, 0.56 mol), water (125 mL), and chloroform (30 mL) was cooled to −15°C and stirred vigorously while the solution of the tris(acid chloride) was added dropwise. When the addition was complete, the reaction flask was removed from the cold bath, allowed to warm to room temperature, and the mixture stirred for two more hours. The supernatant was then decanted from the white solid precipitate, the aqueous layer was separated from the chloroform in the supernatant, and the aqueous layer was combined with the white solid. Concentrated aqueous hydrochloric acid (200 mL) was added to the aqueous mixture which was then cooled in an ice bath for 2 h. The white solid was collected by filtration on a sintered glass funnel, washed with a saturated sodium chloride solution (500 mL), and dried to afford 29.5 g (68%) of the tris(amido acid) **11a** which did not melt below 300°C. IR (KBr): 1731 (CO_2H), 1650 (CONH), 1532 (amide II) cm^{-1}.

^1H NMR (DMSO-d_6/$CDCl_3$, 400 MHz) δ: 12.0 (bs, 3H), 7.95 (s, 3H), 3.42 (bs, 3H), 2.22 (m, 3H), 1.62 (m, 3H), 1.28 (s, 18H). ^{13}C NMR (DMSO-d_6/$CDCl_3$, 100 MHz) δ: 175.6, 173.7, 54.5, 42.1, 31.2, 24.9. High resolution MS *m*/*z*: calcd. for $C_{21}H_{33}N_3O_9Na$ (MNa^+) 494.2114, found 494.2106.

Ethyl chloroformate (5.00 g, 46 mmol) was added dropwise to a stirred mixture of the tris(amido acid) **11a** (7.00 g, 14.8 mmol) in pyridine (75 mL) at −20°C. When addition was complete, the mixture was stirred at room temperature for 1.5 h, and then the pyridine was removed at reduced pressure. The residue was taken up in chloroform (225 mL), washed with a 10% hydrochloric acid solution in water (3 × 50 mL), and then with a saturated sodium bicarbonate solution (1 × 50 mL). The chloroform solution was dried over magnesium sulfate, filtered, and solvent evaporated to leave the tris(oxazolone) **11** (1.71 g, 28%). Mp: 230–233°C. IR (KBr): 1812 (C═O), 1676 (C═N) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.7 (tt, $J = 3.3$, 12.5 Hz, 3H), 2.5 (d, $J = 13.7$ Hz, 3H), 1.7 (dt, $J = 12.5$, 13.7 Hz, 3H), 1.4 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 180.6, 164.3, 65.2, 36.6, 30.2, 24.6. High resolution MS *m*/*z*: calcd. for $C_{21}H_{27}N_3O_6$ (MH^+) 418.1978, found 418.2002.

Oligomerization Reactions

Oligo[4,4-Dimethyl-2-vinyl-5(4H)-oxazolone (**Oligo 1a**)]

Into an 8 oz. amber glass bottle were charged **1a**[2] (130 g; 0.935 mol) and ethyl acetate (193.5 g). A small aliquot (0.5 mL) was removed for GC analysis and comparison

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later. Trifluoroacetic acid (TFA) (5.38 g; 0.047 mol; 5 mol% based on **1a**) was added causing considerable fuming but no warming; the reaction solution was essentially colorless. The bottle was sealed with a metal screw cap equipped with a Teflon film seal, and the solution was placed in the launderometer at 65°C for 24 h. The percent conversion of **1a** to oligomer was determined by GC to be 97% (compared with the earlier withdrawn aliquot utilizing the ethyl acetate solvent as an internal standard); no peaks other than solvent and **1a** were observed at column temperatures up to 250°C. The color of the solution was reddish orange and the viscosity had increased only very slightly to 0.9 cps at 22°C. Removal of solvent in vacuo from an aliquot provided an orange, somewhat friable, foamy solid product. The product was efficiently precipitated by addition of the remaining solution to 20 volumes of heptane forming a light orange solid. Gel permeation chromatographic analysis showed the material to be of very low molecular weight and possessing a relatively narrow distribution: $M_W = 628$, $M_N = 555$, and $P = 1.13$. The reactable oxazolone content of the oligomer was determined by treating a sample with excess standard *n*-butylamine in THF/DMAc. Titration of the remaining amine with standard HCl indicated that 87.0% of the theoretical oxazolone content remained in the oligomer.

Subsequent examination of the overall rate of the TFA catalyzed oligomerization at 65°C using the ReactIR indicated first order depletion of **1a** ($t_{1/2} = 4$ h) by monitoring the disappearance of the vinyl adsorption at 1600 cm^{-1}, and a conversion of 96% was achieved in 24 h.

In a similar fashion, oligo **1a** was obtained using chlorosulfonic acid (CSA) (5 mol%) as catalyst. The oligomerization solution was more intensely reddish orange colored than the TFA catalyzed reaction and exhibited monomer conversions at 2 and 18 hours at 60°C of 95.5% and 98.5%, respectively. The oxazolone content by titration of the CSA material was 79.6%.

Oligo[4,4-Dimethyl-2-isopropenyl-5(4H)-oxazolone (**Oligo 1b**)]

The oligomerization of **1b** required substantially more forcing conditions, i.e., four times the amount of a much stronger acid catalyst, than **1a** to achieve even modest conversions. Monomer **1b** (5.00 g; 0.033 mol) was dissolved in ethyl acetate (5.00 g), ethanesulfonic acid (0.72 g; 0.0065 mol or 20 mol% based on **1b**) was added, and the contents were sealed and heated at 65°C for 96 h. Conversion was 62% and substantially less color developed than with **1a**. A control experiment examining the system with no acid under identical conditions showed no disappearance of **1b**. In an effort to remove unreacted **1b**, the oligomer solution was precipitated into 20 volumes of 2,2,4-trimethylpentane, and the mixture was then warmed to 40°C to extract unreacted **1b** from the slightly yellow precipitated product before filtration. The solid was then dissolved in ethyl acetate and reprecipitated into petroleum ether. The resulting, essentially white solid precipitate was filtered and dried under vacuum. Gel permeation chromatographic analysis indicated the following molecular weight information: $M_W = 789$, $M_N = 691$, and $P = 1.14$. The oligomerization was also conducted in chloroform using trifluoromethanesulfonic acid (10 mol% based on **1b**). After 116 hr 60°C, the colorless solution was examined by GC and the conversion was 70%.

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Derivatization of the Oligomers

Selective Hydrolyses of **Oligo 1a** and **Oligo 1b**

This procedure was conducted in such a fashion, i.e., at room temperature employing only a 10% stoichiometric excess of water, as to selectively hydrolyze only oxazolone groups to corresponding amidoacids and, hopefully, not amide or other groups present in the material. To 52 g of the TFA catalyzed solution above (containing 19.9 g of **oligo 1a** and 0.143 mol of incorporated **1a**) were added THF (104 mL; to maintain a homogeneous reaction solution over the course of the hydrolysis) and 2.84 g (0.157 mol) of water. The TFA present in the original solution was sufficient to catalyze the hydrolysis. After eight days at room temperature, the IR spectrum showed a substantially reduced oxazolone carbonyl absorption at 1821 cm^{-1} and new strong absorption bands observed at 1736, 1650, and 1538 cm^{-1} that were consistent with the desired amide-acid hydrolysis product. The hydrolysis product was precipitated by dropwise addition with stirring into 2 L of diethyl ether. The fine precipitate was collected by filtration and vacuum dried. The dry, slightly yellow solid weighed 22.67 g which represented a 97% hydrolysis yield.

An equivalent procedure was conducted for the chlorosulfonic acid catalyzed **oligo 1a** material, except that only 48 h were required to effect the room temperature hydrolysis until the oxazolone carbonyl had been reduced to a small and constant level. Hydrolysis of **oligo 1b** initiated using ethanesulfonic acid was conducted employing the same conditions as with **oligo 1a**, and a visibly colorless solid product was obtained.

Reaction of **Oligo 1a** with Benzylamine

To 19.5 g of the TFA catalyzed **oligo 1a** solution in ethyl acetate which contained 7.8 g (0.056 mol) of **oligo 1a** were added THF (70 mL) and benzylamine (6.6 g; 0.062 mol). The initial reddish colored solution warmed mildly with addition of the amine and became light yellow in color on standing at room temperature overnight. The reaction solution was precipitated into ether (1200 mL), and a fine-grained yellow solid was collected. After filtering and vacuum drying, the solid weighed 12.4 g (90% recovery/yield). IR analysis revealed a small but persistent C═O absorption at 1825 cm^{-1}.

Experiments Conducted to Investigate the Mechanism of Oligomerization

NMR Examination of Reaction of **1a** and Stoichiometric Excesses of Various Acids

Each acid examined (0.65 mol) was contained in a dry, 10 mL round-bottomed flask equipped with a magnetic stirring bar and fitted with a septum. **1a** (0.28 g; 0.002 mol) was added dropwise via a syringe with efficient stirring at room temperature. After the addition the solutions were stirred for at least 90 min before removing a sample for NMR analysis.

Acetic-d_3 Acid-d: initial concentrations: $[CD_3CO_2D] = 16.3$ M and [**1a**] = 0.5 M; equilibrium concentrations: [**1a**] = 0.1 M (based on integration of remaining vinyl resonances) and [Michael adduct] = 0.4 M based on singlet for $CD_3CO_2CH_2CD_2$ at 4.42 ppm; $K_{eq} = 0.25$.

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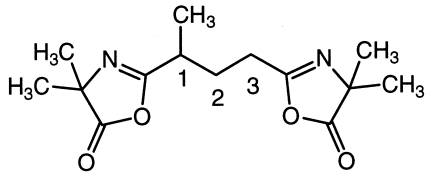
Trifluoroacetic Acid: initial concentrations: [TFA] = 12.3 M and [**1a**] = 0.4 M; equilibrium concentrations: [**1a**] = 0.2 M and [Michael adduct] = 0.2 M based on triplets at 3.32 ($J = 5.6$ Hz) and 4.58 ($J = 5.6$ Hz) ppm (Note: In a repeat experiment in which the temperature may have been less controlled, an amide NH resonance at 7.22 ppm as well as two additional sets of triplets at 2.63 and 4.45 ppm were observed along with the aforementioned sets of triplets; this additional product appeared to be the trifluoroacetate ring-opened Michael adduct.) $K_{eq} = 0.08$.

Chlorosulfonic Acid: No Michael addition products were detected.

Oligomerization of **1a** and **10**

A solution consisting of 4,4-dimethyl-2-ethyl-5(4H)-oxazolone (**10**) (1.41 g; 0.010 mol), chloroform-d (3.94 g), and TFA (1.25 g; 0.011 mol) was cooled to −78°C. Just as a solid was beginning to precipitate, **1a** (1.39 g; 0.010 mol) was added with stirring, causing the emerging precipitate to quickly redissolve. The colorless solution was allowed to warm to room temperature. After 3 h, the solution had become yellow with a slightly increased viscosity. Gas chromatographic analysis (column: 10 ft × 1/8 in, 10% UC W98 on 80–100 mesh Chromosorb W, 50–250° @ 10° min^{-1}; injection port: 250°C; detector: 300°C) showed one unresolved peak for both oxazolones at 6.9 min comprising 69% of the initial oxazolone concentration and a higher boiling material with retention time 18.3 min. Control experiments with **10** and **1a** each alone with TFA established that no reaction took place with **10** and essentially complete oligomerization with **1a** but with no longer retention time peak being observed under the conditions of the GC analysis. Therefore, the higher boiling peak appeared to be a reaction product of **10** and **1a**.

NMR Analysis: Solutions in $CDCl_3$ and also C_6D_6 and C_6D_5N were used for the analysis of the oligomeric mixture.



A doublet resonance at ^1H δ 1.35 ppm and a singlet at ^{13}C δ 16.3 ppm were assigned to the methyl group at position 1. A multiplet at ^1H δ 2.8 ppm and singlet at ^{13}C δ 33 ppm were assigned to the methine (—CH) at position 1. The two protons at position 2, being next to a chiral center, were nonequivalent and assigned to two multiplet resonances at ^1H δ 1.9 and δ 2.2 ppm; its carbon resonance was assigned to the peak at ^{13}C δ 27.7 ppm. A multiplet at ^1H δ 2.7 ppm and singlet at ^{13}C δ 26 ppm were assigned to the methylene ($—CH_2—$) at position 3. The connectivity among the groups at positions 1, 2, and 3 was confirmed by correlations observed in TOCSY, HETCOR, and HMBC NMR spectra. No additional correlations to other proton resonances were observed, confirming the presence of non-protonated groups at both ends of the 1–2–3 segment in the structure shown above.

GC–MS Analysis: The identity of the higher boiling component detected by the GC analysis was examined by GC–MS. The mass spectrum of the component was consistent with the structure indicated by the NMR experiments. A small molecular ion was observed

at 280 along with expected mass fragments at 265 (loss of methyl; 47.7% of base peak @ 58) and 168 (loss of oxazolone; 66.6% of base).

Oligomerization of **1a** Using TFA in the Presence of **11**

Because of solubility problems with **11**, *N*,*N*-dimethylacetamide (DMAc) was employed as oligomerization solvent. A stock solution consisting of DMAc (6.0 g), compound **11** (0.048 g), and 2,2′-*m*-phenylenebis[4,4-dimethyl-5(4H)-oxazolone] (0.048 g; added as an internal standard) was prepared by warming to 90°C for a short time, and a colorless solution resulted. Trifluoroacetic acid (0.16 g; 0.00144 mol) was added, and an aliquot sample (0.5 mL) was removed as a Control sample and placed in a separate vial. To the remainder of the stock solution were added 4.25 g (0.030 mol) of **1a**. An aliquot (0.02 mL) was removed for GC analysis to determine the initial **1a**/solvent ratio, and the remainder of the sample along with the Control vial were sealed and placed in an oven at 90°C for 23.5 h. Gas chromatographic analysis indicated that the extent of oligomerization was 89.5%. At that point, three-fold stoichiometric excesses of water were added to both vials, and the vials were placed in an oven at 65°C for 23 h to effect hydrolysis. The solutions were analyzed by HPLC directly, and the result was that only 6% of the hydrolyzed trimer **11a** remained in the mixture compared to the Control sample.

RESULTS AND DISCUSSION

Effect of Reaction Variables on Rate of Oligomerization

A cursory investigation of the effects of wide ranging reaction parameters was initially conducted to obtain a general understanding of important reaction conditions. The results reported in Table 1 indicated that the acid-catalyzed disappearance of **1a** was favored by increased acid concentration (entries 1–4), increased reaction temperature (entries 5–8), employment of strong acids with pK_a values of less than 1 (entries 9–13), and use of more polar solvents (entries 14–18). The reaction could also be catalyzed by Lewis acids (although more slowly and moisture may not have been rigorously excluded) (entries 19–21) and was unaffected by free radical inhibitors (entries 22–24).

HPLC Analyses

Analyses of the oligomeric mixtures was not just a straightforward matter of performing HPLC on oligomeric solutions because use of reverse-phase techniques employing aqueous solvents was required to resolve the complicated mixtures. Oxazolones are very susceptible to hydrolysis and formation of the corresponding amidoacids, especially in the presence of the very strong acids required to promote oligomerization. Attempting to characterize a "moving target" seemed less than desirable, and even though hydrolysis was observed to cause substantial dissipation of the color and possible loss of chromophores, reaction with water seemed to provide the simplest derivativization possible. The oxazolone oligomers were hydrolyzed in such a manner, i.e., room temperature using a 10% stoichiometric excess of water, that hopefully only oxazolone

Table 1. Effect of reaction variables on the disappearance of **1a**.

Entry	Reaction condition[a]	% **1a** Oligomerized[b]
1	No catalyst	0
2	TFA (1 mol%)	10
3	TFA (5 mol%)	42
4	TFA (7 mol%)	59
5	−78°	5
6	−2°	22
7	22°	43
8	59°	88
9	CH_3CO_2H [$pK_a = 5$[17]]	0
10	$CHCl_2CO_2H$ ($pK_a = 1.3$)	3
11	CCl_3CO_2H ($pK_a = 0.9$)	40
12	TFA ($pK_a = 0$)	42
13	$HClO_4$ ($pK_a = -10$)	72
14	$CHCl_3$ [100, $\varepsilon = 4.7$[18]]	36
15	$CHCl_3$: MEK (75 : 25, $\varepsilon = 8.2$)	45
16	$CHCl_3$: MEK (50 : 50, $\varepsilon = 11.6$)	51
17	$CHCl_3$: MEK (25 : 75, $\varepsilon = 15.1$)	56
18	MEK (100, $\varepsilon = 18.5$)	57
19	$AlCl_3$[c]	25
20	BF_3 etherate	78
21	$ZnCl_2$	21
22	Nitrogen purge[d]	27
23	Oxygen purge	28
24	BHT[e]	30

[a]Unless otherwise indicated, reactions of **1a** were conducted in ethyl acetate solvent (solvent weight fraction = 0.60) at 22°C using TFA (5 mol% based on **1a**) for 18 h.
[b]Disappearance of **1a** was monitored by gas chromatography relative to solvent.
[c]Reactions were conducted in acetonitrile over a 72 h reaction period.
[d]TFA was used as catalyst but at 1.7 mol%.
[e]2,6-Di-t-butyl-4-methylphenol (BHT) was added at 1 wt.% based on **1a**.

rings would be affected and not other linkages that would be diagnostic of the structure of the original oxazolone oligomers.

Having access to an instrument possessing multiple UV detectors was a considerable advantage diagnostically in that the 220 nm detector provided a more universal detector of essentially all components of a mixture, while 340 nm detected those that contributed to visual color. HPLC analyses of hydrolyzed products from TFA and CSA catalyzed oligomerization of **1a** (hereinafter referred to as **oligo 1a**) are shown in Figs. 1 and 2, respectively. The analyses indicated that very different compositions of **oligo 1a** could result depending on the nature of the acid catalyst. For the TFA reaction, three principal oligomeric components were revealed by the 220 nm scan (retention times = 16.46, 19.44, and 39.36 min) and that they furthermore did not contribute to visual color was supported

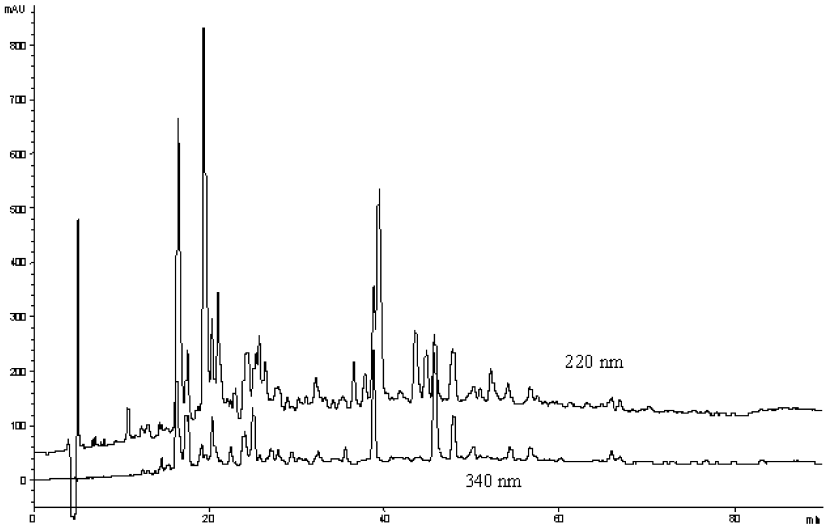


Figure 1. HPLC analyses of hydrolyzed **oligo 1a** catalyzed by TFA. The upper trace was obtained using 220 nm and the lower with 340 nm UV detection.

by the lack of corresponding peaks in the 340 nm scan. The 220 nm scan of the CSA reaction, on the other hand in Fig. 2 and overlayed with the TFA reaction in Fig. 3, revealed that only two of the three principal reaction products were formed (retention times = 16.46 and 39.36 min) and that the concentration of the 16.46 min component was substantially decreased. The 340 nm scan of the CSA material also indicated that a greater

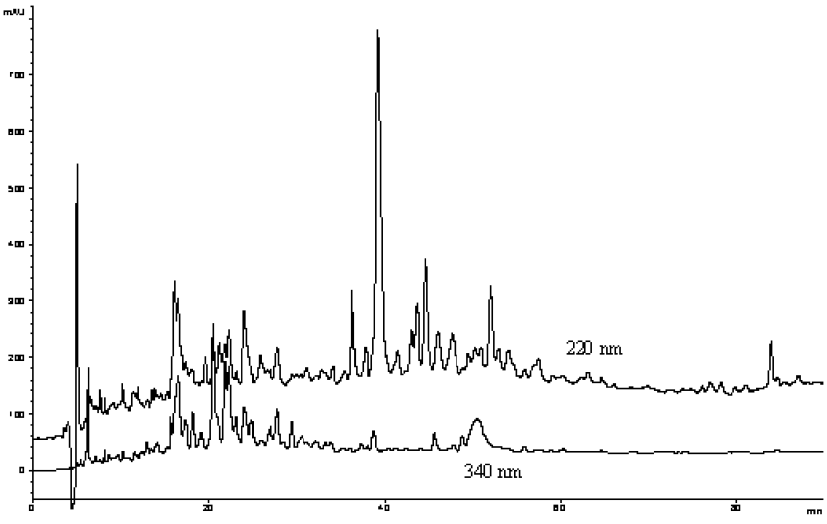


Figure 2. HPLC analyses of **oligo 1a** catalyzed by CSA. The upper trace was obtained using 220 nm and the lower 340 nm UV detection.

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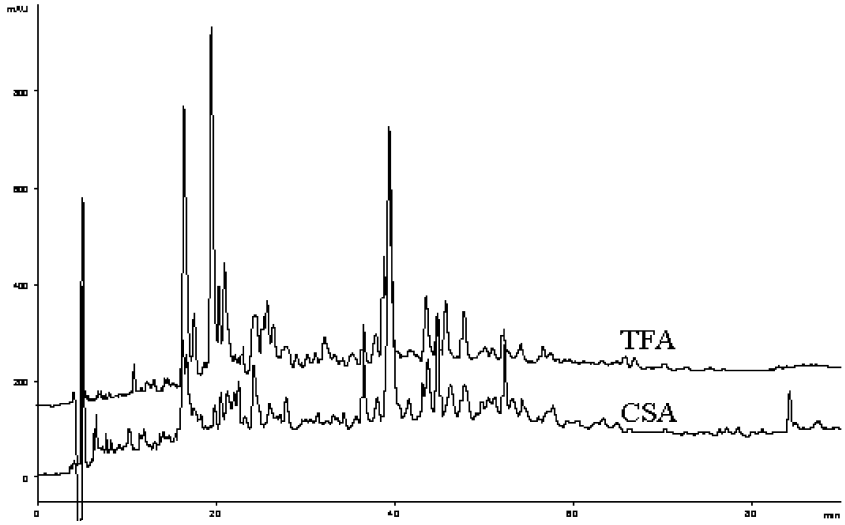

Figure 3. HPLC analyses using 220 nm detection of the TFA (upper) and CSA (lower) catalyzed reactions.

percentage of especially lower retention time components were likely the sources of the color, and their absence in the 220 nm scan indicated that while contributing substantially to visual color they were present only in relatively low concentrations.

HPLC traces shown of **oligo 1b** in Fig. 4 exhibit a better resolved and somewhat less complicated 220 nm trace than with **oligo 1a** and, to support the lack of color in the sample, a flat trace at 340 nm. As is evident from the information contained in Fig. 4, the number of oligomeric products with **oligo 1b** was not substantially decreased and no predominating products were formed as with **oligo 1a**; the first peak in the chromatogram was hydrolyzed **1b**.

Mass Spectral Analyses

As a means of qualitatively assessing the hydrolyzed mixtures of oligomers, electrospray, MALDI, and FAB mass spectrometry were each examined. Electrospray was the most useful from both qualitative and quantitative perspectives. The mass spectrum in Fig. 5 uggested that the oligomer mixture for hydrolyzed TFA-catalyzed **oligo 1a** consisted essentially of tetramers to octamers, with tetramers, pentamers, and hexamers (in order of decreasing amounts) predominating. The following peaks were observed (listed with their possible assignments and relative intensities compared to the base peak): $m/z = 629$ (tetramer $+ 4H_2O + H^+$, base peak); 651 (tetramer $+ 4H_2O + Na^+$, 60%); 768 (pentamer $+ 4H_2O + H^+$, 82%); 786 (pentamer $+ 5H_2O + H^+$, 79%); 808 (pentamer $+ 5H_2O + Na^+$, 56%); 925 (hexamer $+ 5H_2O + H^+$, 50%); 943 (hexamer $+ 6H_2O + H^+$, 50%); 1104 (heptamer $+ 6H_2O + Na^+$, 21%); and 1239 (octamer $+ 7H_2O + H^+$, 17%).

The MALDI spectrum was not as informative because of complications with extraneous peaks associated with the matrix material, to include the largest peak at $m/z = 646$. Common peaks with the positive ion electrospray analysis did exist, however,

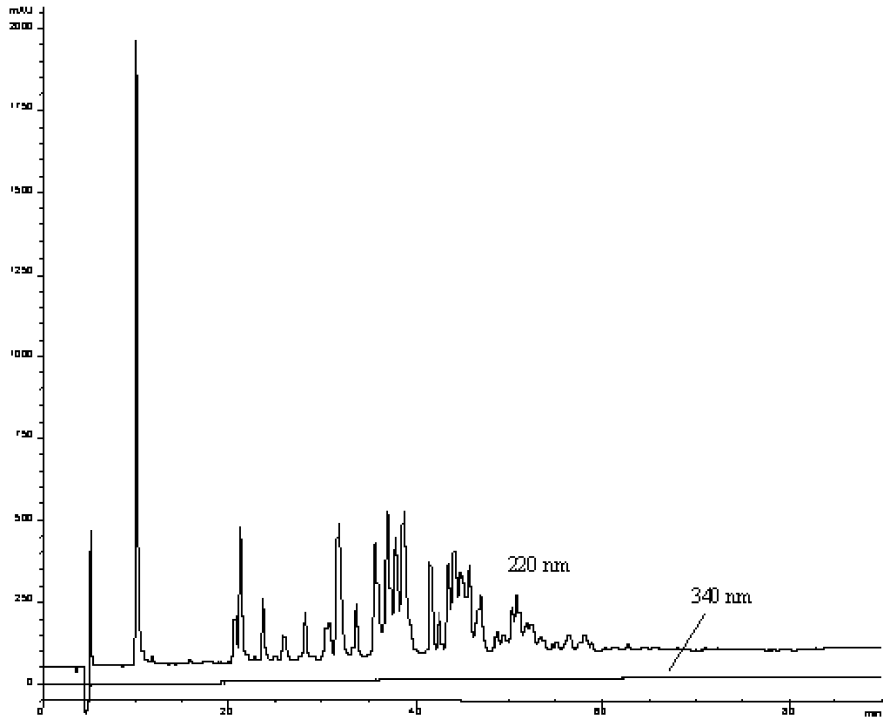

Figure 4. HPLC analyses of hydrolyzed **oligo 1b**. The upper trace was obtained using 220 nm and the lower 340 nm detection.

and included at least one peak which could be assigned to each oligomeric species from tetramer to octamer, i.e., $m/z = 629$, 768, 808, 925, 1104, and 1239.

The positive and negative ion FAB mass spectra provided supporting evidence for the fully hydrolyzed tetramer ($m/z = 629^+$ and 627^-); pentamer + $4H_2O$ (768^+ and 766^-); fully hydrolyzed pentamer (784^-); hexamer + $5H_2O$ (925^+); fully hydrolyzed hexamer (941^-); heptamer + $6H_2O$ (1082^+ and 1080^-); octamer + $6H_2O$ (1221^+); octamer + $7H_2O$ (1239^+); nonamer + $8H_2O$ (1396^+); decamer + $9H_2O$ (1553^+); and fully hydrolyzed decamer (1571^+ and 1569^-).

Concerning the analysis of **oligo 1b**, the electrospray mass spectrum showed a distribution of trimers through hexamers. The following peaks were observed (listed with assignments and relative intensities compared to base peak): trimer + $2H_2O$, 496 (H^+, 41%), 518 (Na^+, 31%); trimer + $3H_2O$, 514 (H^+, 24%), 536 (Na^+, 97%); tetramer + $2H_2O$, 649 (H^+, 27%); tetramer + $3H_2O$, 667 (H^+, 37%), 689 (Na^+, 29%); tetramer + $4H_2O$, 685 (H^+, 29%), 707 (Na^+, 66%); pentamer + $3H_2O$, 820 (H^+, 40%), 842 (Na^+, 41%); pentamer + $4H_2O$, 838 (H^+, 67%), 860 (Na^+, 71%), 876 (K^+, 21%); pentamer + $5H_2O$, 856 (H^+, 43%), 871 (Na^+, 100%), 894 (K^+, 32%); hexamer + $3H_2O$, 973 (H^+, 21%); hexamer + $4H_2O$, 991 (H^+, 27%), 1013 (Na^+, 28%); hexamer + $5H_2O$, 1009 (H^+, 31%), 1031 (Na^+, 48%); and hexamer + $6H_2O$, 1027 (H^+, 25%), 1049 (Na^+, 62%), 1065 (K^+, 26%).

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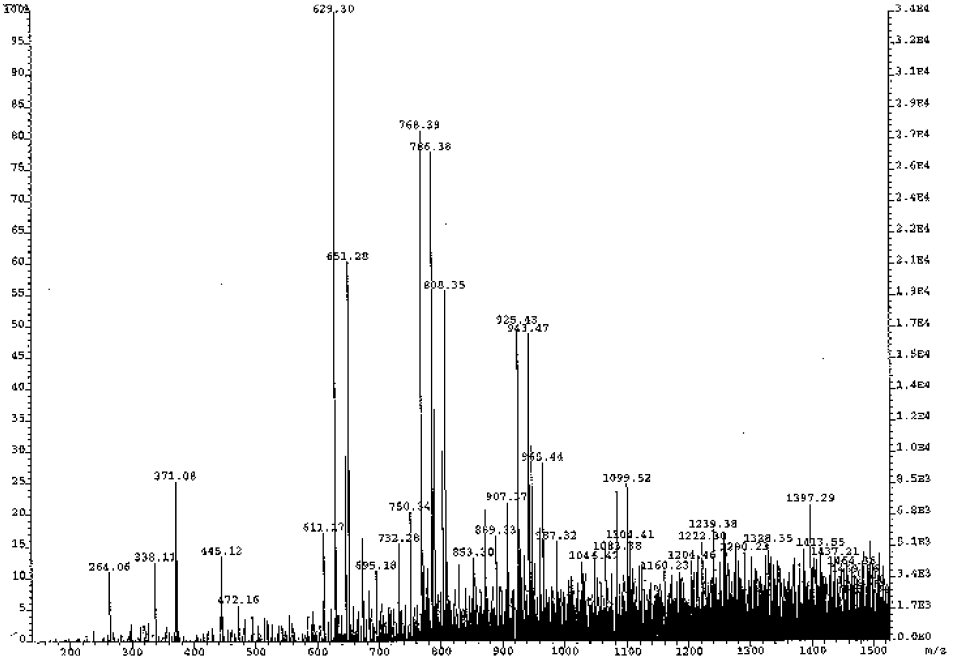

Figure 5. Positive ion electrospray mass spectrum of hydrolyzed **oligo 1a** (TFA catalyzed).

The LC–MS results using electrospray MS detection for hydrolyzed **oligo 1a** prepared using TFA are given in Table 2 (HPLC—Fig. 1), and the corresponding results on **oligo 1b** are given in Table 3 (HPLC—Fig. 4).

It was apparent from the mass spectra that essentially every oligomeric component was present in which not all (usually only one, sometimes two) of the oxazolone groups had not been hydrolyzed, e.g., trimer + $2H_2O$, tetramer + $3H_2O$, pentamer + $4H_2O$, hexamer + $5H_2O$, heptamer + $6H_2O$, and octamer + $7H_2O$, etc., either due to incomplete hydrolysis or possibly that one or more of the oxazolone groups might be chemically different and more resistant. While this possibly incomplete reaction served a useful purpose to some extent in providing multiple m/z markers for a given oligomer, the complexity of the mixture as shown by the HPLC traces of Figs. 1–4 was substantial.

In order to reduce the number of components in the mixture and to probe the question concerning the possible difference of some of the oxazolone units present in the oligomers, the hydrolysis was repeated employing conditions of slightly increased severity—reaction being conducted at 50°C instead of 22°C. This condition did not result in any substantial improvement in the complexity or change in the product mixture.

It was then decided to examine a primary amine as a derivatizing reagent, and benzylamine was chosen because the ^{1}H-NMR spectra of the resultant *N*-benzyl amide derivatives would result in uncomplicated singlet resonances for the benzylic hydrogens and the aromatic ring would provide a chromophore that would facilitate UV detection in the HPLC. The result was the obtention of a light yellow solid amidoamide product upon reaction with **oligo 1a** which retained a C=O absorption at 1825 cm^{-1} that was more

Table 2. LC–MS analysis of hydrolyzed **oligo 1a**.

			Molecular ion identification peaks present						
Peak	VE (min)	MS assignment	M_w	M + H	M + Na	M + K	M + H − H_2O	M + H − 2H_2O	M + H − 3H_2O
1	10.78	Trimer + 3H_2O	471	x					
2	16.46	Tetramer + 4H_2O	628	x	x	x			
3	17.51	Tetramer + 4H_2O	628	x					
4	19.44	Tetramer + 4H_2O	628	x	x	x			
5	19.44	Tetramer + 3H_2O	610				x		
6	20.38	Pentamer + 5H_2O	785	x					
7	20.99	Pentamer + 5H_2O	785	x	x				
8	25.35	Pentamer + 5H_2O	785	x					
9	25.76	Pentamer + 4H_2O	767				x		
10	26.39	Pentamer + 2H_2O	731						x
11	37.85	Hexamer + 5H_2O	924				x		
12	38.80	Pentamer + 3H_2O	749					x	
13	39.36	Pentamer + 4H_2O	767				x		
14	43.56	Hexamer + 5H_2O	924				x		
15	44.73	Hexamer + 5H_2O	924				x		
16	52.19	Hexamer + 5H_2O	924				x		

Table 3. LC–MS analysis of hydrolyzed **oligo 1b**.

			Molecular ion identification peaks present				
Peak	VE (min)	MS assignment	M_w	M + H	M + Na	M + H − H_2O	M + H − 2H_2O
1	10.10	Monomer + H_2O	171	x		x	x
2	20.73	Trimer + 3H_2O	513	x		x	
3	21.28	Trimer + 3H_2O	513	x		x	x
4	23.67	Trimer + 3H_2O	513	x	x	x	x
5	25.90	Trimer + 3H_2O	513	x	x	x	
6	28.14	Tetramer + 4H_2O	684	x	x	x	x
7	30.52	Tetramer + 4H_2O	684	x	x	x	
8	30.83	Tetramer + 4H_2O	684	x	x	x	
9	31.81	Tetramer + 4H_2O	684	x	x	x	
10	33.73	Tetramer + 4H_2O	684	x		x	x
11	35.86	Pentamer + 5H_2O	855	x	x	x	x
12	36.93	Pentamer + 5H_2O	855	x		x	
13	37.07	Pentamer + 5H_2O	855	x	x	x	x
14	37.85	Pentamer + 5H_2O	855	x	x	x	x
15	38.68	Pentamer + 5H_2O	855	x	x	x	x
16	39.40	Pentamer + 5H_2O	855	x	x	x	x
17	41.59	Hexamer + 6H_2O	1,026	x	x	x	x
18	42.62	Hexamer + 6H_2O	1,026	x	x	x	x
19	43.64	Pentamer + 5H_2O	855	x	x	x	x
20	44.28	Hexamer + 6H_2O	1,026	x	x	x	x
21	44.90	Hexamer + 6H_2O	1,026	x	x	x	x
22	45.21	Hexamer + 6H_2O	1,026	x	x	x	x
23	45.84	Hexamer + 6H_2O	1,026	x	x	x	x
24	50.42	Heptamer + 7H_2O	1,197			x	
25	50.99	Heptamer + 7H_2O	1,197			x	x

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obvious than in the hydrolyzed samples because an amide C═O stretch absorption occurs at lower frequency and is better resolved from the oxazolone C═O than a carboxylic acid C═O absorption. This provided additional support that residual absorptions in this region did not result from incomplete reaction of the oxazolone groups but were due to a nucleophilically less reactive "oxazolone" moiety. This proposal was also supported by 13–20% of the oxazolone groups not responding to the *n*-butylamine reactant (See Experimental). HPLC analysis, however, still indicated a very complex (ca. 100 peaks) mixture of products and one that contained significant amounts of residual benzylamine and longer retention time products that seemed to adsorb onto and foul the column. Mass spectral analysis of the material was evidently hampered somewhat compared to the hydrolyzed derivatives due to increased molecular weight and/or changes in ionization efficiency for the *N*-benzylamide derivatives. The overall result was detection of tetramers through octamers and not the wider distribution of oligomers observed in the hydrolyzed samples.

Comparison of Oligomeric and Polymeric 2-Alkenyl-5(4H)-Oxazolone Products

Since oligomerization can be regarded as a special kind of polymerization in which the MW is very low, it seemed reasonable to compare the oligomeric materials with the corresponding high MW homopolymers made using solution free radical polymerization techniques.[1a] Because oligomerization occurred much more readily in terms of rate and degree of conversion with **1a** compared to **1b**, initial characterization efforts were primarily focused on **1a**.

Visually, the most obvious differences between **oligo 1a** and the high MW **poly 1a** were the intense reddish orange color and extremely low viscosity, e.g., about 1 cps of a 40% solids solution, of **oligo 1a**. **Poly 1a** was essentially colorless and exhibited a relatively high solution viscosity at room temperature, e.g., 1280 cps at 40.9% solids. Comparative UV spectroscopic evaluation of **oligo 1a** and **poly 1a** provided a basis for the reddish orange color of **oligo 1a**; significant absorptions in the near UV with $\lambda_{max} = 331$ nm (acetonitrile; $a = 2.52\ L\,g\,cm^{-1}$) were observed with **oligo 1a**, while **poly 1a** showed only modest absorption at 220 nm before cut off absorption by the solvent. The qualitatively more intense color of **oligo 1a** initiated using CSA was also confirmed by a UV spectrum that was very similar to that initiated using TFA in terms of λ_{max} and absorptivity but was substantially broader, extending almost to 500 nm. The absorption bands and corresponding color, of course, indicated formation of a new chromophore of some kind, although in relatively low concentration as determined by HPLC analysis and with the caveat that hydrolysis appeared to destroy color-contributing components. One other important observation regarding color was that the methyl group present in **1b** apparently prohibited formation of contributing chromophores because color and corresponding 340 nm absorptions were not observed in samples of hydrolyzed **oligo 1b** (Fig. 4).

The very low viscosity of relatively high solids solutions of **oligo 1a** was certainly suggestive of low MW and possibly highly branched structures that do not associate intermolecularly very well. Gas chromatographic analyses conducted using column temperatures up to 250°C showed essentially no peaks other than solvent and residual **1**. This indicated that dimers, perhaps trimers, and other products resulting from non-propagating organic transformations such as Diels-Alder reactions were probably not

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present in the oligomeric mixtures to any significant extent since such products would be expected to be sufficiently volatile to be detected employing the GC conditions.

Figure 6 displays the IR spectra of two materials that are remarkably similar and very supportive of analogous fundamental structures for **oligo 1a** and **poly 1a**, i.e., that oxazolone rings are predominantly intact in both species—an observation also confirmed by chemical titration. The C═O and C═N absorptions of both are intense and energetically virtually identical (at 1825 and 1667 cm^{-1}, respectively); even the fingerprint regions are quite similar with only signal intensity variations being observed. The IR spectrum for **oligo 1a** also shows evidence of partial hydrolysis (probably occurring during handling and sample preparation) due to absorption bands at 1736 (carboxylic acid C═O) and 1527 (amide II band) cm^{-1}.

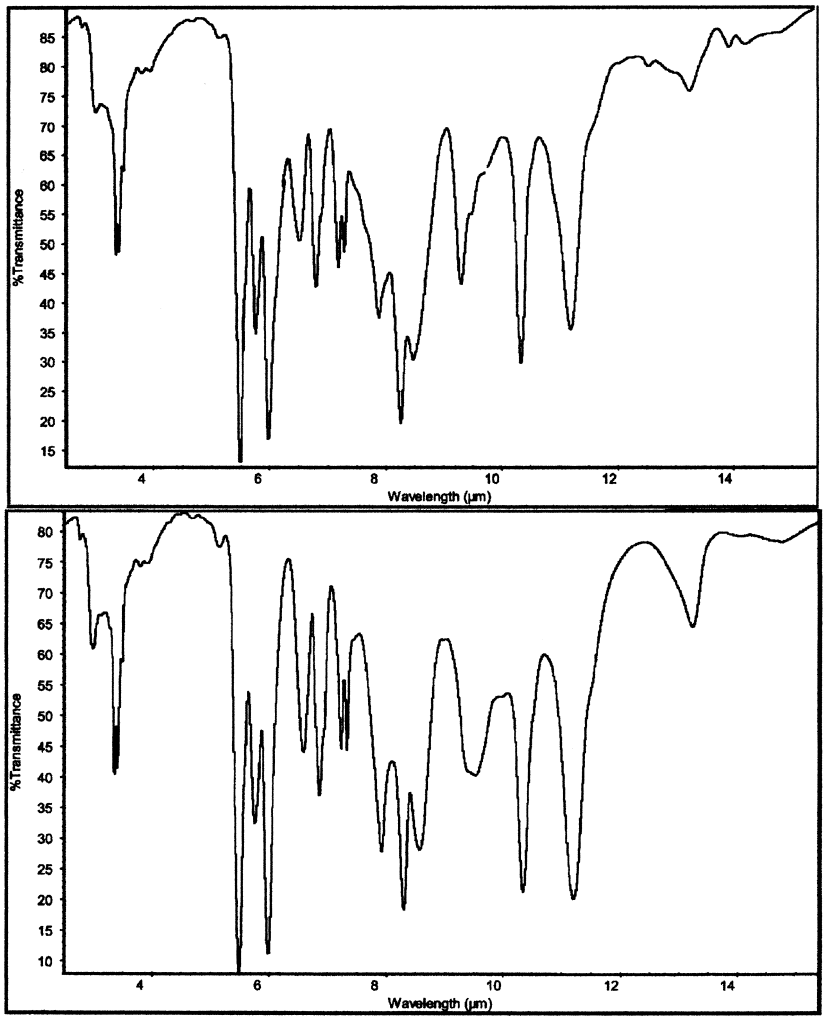

Figure 6. IR spectra of **oligo 1a** (upper) and **poly 1a** (lower).

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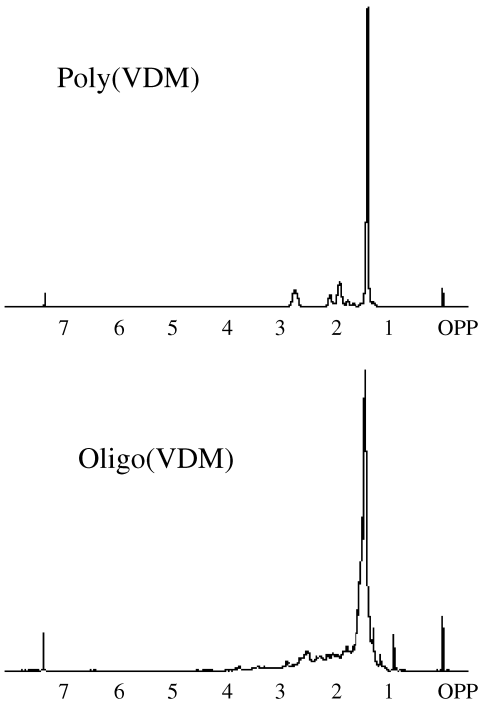
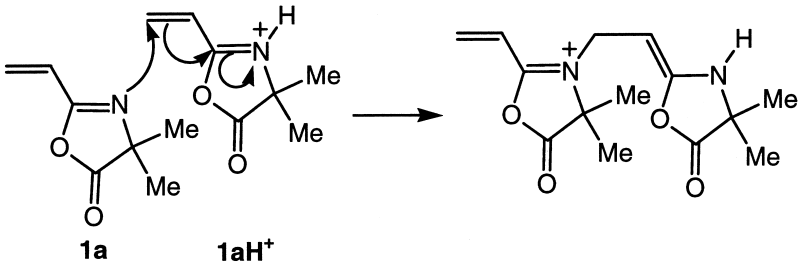


Figure 7. ^{1}H-NMR spectra of **poly 1a** (upper) and **oligo 1a** (lower).

The ^{1}H-NMR spectra of Fig. 7, on the other hand, show distinctive differences supportive of other structural elements present in **oligo 1a**. **Oligo 1a** is characterized by having several major resonances between 1.5 and 3.0 ppm and minor resonances from 3.0 to 4.2 ppm. Significantly absent in the spectrum for **oligo 1a** are any substantial olefinic CH resonances of the kind that were observed by Tomalia et al., with oxazoline-based products.[9] The minor downfield resonances from 3.0 to 4.2 ppm could be assigned to various N—CH_2 methylenes resulting from structures derived from Michael addition of **1a** to **1aH**$^{+}$ as shown below in Eq. (1).



(1)

Similar assignments were made by Saegusa et al.,[10] who curiously did not report any end group resonances despite the very low molecular weight ($\eta_{sp}/c = 0.03$) of the acid-catalyzed 2-vinyl-2-oxazoline products obtained.

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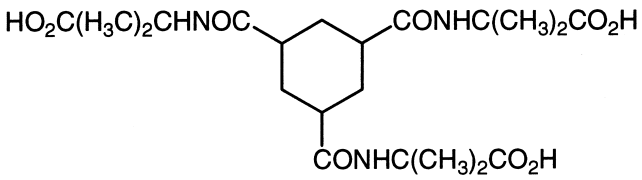
The ^{13}C-NMR spectra of the unresolved mixtures were unremarkable, except for additional downfield hetero-substituted sp^2 carbon resonances around 164 and 176 ppm, although the signal-to-noise levels did not permit rigorous exclusion of other structural elements present in low concentration.

Isolation and Characterization of Specific Oligomer Components

Compound **11a** was actually shown to be among the hydrolyzed **oligo 1a** products by HPLC comparison of an authentic sample with the oligomeric mixture; the component exhibited a retention time of 10.78 min (Fig. 1).



11a

Preparative HPLC separation of the components of the hydrolyzed, TFA-catalyzed **oligo 1a** sample of Fig. 1 was conducted, and three fractions were collected corresponding to the three major components with retention times 16.46, 19.44, and 39.36 min.

From the LC–MS analysis (Table 2), the fraction with retention time 16.46 min was known to be a completely hydrolyzed tetramer. The compound was determined to have the structure shown along with its ^{13}C-NMR spectrum in Fig. 8; DEPT and 2D NMR techniques including COSY, HMQC, and HMBC were used to confirm assignment (Table 4) of the observed resonances for both ^{1}H- and ^{13}C-NMR spectra.

The second and largest peak in the HPLC was also a completely hydrolyzed tetramer with retention time 19.44 min. A fraction was separated but, unfortunately, was apparently a mixture of components, and no structures could be assigned.

The third largest component in the chromatogram was a pentamer in which only four oxazolone groups were hydrolyzed. The component with retention time 39.36 min was separated, and the structure shown in Fig. 9 was indicated based on NMR assignments (Table 5) using DEPT, COSY, TOCSY, gHSQC, and gHMBC NMR experiments. TOCSY experiments at higher fields (600 MHz) were important for resolution to identify three spin systems in the core of the molecule (4–6, 8–11, and 16–17; see numbering in Fig. 9). These three spin systems had numerous long range ^{1}H–^{13}C correlations in gHMBC experiments to two quaternary carbons that were only reasonably linked together via a bicyclic structure. Furthermore, this bicyclic structure was the only one consistent with DEPT analysis for the number of quaternary, methine, and methylene carbons. A distinctive feature of this molecule was the 99.3 ppm resonance of carbon 2 with a ketal-like structure.

Only one component of **oligo 1b** could be isolated in sufficient purity for structure determination. That component was a fully hydrolyzed trimer with retention time 21.28 min. The structure indicated in Fig. 10 was confirmed (Table 6) by NMR spectra (DEPT, COSY, TOCSY, gHSQC, and gHMBC experiments). Key aspects of the NMR spectrum were amide-type diastereotopic resonances at 3.7/3.1 ppm, indicative of Michael

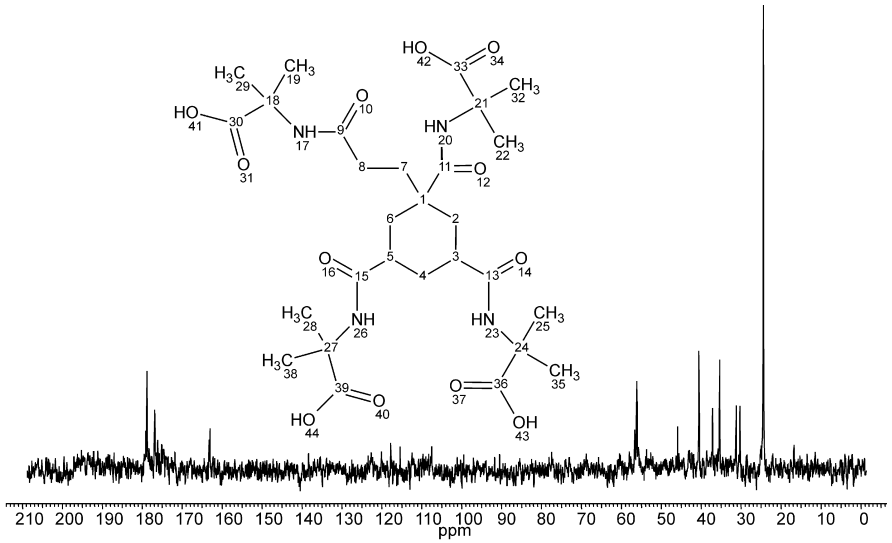


Figure 8. ^{13}C-NMR spectrum in D_2O of fully hydrolyzed tetramer with retention time of 16.46 min.

Table 4. ^{13}C and ^{1}H NMR assignments for the fully hydrolyzed tetramer.

Position	^{1}H shift	^{13}C shift
1	NA	45.8
2, 6	2.07/1.94	35.3
3, 5	2.29	40.4
4	1.77/1.30	30.2
7	1.69	37.0
8	2.07	31.1
9	NA	174.9
11	NA	176.0
13, 15	NA	176.7
18	NA	56.4
21, 24, 27	NA	55.9
19, 29	1.37	24.2
22, 32, 25, 35, 28, 38	1.3	24.2
30	NA	178.8
33, 36, 39	NA	178.6

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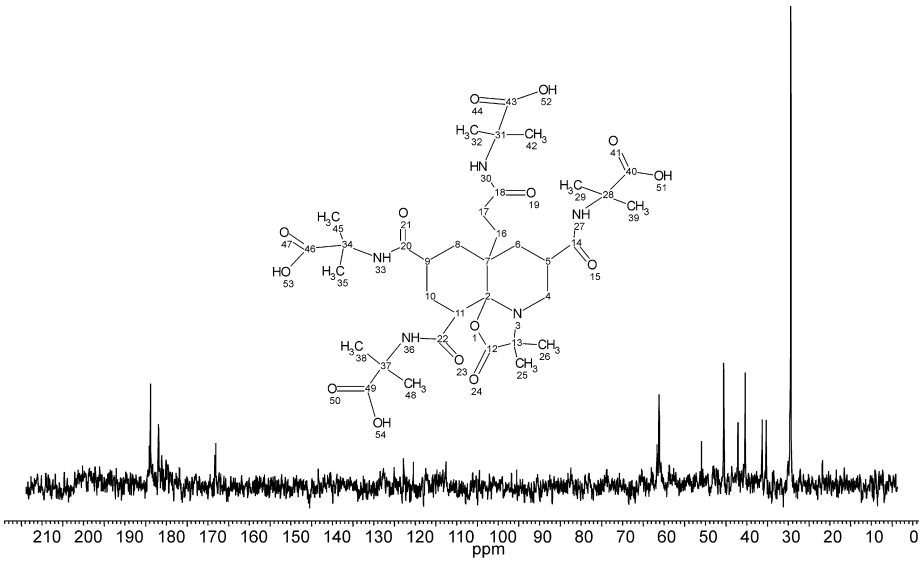

Figure 9. ^{13}C-NMR spectrum in D_2O of pentamer with retention time 39.36 min wherein four of the oxazolones were hydrolyzed (multiplets at 120 and 165 ppm are residual trifluoroacetic acid ($^{1}J_{CF}$ and $^{2}J_{CF}$ splittings).

Table 5. ^{13}C and ^{1}H NMR assignments for the partially hydrolyzed pentamer of **oligo 1a**.

Position	^{1}H shift	^{13}C shift
2	NA	99.3
4	3.24/2.97	42.5
5	2.55	40.5
6	1.95/1/57	33.0
7	NA	41.9
8	1.60	38.5
9	2.55	40.9
10	1.88/1.83	32.1
11	3.30	47.4
12	NA	183.4
13	NA	61.9
14	NA	177.7
16	1.87/1.49	31.3
17	2.12/2.05	32.2
18	NA	178.3
20	NA	179.1
22	NA	175.7
25, 26	1.33/1.12	28.3/27.4
28, 31, 34, 36	NA	58.6–58.8
29, 32, 35, 37, 39, 42, 45, 48	NA	26.8–27.0
40, 43, 46, 49	NA	180.8–181.2

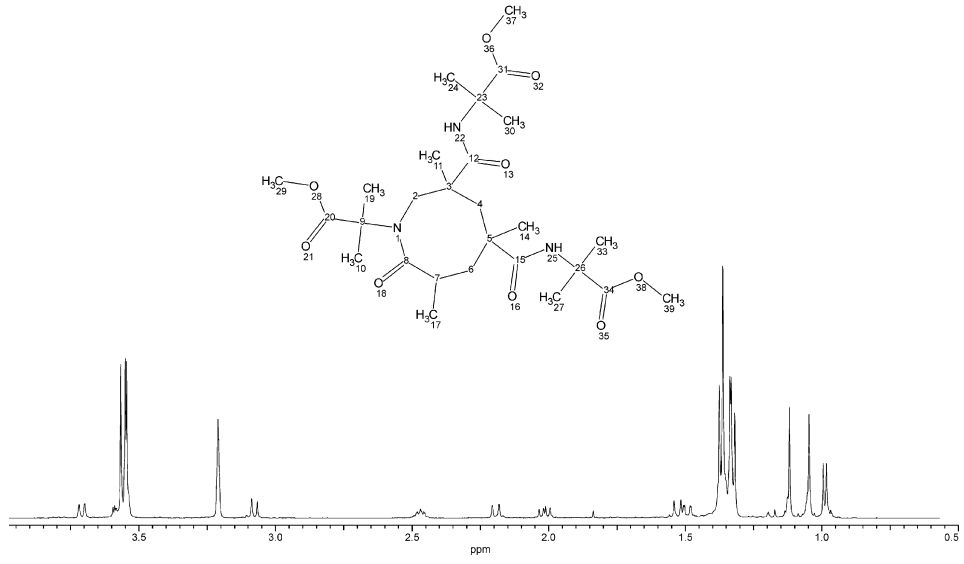

Figure 10. ^{1}H-NMR spectrum of the fully methanolyzed trimer of **oligo 1b** in D_2O.

Table 6. ^{13}C and ^{1}H NMR assignments for the fully hydrolyzed trimer of **oligo 1b**.

Position	^{1}H shift	^{13}C shift
2	3.70, 3.07	49
3	NA	42
4	2.20, 1.53	42
5	NA	41
6	2.02	42
7	2.46	36
8	NA	178
9	NA	62
10, 19	1.45	23
11	1.25	24
12	NA	176
14	1.15	26
15	NA	176
17	1.10	20
20, 31, 34	NA	175.5
23	NA	55
24, 30	1.45	24
26	NA	55
27, 33	1.45	24
29, 37, 39	3.7	51

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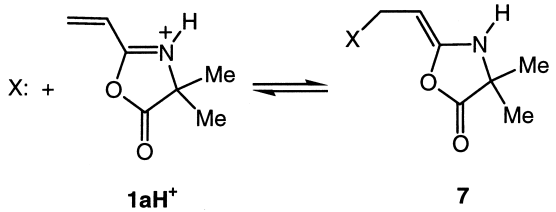
addition. The consequence of Michael addition by one monomer was production of a methine/methyl-methylene spin system (6, 7, and 17; see Fig. 10). A clear marker for this spin system was the double methyl at 1.0 ppm.

Effect of Reaction Variables on Oligomer Composition

In order to understand the effects of key oligomerization reaction variables on the distribution of oligomers obtained, experiments were conducted examining initiating acid concentration ([TFA] = 5 and 10 mol%), oligomerization time (2, 9, and 24 h), and concentration of **1a** in ethyl acetate solvent (**1a** weight fractions of 0.25, 0.30, 0.40, 0.48, and 0.55). Electrospray mass spectra of precipitated, hydrolyzed samples were examined to detect any systematic variation in the distributions trimer, tetramer, pentamer, and hexamer products. The general conclusion from these studies was that the system was fairly unresponsive to changes in these variables. Only the effect of concentration of **1a** indicated some possible trend in distribution. At [TFA] = 5 mol% and 24 h reaction time, low **1a** concentration (weight fraction = 0.25) provided more pentamer compared to tetramer (50% vs. 39%), whereas with a more concentrated system (weight fraction = 0.55) the values were essentially reversed (33% vs. 57%). This result may indicate that tetrameric products predominate under conditions favoring equilibrium control. That a higher homolog would predominate under kinetically controlled conditions was surprising.

Discussion of the Reaction Mechanism

Given that a catalytic amount of acid promoted high conversions of **1** to oligomers and that fragments of initiating acids were not found in any products' structures, it was evident that turnover of the acid was occurring during the oligomerization. The oligomerization was apparently specific acid catalyzed, as evidenced (from Table 1) by the observations that only acids were effective that were sufficiently strong to actually protonate the oxazolone nitrogen, that oligomerization rates were accelerated with increasing acid concentrations, and that rates increased in more polar solvents that could better solvate an oxazolinium salt conjugate acid product. Protonation alone, however, was insufficient for initiation, as evidenced by formation of only the oxazolinium salt and no oligomerization when **1a** was added to excess chlorosulfonic acid. Protonation amounted to activation of the system, and either a non-protonated oxazolone or a nucleophilic gegenion [collectively referred to as "X:" in Eq. (2)] were required for Michael addition to the oxazolinium salt forming a ketene-aminal product **7** which was the actual initiator for oligomerization.

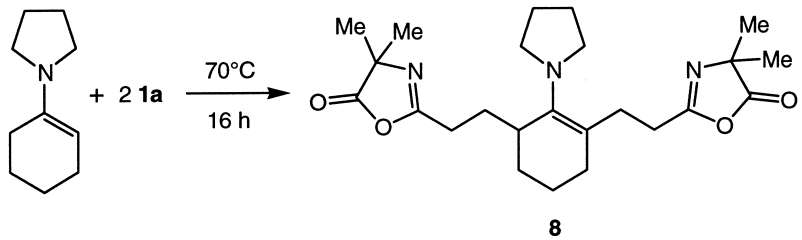


(2)

The more sluggish tendency of **1b** to undergo oligomerization, requiring increased monomer concentrations, higher reaction temperatures, and being promoted only by employing greater concentrations of very strong Brønsted acids such as ethanesulfonic acid, also supported the Michael addition proposal. It had been shown in earlier work[17] examining the acid-catalyzed reactions of **1** and alcohols just how dominating the inductive effect of α-methyl substitution in **1b** could be. In that study irreversible ring-opening addition of the alcohol was observed exclusively with **1b**, while Michael addition was a major pathway with **1a**. In the present work, ring opening does not occur with the weak nucleophiles available, so oligomerization proceeds at a very slow rate by interception of a highly reversible Michael adduct of **1b–1bH**$^+$.

As a means of understanding whether Michael addition was a sufficient condition itself to promote the oligomerization, propensities of gegenions of the following acids to undergo Michael addition to **1a** were examined by NMR: acetic acid, TFA, and CSA. The latter two had been shown to be effective catalysts, while acetic acid was not. Especially with the stronger acids which promoted oligomerization, dropwise addition of **1a** to at least a 30 fold excess of the particular acid created a condition in which unprotonated **1a** would not be present to compete with Michael addition by the anion. The results were that despite acetic acid's weak acidity and inability to protonate **1a** Michael addition proceeded most effectively ($K_{eq} = 0.25$). Trifluoroacetic acid was less effective ($K_{eq} = 0.08$) and CSA formed only **1aH**$^+$ and no Michael addition of chlorosulfonate took place. This latter result indicated that in the normal oligomerization reaction with CSA only **1a** was adding to **1aH**$^+$ to initiate reaction. It also further confirmed the proposal that the initiation process with **1bH**$^+$ involved only Michael addition of **1b**, since very strong acids were required as catalysts and their corresponding conjugate base anions were very poor nucleophiles. Therefore, since acetic acid underwent relatively efficient Michael addition to **1a** but did not catalyze oligomerization, this series of experiments suggested that propensity for Michael addition alone was an insufficient condition to promote oligomerization. Although the effect of strong acid on the enolization of the Michael adduct was unknown and could be substantial, one rationalization of this result was the restatement of a criterion offered earlier—that a Michael adduct must also be formed in the presence of protonated **1** for oligomerization to occur.

That a ketene-aminal intermediate could be involved and was capable of Michael addition seemed very plausible based on earlier studies examining reactions of related enamine nucleophiles with **1a.**[18] 1-Pyrrolidono-1-cyclohexene, for example, cleanly reacted with two equivalents of **1a** to form bisadduct **8** [Eq. (3)].



8 (3)

One problem, however, with continued propagation of a ketene-aminal would be competitive tautomerization of this *enolic* form to a seemingly unreactive *keto* form as

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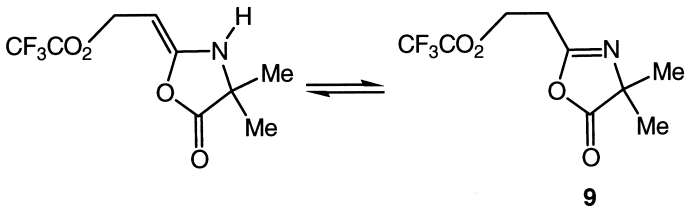
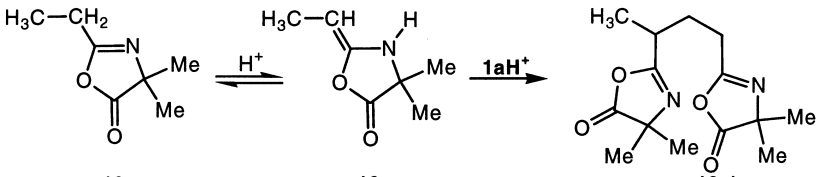
illustrated in the formation *keto* tautomer **9** in Eq. (4), and tautomerization would be expected to be much faster than oligomerization especially at elevated temperatures.



9 (4)

Enolic species such as vinyl alcohol have been shown to participate as comonomers but only under special circumstances.[19] When monomeric vinyl alcohol was generated instantaneously in high yield from appropriate precursors and allowed to interact with appropriate comonomers under suitable conditions such that copolymerization was faster than tautomerization, vinyl alcohol could be effectively incorporated into a copolymer. An experiment more analogous to the present oxazolone system in which corresponding utilization of equilibrium concentrations of vinyl alcohol from acetaldehyde was not examined because of the very small equilibrium concentration (ca. 10^{-7} M) of vinyl alcohol.

To explore the potential involvement of an equilibrium concentration of *enol* tautomer derived from the *keto* tautomer, a 1 : 1 mixture of 4,4-dimethyl-2-ethyl-5(4H)-oxazolone (**10**) and **1a** was reacted with TFA in $CDCl_3$; a separate control experiment examining **10** alone with TFA produced no reaction other than protonation. If "enolic" **10a** was to form and participate in a co-oligomerization with **1a**, the unit should function as a chain initiating species [Eq. (5)].



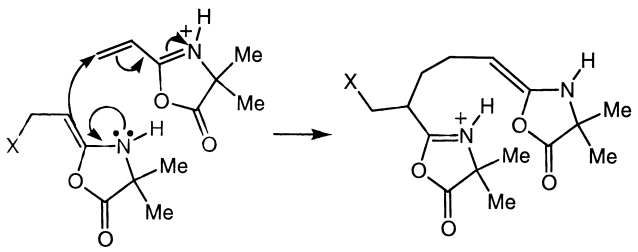
10 **10a** **10-1a** (5)

In selecting experimental conditions to examine this issue, it was desired that a **10–1a** dimer be produced in as high yield as possible. Such an adduct would in principle be relatively easy to separate because its molecular weight would be low and its volatility high. Identification in the mixture would also be greatly facilitated by observing a methine-split methyl doublet in the ^{1}H-NMR spectrum as a signature for the initiating **10a** unit. The co-oligomerization reaction was therefore conducted using a relatively high TFA concentration (110 mol% based on **10**) to hopefully maximize the concentration of **10a** and by adding an equimolar amount of **1a** to facilitate dimer formation. After 3 h at room temperature, GC analysis showed that **1a** had been completely depleted as well as 31% of **10**. Furthermore, a higher boiling product was indicated by GC. A doublet resonance at δ 1.35 ppm in the ^{1}H-NMR was observed that corresponded to the expected methine-split methyl resonance in the **10–1a** dimer unit from correlations employing TOCSY, HETCOR, and HMBC NMR techniques. The higher boiling product also provided a GC–MS that was consistent with the **10–1a** dimer. A molecular ion at $m/z = 280$ supported formation of the desired dimer structure, as well as a fragmentation

pattern consistent with the structure, i.e., loss of methyl (265) and oxazolone (168). This experiment therefore confirmed that "enolizable" oxazolone compounds could participate in the oligomerization reaction and constituted an important mechanistic element in understanding this novel oligomerization. This observation also confirmed that propagation could continue as long as $\mathbf{1H}^+$ and α hydrogens exist on 2-alkyl substituted oxazolones. In this respect, the oligomerization can be regarded as being a "living" system.

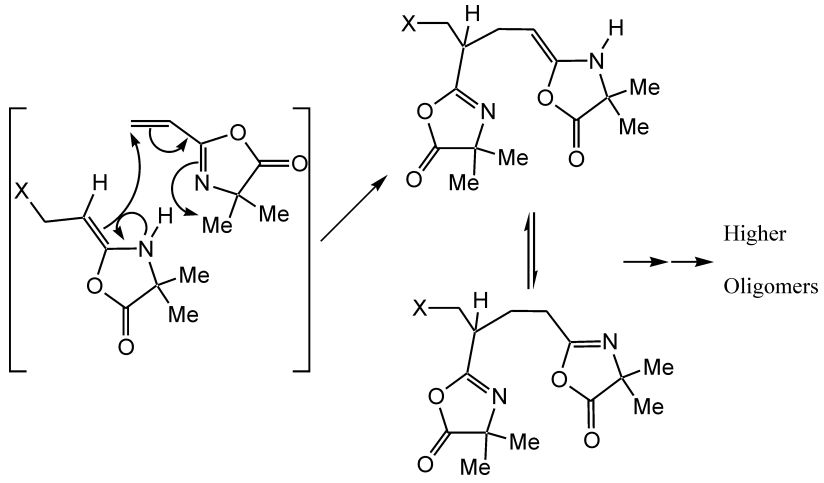
It is tempting to represent a transition state for propagation, shown in Sch. 1 below, as an eight membered ring assembly analogous to group transfer polymerization,[20] except that a proton is substituted for a silicon atom as the transferred moiety. This proposed scheme was not supported, however, by the acetic acid results in which Michael addition occurred but not oligomerization, again with the caveat that the effect of strong acid on increasing ketene-aminal enol concentration could be significant especially when the ring nitrogen can be protonated and these factors were not present in the acetic acid experiment.

A proposal more consistent with the results obtained thus far involves nucleophilic addition of a ketene-aminal to $\mathbf{1aH}^+$ [Eq. (6)] which is analogous to the mechanism proposed for the Me_3SiOTf initiated polymerization of 2-vinyl-2-oxazoline.[10]



(6)

By this route, the penultimate oxazolone unit in a propagating oligomer is required to lose a proton, preferably to monomer **1a**. At least from an inductive standpoint, a potential



Scheme 1.

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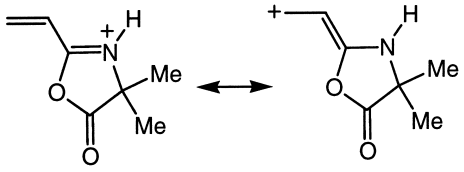
problem with this proton transfer to **1a** involves a perceived energetically "uphill" acid–base reaction. The basic strength of **1a** would be expected to be less than oligomerized oxazolones based on the greater electron withdrawing tendency of a 2-vinyl compared to a 2-alkyl group. This effect, however, is apparently more than compensated by the base strengthening delocalization of the positive charge capable with $\mathbf{1aH}^+$ [Eq. (7)].

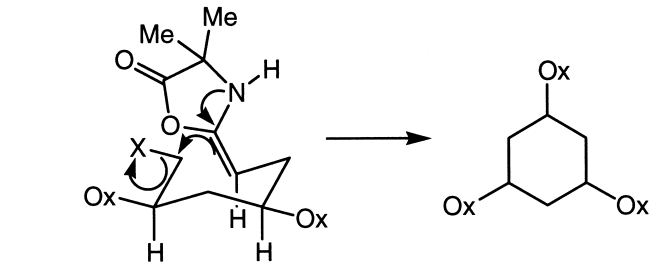


(7)

Two Michael addition products have been shown to be possible in these systems, one in which a relatively nucleophilic gegenion such as trifluoroacetate is involved and the other when monomer **1** itself adds to $\mathbf{1H}^+$.

Gegenion Addition

Based on detecting hydrolyzed trimer **11a** which was derived from tris(oxazolone) **11** among the products of the TFA-initiated oligomerization of **1a**, it was apparent that trifluoroacetate could be displaced in a substitution process by a carbon nucleophile as shown in Eq. (8). A driving force for this reaction, of course, is six-membered ring formation.



X = trifluoroacetate or N-alkylated **1**

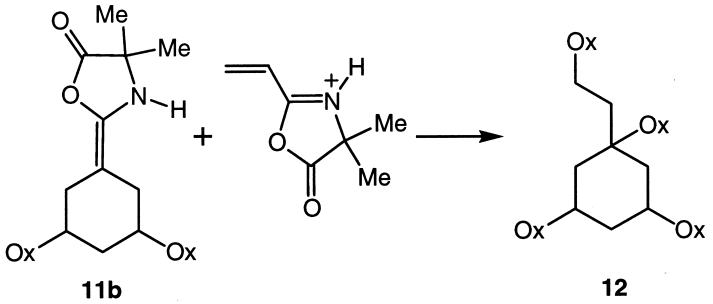
cis, cis

11

(8)

Another product in the same oligomerization reaction formed in much greater quantity was the tetramer **12**. This product presumably arose from displacement of a gegenion in the manner shown above because **12** contained no ring nitrogens attributable to an intermediate derived from Michael addition of **1a** to $\mathbf{1aH}^+$, although displacement of **1a** as a leaving group in the manner of trifluoroacetate could not be excluded. In fact, support for this proposed displacement of **1a** was obtained in the oligomerization using CSA. The very poorly nucleophilic chlorosulfonate gegenion of this very strong acid was shown not to engage in Michael additions (at least at the limit of detection by NMR), and yet the observed hydrolyzed tetramer 12 peak as a minor product in the HPLC (Fig. 3; retention time = 16.46 min) indicated that displacement of **1a** did occur in low yield.

To probe the question whether tetramer **12** resulted from cyclic trimer **11** or perhaps from cyclization of a linear tetrameric oligomer, an experiment was conducted in which authentic trimer **11** was independently synthesized. Since hydrolyzed trimer **11a** had already been identified among the hydrolyzed products albeit in very low concentration (Table 2, peak 1), the expectation was that if tris(oxazolone) **11** was not involved as a reaction intermediate its concentration would be increased, given its production during oligomerization plus the addition of **11** to the oligomerization reaction. When compound **11** was added to the solution before addition of the TFA initiator, the result was the concentration of trimer **11** actually decreased in the oligomeric mixture to only 6% of its initial concentration. This result indicated that enolate **11b** was a likely intermediate to tetramer **12** in the manner shown by Eq. (9) and that tris(oxazolone) **11** may be functioning as an intermediate to higher homologs and that its concentration remains relatively low and constant over the course of the reaction. Presumably, pentamers and hexamers would result from enolization of hydrogens in the 3- and 5-positions of tetramer **12**. The side chain oxazolone of the tetramer can also enolize and propagate to still higher oligomers, and the resultant "living" aspect and complexity of the product mixtures depicted by the HPLCs begin to be rationalized.



11b **12** (9)

Michael Addition by 1

This mode of reaction was clearly indicated by products identified that contained at least one nitrogen within a carbocyclic ring system. Obtention in the oligomerization of **1b** of the completely methanolyzed trimer **14** derived from **13** illustrated this point. With **1b** and the very strong acids required to effect oligomerization, only **1b–1bH**$^+$ addition is possible. A trimerization sequence shown in Sch. 2 culminates in ring closure by addition of a ketene-aminal intermediate to an *enone* system formed from initial Michael addition, rather than displacement of **1b**.

This type of ring closure involving an enone formed from initial Michael addition of an oxazolone was also observed with **1a**, as indicated by the structure of the pentamer **19** in which only four of the oxazolones had been hydrolyzed. This product also provided insight into the nature of the "oxazolones" that resisted hydrolysis and were seemingly unreactive to nucleophilic reagents. A mechanistic sequence in which a dimer **15** is capable of additional Michael addition is depicted in Sch. 3. Trimer **16** also contains an active carbon nucleophile that can add to **1aH**$^+$. In the oligomerization of **1b** in Sch. 2 above, trimer **13** was unreactive and isolable at this point primarily due to the lack of a good Michael acceptor in **1bH**$^+$. In the **1a** system, **1aH**$^+$ is a better acceptor and can

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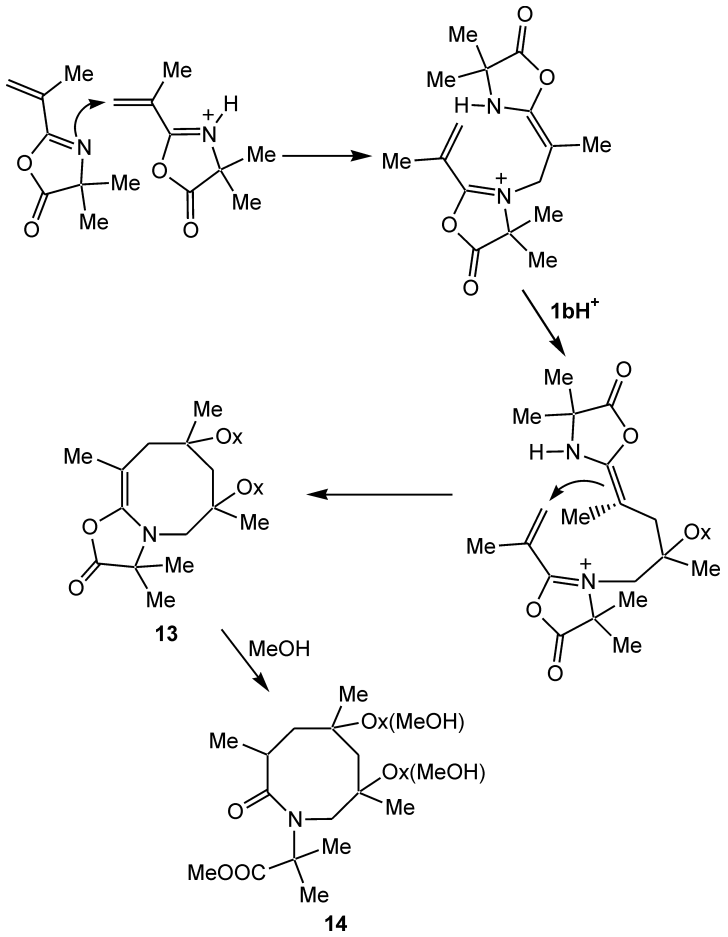
engage trimer **16** to form the oxazolinium tetramer **17**. This compound is probably stable and could be among the oligomeric products or it can enolize on one of its side chains and add $\mathbf{1aH}^+$ which is facilitated by ring closure and destruction of the positive charge to form the tricyclic structure **18**. Hydrolysis of the unique oxazolidinone ring is difficult because it is electronically and sterically deactivated. Also, a displaced alkoxide leaving group resulting from nucleophilic attack at the carbonyl cannot be stabilized by tautomerization to an amide structure as with oxazolones.

The Issue of Color Formation

The color formed during these oligomerizations and the nature of the chromophores involved remains unknown. The following observations can be made regarding color:

1. From HPLC analyses it was shown that color contributors were minor products.



Scheme 2.

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2. The color seemed to be associated with oxazolone rings in some way because it largely dissipated when the rings were opened by reaction with water or amines.
3. Protonation of oxazolones and perhaps other nitrogen bases was contributing because color was lightened when triethylamine was added to oligomer solutions.
4. Color seemed to be associated with facile Michael addition because color and 340 nm HPLC absorbing components were significantly increased with **1a** compared to **1b** which is much less effective as a Michael acceptor.

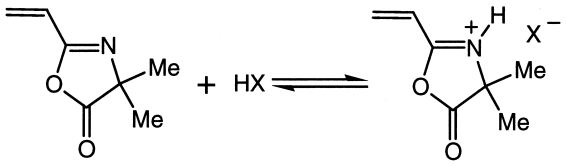
Early in the study of the mechanism of the oligomerization and as ketene-aminals (or ketene cyclic *N*,O-acetals) were indicated, it was conjectured that those species were responsible for the orange-red colors that formed during oligomerization. Isolation of an actual oligomeric product in trimer **12** that was directly derived from a stable ketene-aminal in the oligomerization of **1b** dispelled this conjecture because there was essentially no color associated with the oligomerization of **1b**. Also, ketene cyclic *N*,O-acetals have been examined by others,[23] and compounds and polymers were prepared containing this structural unit. Generally, little or no colored solutions or products were reported.

CONCLUSION

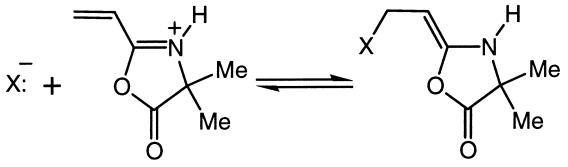
The acid-catalyzed oligomerization of 2-alkenyl-5(4H)-oxazolones is similar to controlled radical polymerizations[22] in at least two respects: (1) the kinetics involves first order disappearance of **1a** and; (2) the system is "living" as long as $\mathbf{1H}^+$ and species with hydrogens on carbons in position-2 of oxazolones are present. Predictabilitiy and control of molecular weight seem not to be present and may be a peculiarity of the oligomeric systems behaving more like small molecules that can undergo limited rearrangements than polymers.

The overall mechanism of this living nucleophilic oligomerization mechanism seems best characterized as paralleling the activated monomer mechanism proposed by Miyamoto et al.[10] for the Me_3SiOTf catalyzed polymerization of 2-alkenyl-2-oxazolines.

(A) Monomer Activation:



(B) Initiation:



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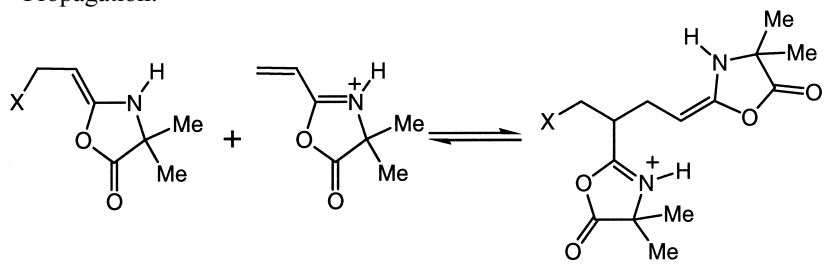
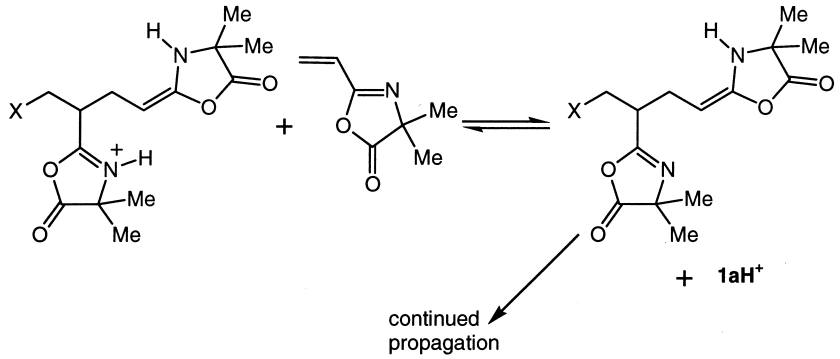
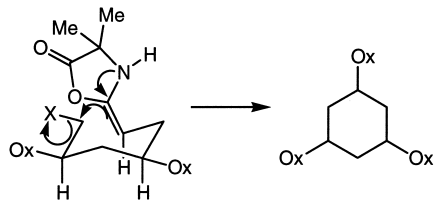
(C) Propagation:



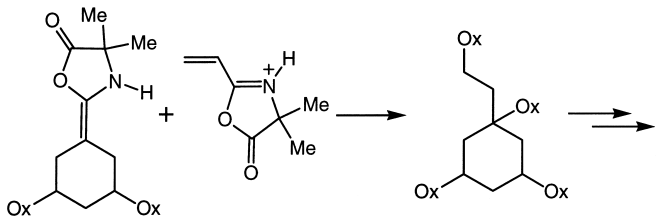
(D) Proton Transfer:



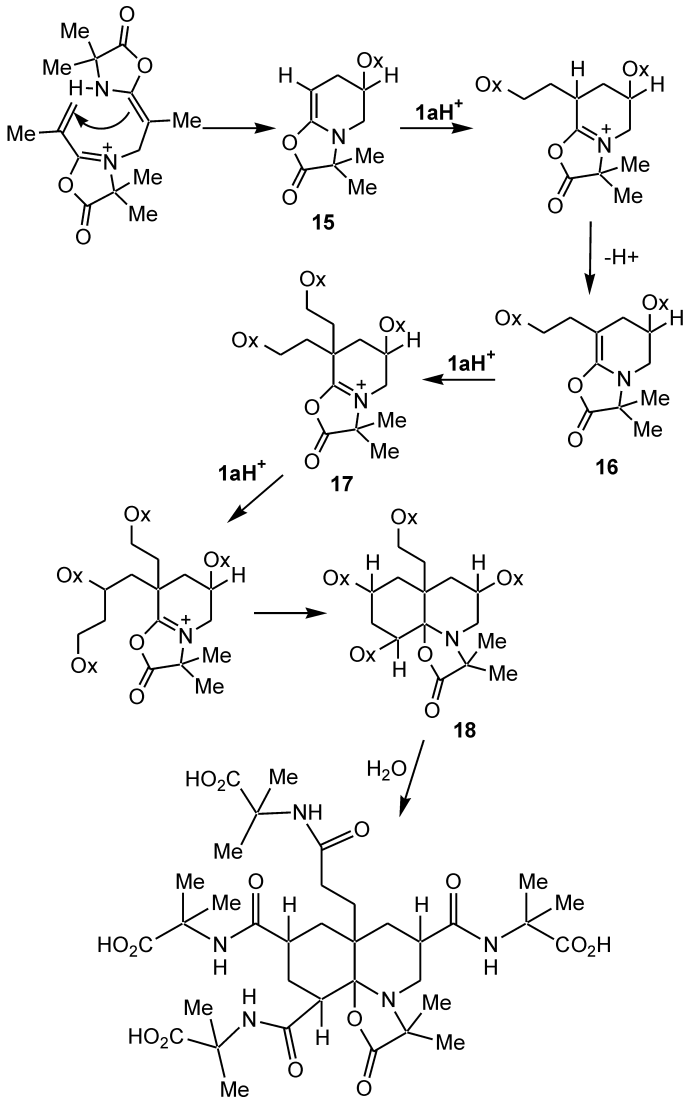
(E) Cyclization at the Trimer Stage:



(F) Continued Propagation via Enolization:



In the final analysis and explanation, differences in the chemistries of analogous systems are generally due either to electronic or steric factors (or both). In comparing responses of 2-alkenyl-2-oxazolines and 2-alkenyl-4,4-dimethyl-5(4H)-oxazolones to strong acids, differences are predicted to result primarily from steric factors since the electronically sensitive 5-position is not involved in any ring-opening reaction. To a large



Scheme 3.

degree, the observations of exclusive poly(*N*-alkylation) with 2-isopropenyl-2-oxazoline and predominant poly(*N*-alkylation) with 2-vinyl-2-oxazoline can be rationalized with the results of the present study. In the present study with gem-dimethyl groups at position-4, a substantially more sterically encumbered nitrogen nucleophile is present, and reaction occurs predominantly by the ketene-aminal intermediates behaving as C-nucleophiles leading to vinyl propagated oligomers. The results observed by Miyamoto et al. [10] with 2-vinyl-4,4-dimethyl-2-oxazoline that exclusive C-alkylation and vinyl propagation also occurred with a sterically encumbered oxazoline were in accord with the present work, but it was surprising that cyclized products were not observed!

It would be desirable to extend principles learned from the present study to other monomeric systems, especially acrylates and methacrylates. Miyamoto et al.,[23] have shown that methyl methacrylate can be polymerized in modest yield in the presence of very strong Brønsted acids and suitable initiators. These systems were described as not being living and that termination occurred upon tautomerization of a propagating *enol* to ester *keto* form. Despite the absence of basic nitrogen in an acrylate monomer, it would seem that the proper combination of initiator and very strong acid should lead to similar kinds of oligomeric products as have been observed in the present study.

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2. 4,4-Dimethyl-2-vinyl-5(4H)oxazolone **(1a)** is commercially-available from SNPE, Inc.: Princeton, NJ.
3. This compound is a well-known radical scavenger in the presence of oxygen [cf. Hammond, G.S.; Boozer, C.E.; Hamilton, C.E.; Sen, J.N. Air oxidation of hydrocarbons. III. Mechanism of inhibitor action in benzene and chlorobenzene solutions. J. Am. Chem. Soc. **1955**, *77*, 3238–3244] and the presence of the t-butyl groups prevents ring-opening of the oxazolone ring.
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