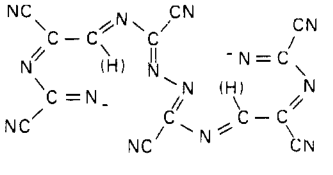
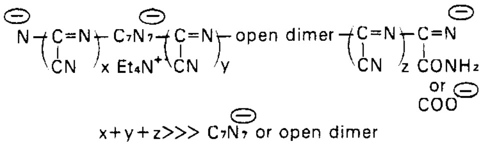


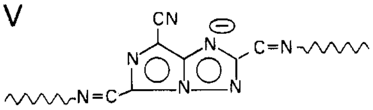
III

IV

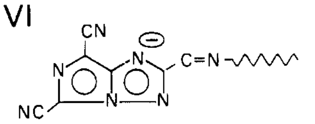


which could be formed at the anode by oxidation of $C_7N_7^-$, leading to occasional carbon–carbon and nitrogen–nitrogen links in the backbone. Our view of the "real" polymer is shown in IV. $C_7N_7^-$ anion that is not dimerized can be incorporated at a chain end or within the chain in two forms (V and VI).

V



VI



The results of DSC and ^1H NMR studies suggest that the concentrations of $C_7N_7^-$ related species and Et_4N^+ in the polymer are essentially the same and that there is approximately one $C_7N_7^-$ anion per 40 C_2N_2 units. It is the incorporation of tetraalkylammonium groups that explains the C/N ratios being greater than 1:1 as well as the hydrogen content (~2%) of PCN. Adventitious protons are undoubtedly also responsible for chain termination.

Using HC_7N_7 as an electrolyte instead of the tetraethylammonium salt leads to the molecular weight decreasing by a factor of 2. It has been noted by Sato et al.[6] in studies of electropolymerization of acrylonitrile that polymerization rate and molecular weight increase with increasing size of the alkylammonium ion in the supporting electrolyte.

The fact that a polymer of such low molecular weight still forms fibers implies that dipole–dipole interactions between —C═N groups on neighboring chains are important in giving this interesting new polymer cooperative properties.

Acknowledgment. This work was supported by the National Science Foundation, Solid State Chemistry, under Grant No. DMR83-02329.

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Mesoionic Polymerization. Poly(oxyvinylene) Lactams from *N*-(Chloroacetyl) Lactams through an Isomunchnone Intermediate

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ABSTRACT: The polymerization of *N*-(chloroacetyl) lactams to yield poly(oxyvinylene) lactams is described. Evidence for the polymer structure includes spectral characterization by IR, ^1H NMR, and ^{13}C NMR, and degradation behavior. Polymerization was found to occur for 2-haloacyl-substituted lactams only and not for 3- or 4-haloacyl derivatives. *N*-(Chloroacetyl) lactams of ring size six, seven, and eight were found to polymerize spontaneously at ambient temperature and at higher temperatures. The five-membered lactam failed to polymerize under any conditions. Polymers synthesized from *N*-(chloroacetyl)caprolactam exhibited inherent viscosities in the range 0.03–0.07 dL/g and were soluble in a wide variety of organic solvents, including ketones, aromatics, lower alcohols, tetrahydrofuran, and dimethyl sulfoxide. The polymerization mechanism postulated involves formation of a mesoionic 1,3-oxazolium-4-oxide or "isomunchnone" intermediate. Polymer is formed by sequential Michael addition and ring opening of this species. Support for the isomunchnone intermediate involved trapping with dimethyl acetylenedicarboxylate. The initial 1,3-dipolar cycloaddition product rearranged to a pentahydro-3-hydroxy-4,5-bis(methoxycarbonyl)cyclohepta[*a*]pyridin-2-one.

Introduction

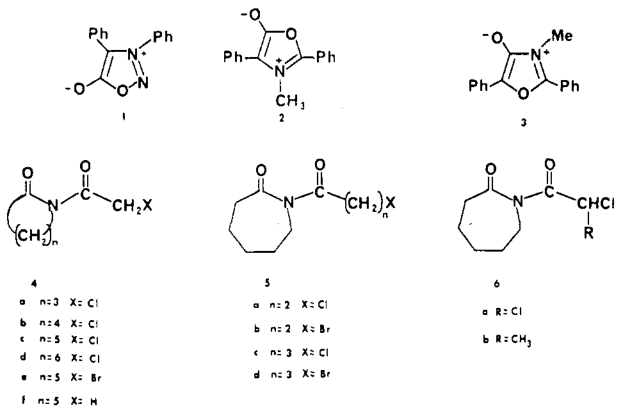
The variety of polymerization mechanisms that have so far been demonstrated include almost all those that can be imagined. Neutral, radical, cationic, anionic, complexed, and zwitterionic intermediates have been postulated or demonstrated for a range of chain-growth and step-growth systems. We report in this paper what we believe to be the first polymerization in which a *mesoionic* intermediate is involved.

A mesoionic compound is usually a heterocyclic species for which an unusual bonding structure can be drawn that possesses formal charge separation. "Sydnones" (1) are considered to be one of the first families of mesoionic compounds to be discovered.[1] Following the serendipitous

Table I
Properties of Haloacyl Lactams

compd	mp, °C	lactam mp, °C	polymerizability		$\nu_{C=O}$, cm^{-1}	
			ambient	100 °C	monomer	polymer
4a	44–46	23–25	–	–	1740, 1704	
4b		38–40	+	+	1699	1704
4c		70–72	+	+	1701, 1697	1704
4d	61–64	35–38	+	+	1691, 1682	1707
4e		70–72	+	+		1704
4f		70–72	–	–	1695	
5a		70–72	–	–	1699	
5b		70–72	–	–	1698	
5c		70–72	–	–	1702, 1693	
5d		70–72	–	–	1701, 1694	
6a		70–72	–	+	1704	1734, 1699, 1652
6b		70–72	–	+	1698	1737, 1704 1663

Chart I



discovery of the polymer-forming reaction described in this paper,[2] we became acquainted with two additional families commonly called "munchnones" (**2**)[3] and "isomunchnones" (**3**).[4] The chemistry of these compounds has been widely explored, especially cycloaddition reactions. While polymerizations involving cycloadditions of bis-mesoionic compounds with bis-dipolarophiles have been described,[5,6] there have been no reports dealing with polymerizations in which a mesoionic intermediate undergoes self-addition. In this article we fully describe monomer and polymer structures, polymerization conditions, and evidence for the highly reactive intermediate proposed for polymer formation.

Experimental Section

Monomer-grade caprolactam was donated by Akzo Chemical Co. and was recrystallized from cyclohexane and dried before use. The haloacyl halides were distilled just prior to use. All other reagents and solvents were reagent grade and were used as received.

^{13}C NMR spectra were obtained on a JEOL FX90Q and ^1H NMR spectra were obtained on a Varian EM-360. FTIR spectra were recorded on a Nicolet 5DX. UV spectra were obtained on a Perkin-Elmer 320 interfaced to a Nicolet 1200S computer. TGA and DSC data were obtained on a Du Pont 951 TGA and Du Pont 910 DSC interfaced to a Du Pont 9900 data station. Elemental analyses were performed by MicAnal Laboratories, Tuscon, AZ.

Monomer Synthesis. *N*-(Chloroacetyl)pyrrolidone (4a). The synthesis of this monomer is typical of the syntheses for the six-, seven-, and eight-membered-ring lactams. Benzene (65.04 g) and 2-pyrrolidone (17.02 g (0.2 mol)) were charged to a 250-mL, three-necked, round-bottom flask equipped with a nitrogen inlet, drying tube, thermometer, addition funnel, and stirring bar. The stirring solution was cooled to 3–5 °C in an ice bath and purged with nitrogen. Freshly distilled chloroacetyl chloride (11.3 g (0.1 mol) was added over a 20-min period. After 1 h at 5 °C the solution was brought to room temperature and allowed to react for 24 h. The resulting solution was filtered free of pyrrolidone hydrochloride and stripped of benzene. The resulting solid was recrystallized from diethyl ether to yield 12.01 g of *N*-(chloroacetyl)pyrrolidone: mp 44–45 °C; IR 2964, 2898, 1739, 1706, 1364, 1343, 1221, 787 cm^{-1}; ^1H NMR 4.55 s (2 H), 3.78 t ($J = 12$ Hz, 2 H), 2.49 t (2 H), 2.04 m (2 H); ^{13}C NMR 175.3, 169.4, 48.2, 44.9, 32.4 ppm. Anal. Calcd for $C_6H_8NO_2Cl$: C, 44.60; H, 4.95; N, 8.67; Cl, 21.98. Found: C, 44.48; H, 4.69; N, 8.68; Cl, 21.05.

In order to prepare pure *N*-chloroacetyl derivatives of valerolactam, caprolactam, and enantholactam, the molar ratio of chloroacetyl chloride to lactam was adjusted to 1.126:2. This routinely led to yields of pure material in excess of 80%.

Polymer Synthesis. Polymerizations of chloroacetyl lactams were carried out under a wide variety of conditions in an attempt to obtain high molecular weight polymer. For consistency, *N*-(chloroacetyl)caprolactam(**4c**) was utilized in these studies. As an example, 4.75 g (0.0251 mol) of **4c** and 10 g of dimethylformamide were charged to a 100-mL, single-necked, round-bottom flask. The solution was heated to reflux for 1 h, cooled, and poured into rapidly stirring water. The precipitated polymer was collected and dried in vacuo for 24 h at 45 °C. Yield was 2.71 g, 57.1% based on monomer. The inherent viscosity (0.5 g/dL in dimethyl sulfoxide) was 0.046 dL/g. Anal. Calcd for $C_8H_{11}NO_2$: C, 62.75; H, 7.19; N, 9.15. Found: C, 60.97; H, 7.16; N, 8.24; Cl, 0.04.

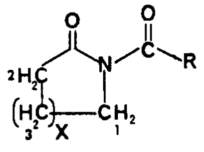
Results and Discussion

Monomer Synthesis. The chloroacetyl compounds were initially designed as grafting agents capable of subsequent initiation of nylon 6 polymerization. While a variety of techniques have been reported for the preparation of acyl lactams, no prior report of the synthesis of these compounds was found. Straightforward application of a method previously described for *N*-acetylcaprolactam[7] was therefore applied and found to work very well. In this procedure, excess caprolactam is used both as the substrate for the reaction and as base for removing the liberated HCl as the caprolactam salt. The use of pyridine or triethylamine as the acid scavenger resulted in reduced yields and impure products. The initially isolated *N*-(chloroacetyl)caprolactam derivative was obtained as a clear, free-flowing liquid. On standing for several days, this liquid gradually became more viscous and finally solidified. Attempted vacuum distillation of this monomer resulted in polymerization prior to the boiling point.

Application of this method to the monomers listed in Table I gave compounds that were initially obtained pure (as indicated by TLC and spectroscopy) and possessed the physical properties listed. It is interesting to point out that those monomers that are made from lower melting lactams gave higher melting 2-chloroacetyl derivatives (compounds **4a** and **4d**) while the higher melting lactams gave lower melting derivatives (**4b** and **4c**).

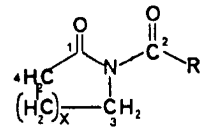
Tables II and III show the ^1H and ^{13}C NMR chemical shifts for the various *N*-haloacyl derivatives synthesized

Table II
^{1}H NMR of Haloacyl Lactams



compd	x	chem shift (ppm from Me_4Si) 1	2	3	R
4a	1	3.78	2.49	2.04	4.55 (CH_2Cl)
4b	2	3.72	2.56	1.82	4.70 (CH_2Cl)
4c	3	3.83	2.69	1.70	4.51 (CH_2Cl)
4d	4	3.90	2.65	1.52	4.60 (CH_2Cl)
4f	3	3.91	2.70	1.77	2.49 (CH_3)
5a	3	3.95	2.70	1.75	3.80 (CH_2Cl), 3.30 (CH_2)
5c	3	3.80	2.65	1.70	3.55 (CH_2Cl), 3.00 (CH_2CO), 2.05 (CH_2)
5d	3	3.90	2.75	1.80	3.5 (CH_2Br), 3.08 (CH_2CO), 2.25 (CH_2)
6a	3	3.90	2.65	1.76	7.21 (CH)

Table III
^{13}C NMR of Haloacyl Lactams



compd	x	chem shift (ppm from Me_4Si) 1	2	3	4	R
4a	1	175.3	169.4	44.9	32.4	48.2 (CH_2Cl)
4b	2	172.5	169.4	44.7	34.2	48.1 (CH_2Cl)
4c	3	177.1	168.7	43.6	38.8	47.8 (CH_2Cl)
4d	4	177.1	168.2	43.2	35.7	46.1 (CH_2Cl)
4f	3	178.2	172.9	44.4	38.5	27.8 (CH_3)
5a	3	177.7	172.5	42.2	39.5	43.1 (CH_2CO), 39.5 (CH_2Cl)
5b	3	177.3	172.6	43.1	39.5	43.3 (CH_2CO), 27.9 (CH_2Br)
5c	3	177.6	174.7	43.2	39.8	45.1 (CH_2CO), 36.5 (CH_2Cl), 30.8 (CH_2)
5d	3	178.7	175.7	44.5	39.0	35.5 (CH_2CO), 33.4 (CH_2Br), 29.3 (CH_2)
6a	3	176.9	165.6	44.4	38.5	66.8 ($CHCl_2$)
6b	3	176.6	171.5	43.2	38.4	53.4 (CH), 20.2 (CH_3)

(compounds 4–6). The additional methylene peaks in the ^{13}C spectra of the monomers have been omitted. These peaks all fall between 20 and 30 ppm and contain little useful structural information other than confirming the presence of all expected carbons.

Polymer Formation. Spontaneous polymerization at ambient temperature and pressure was observed only for the *N*-(chloroacetyl) derivatives **4b–d** (Tables I and IV). In most cases, polymerizations performed at elevated temperatures resulted in increased color formation without markedly increasing polymer viscosity.

Acyl substituents containing halo groups further removed from the α-position did not polymerize or underwent HCl loss followed by vinyl polymerization (the 3-chloropropionyl compound). Most surprising was the complete lack of polymerizability of the pyrrolidone derivative even at temperatures up to 150 °C. We believe this is due to its inability to form the mesoionic intermediate required for oxyvinylene generation.

In addition to the chloroacyl compounds, the corresponding bromides were synthesized in several cases. While these monomers were even more reactive, the formed polymers could only be obtained in highly colored form. We eventually concluded that color formation is indicative of residual ionic repeat units or end groups or involves side reactions not yet elucidated. In any event, the chloro compounds gave the cleanest polymerizations and were used for additional investigation.

Polymers prepared from these monomers have all exhibited low viscosities (<0.1 dL/g) and seem to be of low molecular weight. As can be seen from Table IV, the highest yields and best viscosities were produced in neat polymerizations, carried out under vacuum to help remove HCl. The addition of a variety of bases and proton-abstracting reagents did not increase yields or viscosities. The most probable reason for the failure to reach high molecular weight is that an inherently unstable intermediate (the actual monomer) is never built up in high concentrations. This "monomer" is therefore not available to sustain the reaction. In addition, the HCl and chloride anions liberated may terminate the reaction or cause side reactions with the intermediates. These possibilities are

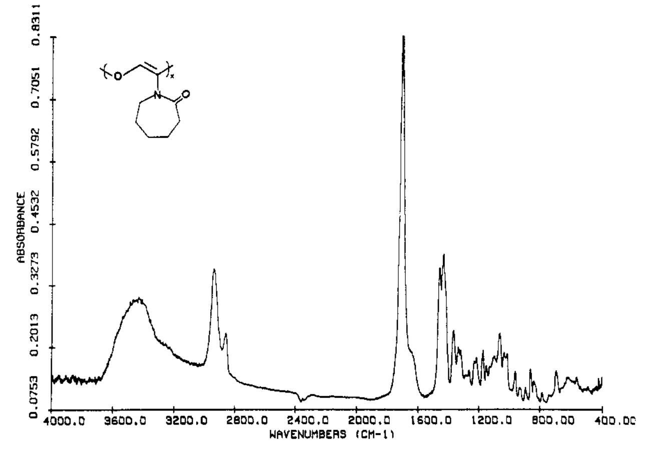


Figure 1. FTIR spectrum of poly(oxyvinylene)caprolactam.

Table IV
Haloacyl Lactam Polymerization Data[a]

monomer	solvent	base	temp, °C	yield, %	color	η_{inh},[d] dL/g
4c			25	56.2	white	0.034
4c			25		white	0.020
4c			25	46.9	white	0.024
4c	b		150		white	0.073
4c	b		80	69.2	white	0.032
4c	b		100	74.0	white	0.051
4c	b		210	65.9	tan	0.035
4c	b		100		white	0.047
4c	benzene		80		white	0.055
4c	benzene	KOH/18 crown 6	80	c		
4c	benzene	KF/18 crown 6	80	c		
4c	benzene	triethylamine	80	c		
4c		triethylamine	100		tan	0.035
4c	dioxane		100	35.5	white	0.037
4c	DMF		150	57.1	white	0.046
4c	DMF		100	35.9	white	0.040
4c	DMF	NaAc	150	20.6	brown	0.016
4c	DMF	NaAc	25	c		
4c	DMAc		100	16.0	white	
4c	Me_2SO		100	20.0	black	
4c	TMU		100	53.6	white	0.036
4e	b		150		black	0.046
4d			25		white	0.018
4d	b		150	55.2	gold	0.021
4b	b		100	c	red	
4b	DMF		150	2.8	red	0.027
6a	b		150	36.3	black	0.046
6b	b		150	c	brown	

[a] DMF = dimethylformamide, Me_2SO = dimethyl sulfoxide, DMAc = dimethylacetamide, TMU = tetramethylurea, NaAc = sodium acetate. [b] Reaction performed at reduced pressure (0.1–0.01 mmHg). [c] Polymer would not precipitate when treated with nonsolvent. [d] 0.5 g/dL in Me_2SO.

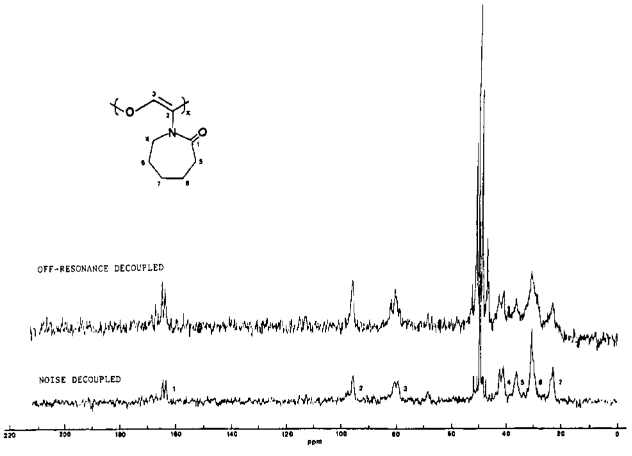
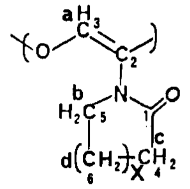


Figure 2. ^{13}C NMR spectrum of poly(oxyvinylene)caprolactam noise and off-resonance decoupled (peak at 49 ppm is methanol).

Table V
Poly(oxyvinylene) Lactam NMR Data



^1H NMR Data

x	chem shift (ppm from Me_4Si) a	b	c	d
2[a]	4.05	3.29	2.33	1.78
2[b]	5.45	4.35	3.60	1.95
3[a]	4.15	3.25	2.50	1.80
3[b]	5.40	3.95	3.25	1.95
4[b]	5.45	4.15	3.15	1.75

^{13}C NMR Data[c]

x	chem shift (ppm from Me_4Si) 1	2	3	4	5	6
2	169.0	95.0	78.8	38.7	31.6	24.2 (a), 21.4 (b)
3	169.1	98.9	80.0	40.3	35.3	29.4 (a, b), 21.5 (c)
4	169.2	96.1	79.7	41.2	29.5	26.7 (a, b), 24.8 (c), 21.0 (d)

[a] In $CDCl_3$. [b] In trifluoroacetic acid. [c] In CH_3OH.

discussed in more detail later.

Polymer Characterization. The IR and ^{13}C NMR spectra of poly(oxyvinylene)caprolactam are shown in Figures 1 and 2. Table V shows NMR chemical shift data for the poly(oxyvinylene) lactams produced.

The IR spectrum of the polymer is quite similar to that of the monomer as regards the main structural bands. The carbonyl and methylene absorbances remain practically unchanged, and the only disappearance noted is that of the C–Cl band at 750 cm^{-1}. The appearance of a broad absorption at ca. 3500 cm^{-1} is also seen in the polymer. This absorption is probably due to OH end groups or hydrolyzed side chains in the polymer.

Figure 3 shows ^1H NMR spectra of **4c** in $CDCl_3$ solution taken over a period of 6 weeks. The spectra show the disappearance of the two chloroacetyl protons at 4.51 ppm and the appearance of a sharp singlet at 4.15 ppm. This information combined with the ^{13}C NMR spectrum showing the disappearance of resonances at 47.8 and 177.1 ppm in the monomer and the appearance of new resonances at 98.9 and 80.0 ppm in the polymer (which appear as a singlet and doublet in the off-resonance spectrum, respectively) is indicative of the transformation of the acyl halide side chain to the indicated oxyvinylene polymer backbone. This assignment was confirmed by degradation studies of the polymer. The use of refluxing 85% phosphoric acid resulted in dissolution of the polymer whereby a homogeneous degradation reaction could be carried out.

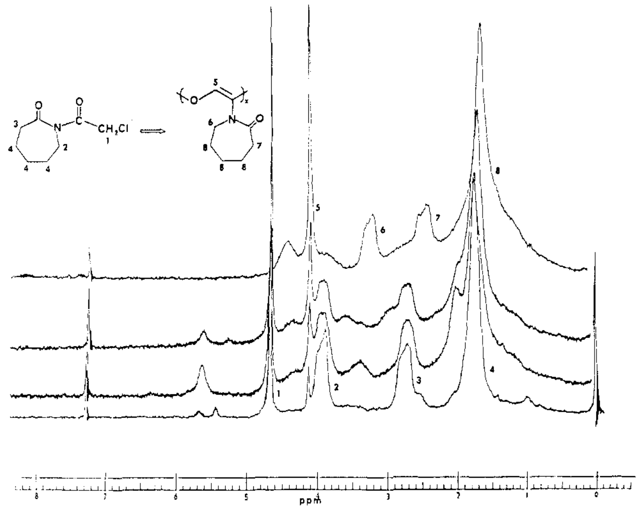


Figure 3. ^{1}H NMR spectra of **4c** taken intermittently during a 6-week period of storage at 25 °C. Bottom scan, initial solution; top scan, final solution.

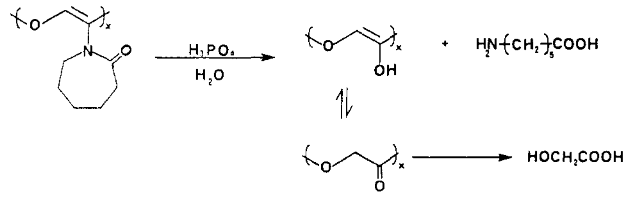


Figure 4. Proposed degradation mechanism for poly(oxyvinylene)caprolactam in refluxing phosphoric acid solution.

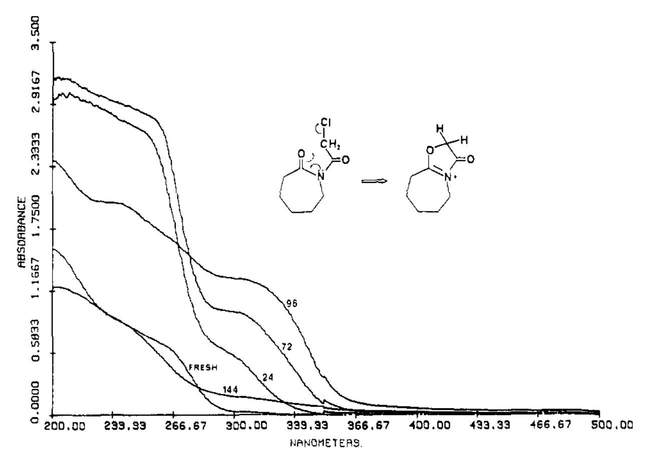
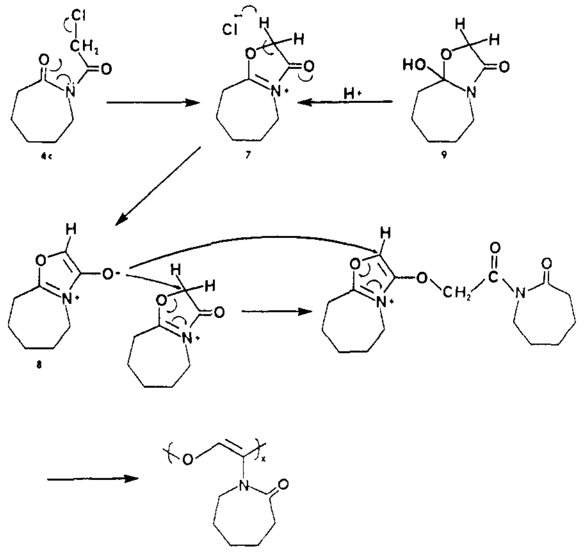


Figure 5. UV spectra of neat **4c** taken after preparation and storage at 25 °C for 24, 72, 96, and 144 h.

Scheme I



After reaction for 8 h the solution was diluted with water and the unreacted polymer was filtered off. The remaining solution was then neutralized with barium hydroxide and the insoluble barium salt was filtered off. Analysis of the water-soluble layer after extraction with ether revealed the presence of 6-aminocaproic acid and glycolic acid. The proposed degradation process is shown in Figure 4. Degradation in methanolic sodium hydroxide and benzylamine failed to yield any transformation of the polymer, indicating the absence of imide type structures, which have been shown to be labile to attack by benzylamine.[8]

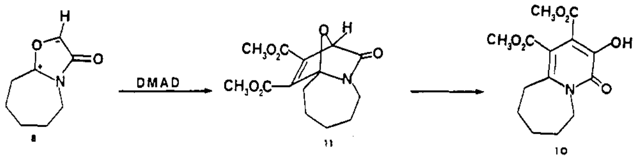
The question of polymerization mechanism posed an interesting problem at this point. Previous work reported on the polymerization of *N*-acyl lactams utilizing carboxylic acid initiators and high reaction temperatures indicated the formation of *N*-acyl polyamides by an ordinary acid-catalyzed acyl-exchange step-growth process.[8] This mechanism could not explain the formation of oxyvinylene type polymers as was found in our case. In order to study the chemical changes that occurred during the polymerization, UV spectra of neat **4c** were taken periodically over 144 h. These spectra are shown in Figure 5. The appearance of absorption bands at 270 and 320 nm is similar to that reported by Griot and Frey, who studied the UV behavior of 7-hydroxy-8-oxa-1-azabicyclo[5.3.0]decan-10-one (**9**) in ethanol and sulfuric acid solution.[9] The spectrum in sulfuric acid showed a bathochromic shift of the imide carbonyl from 192 to 217 nm, with the appearance of a weaker absorption maximum at 317. They interpreted this as evidence for an exchanging OH group through the 5-hydro-1,3-oxazolium-4-oxide carbonium ion **7** shown in Scheme I. Further evidence for this intermediate came from the ability of acidic solutions of **9** to yield 8-oxa-1-azabicyclo[5.3.0]decan-10-one) on hydrogenation over palladium. Further reaction of this intermediate with chloride anion and liberation of HCl results in the formation of a mesoionic 1,3-oxazolium-4-oxide or "isomunchnone" compound, **8**. The name isomunchnone was coined by Japanese workers[4] to describe these compounds, which are isomeric to the 1,3-oxazolium-5-oxide "munchnones" originally described by Huisgen and coworkers.[3]

Two synthetic routes to these compounds have been described in the literature, namely catalytic decomposition of diazoimide compounds[4] and the triphenyl phosphite transformation of *N*-(aroylaryl)glyoxanilides.[10] Additionally, Potts has described the 2-aryl-4(5*H*)-oxazolone compound existing in tautomerization with its mesoionic counterpart.[11,12] Proof for this tautomerization came in the discovery that these compounds undergo cycloaddition reactions with olefinic dipolarophiles.

Polymerization of isomunchnones or 2-aryl-4(5*H*)-oxazolones either on heating or at ambient conditions has not been previously described. One possible reason for this is that no isomunchnone has been described that is substituted at the 5 position with a proton and the 2 position with an alkyl group. Isomunchnones are commonly prepared with aryl substituents in these positions to enhance their poor stability.

The proposed polymerization mechanism shown in Scheme I involves attack of the oxygen of isomunchnone **8** on intermediate **7** to initiate the polymerization. Direct attack of the isomunchnone on itself is improbable due to the possibility for the 5 position to possess a negative charge in the canonical form shown in Scheme II. Propagation then occurs by attack of **8** on this charged and

Scheme II



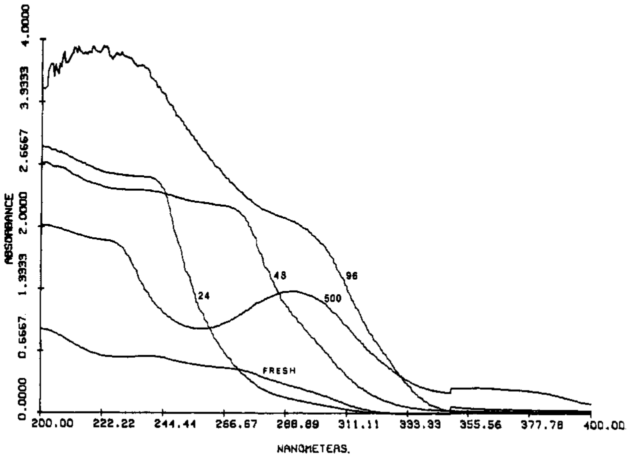


Figure 6. UV spectra of neat **4b** taken after preparation and storage at 25 °C for 24, 48, 96, and 500 h.

unsaturated end group as shown.

The presence of isomunchnone **8** in the decomposition of *N*-(chloroacetyl)caprolactam was demonstrated by trapping the intermediate using the well-known propensity of mesoionic compounds to undergo 1,3-dipolar cycloaddition reactions with acetylenes and dienes. The reaction of *N*-(chloroacetyl)caprolactam with dimethyl acetylenedicarboxylate (DMAD) resulted in the formation of a crystalline, high-melting (200 °C) compound which was found to be 7,8,9,10,11-pentahydro-3-hydroxy-4,5-bis(methoxycarbonyl)cyclohepta[*a*]-pyridin-2-one (**10**).[13] This compound resulted from the acid-catalyzed rearrangement of the 1,3-dipolar cycloaddition product **11** as shown in Scheme II. The ordinary behavior of *N*-methyl-substituted isomunchnones reacted with DMAD is to undergo retro-Diels–Alder reaction and liberate methyl isocyanate to form substituted furans.[11,12,14] The formation of pyridone **10** is facilitated by the lactam ring effectively preventing retro-Diels–Alder formation and the presence of a proton at the 5 position of the isomunchnone which allows the bicyclic protonated oxygen to migrate to the 5 position during the rearrangement. Reaction of DMAD with *N*-(chloroacetyl)valerolactam also yielded a substituted pyridone similar to **10**.

In the case of the *N*-(chloroacetyl)valerolactam system, the polymer yield and viscosity are found to be low. The UV spectra of this monomer over time are shown in Figure 6. In contrast to the *N*-(chloroacetyl)caprolactam monomer, this material retains significant absorbance at 280 and 375 nm even after 2 months of storage at ambient temperature. The spectrum of a polymer precipitated into water from its dimethylformamide polymerization solvent also shows a broad absorption in this region and this polymer retains its red color. This is indicative of a highly stabilized isomunchnone chain end or intermediate for this polymer and may account for its low yield and viscosity.

The polymerization of caprolactam-based monomers with alternative haloacyl side chains gave mixed results. The use of *N*-(bromoacetyl)caprolactam and *N*-(dichloroacetyl)caprolactam gave very dark polymers that were difficult to characterize. 1-(2-Chloropropionyl)-caprolactam gave a dark brown tacky solid on heating that was also difficult to characterize. Caprolactam derivatives with 3-halopropionyl and 4-halobutyryl side chains failed to polymerize, as did the *N*-(chloroacetyl)pyrrolidone. Griot and Frey reported that (α-hydroxyacyl)pyrrolidones failed to give cyclols with structures similar to **9** while (α-hydroxyacyl)piperidones and -caprolactams cyclized in good yields. They also reported that a six-membered cyclol could not be formed from *N*-(β-hydroxyacyl)caprolactam but the large-ring compound 8-oxa-1-azacycloundecane-7,11-dione could be isolated after standard cyclization reaction conditions had been carried out.[9] This product results from cleavage of the bicyclic C–N bridgehead bond resulting in the six- and seven-membered rings opening to an eleven-membered macrocycle.

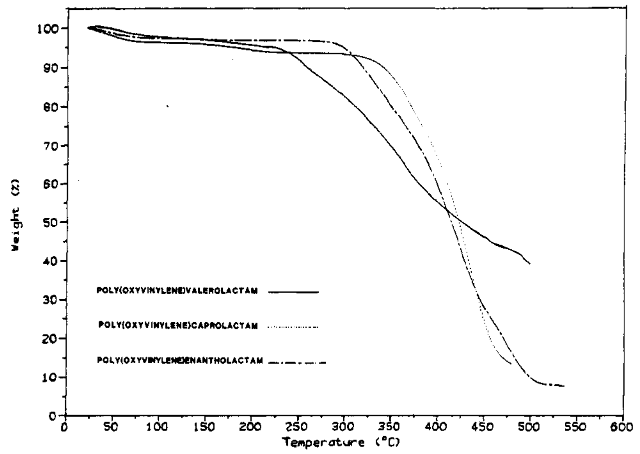


Figure 7. TGA analysis of poly(oxyvinylene) lactams (nitrogen atmosphere, heating rate 20 °C/min).

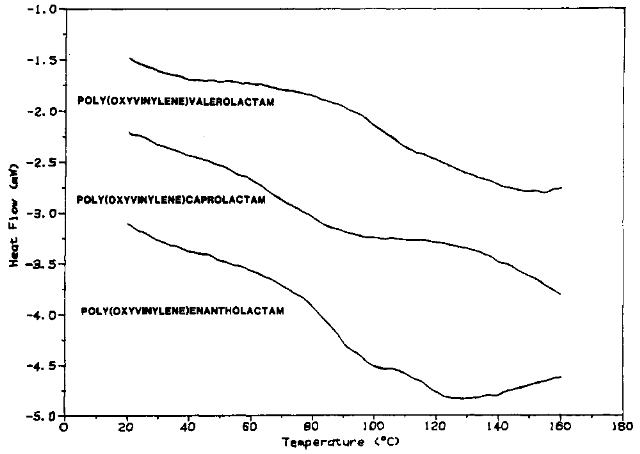


Figure 8. DSC analysis of poly(oxyvinylene) lactams (nitrogen atmosphere, heating rate 10 °C/min).

TGA and DSC scans for poly(oxyvinylene) lactams are shown in Figures 7 and 8. The TGA data indicate good stability of the poly(oxyvinylenes) of caprolactam and enantholactam, with poorer initial stability observed for the valerolactam-based polymer. This polymer showed interesting char formation, however, as the polymer retained ca. 40% of its weight after exposure to temperatures of 500 °C. The char had a silvery texture in bulk but appeared black with no distinguishing features when examined with polarizing light microscopy. The polymers exhibited definite breaks in the DSC curves indicative of glass transitions with values of 60–100 °C. Poly(oxyvinylene)caprolactam could be melt pressed into films at temperatures of 200 °C but these films were brittle and displayed no significant strength. The polymers showed no birefringent or spherulite behavior under the polarizing light microscope and are apparently noncrystalline. The polymers were found to be soluble in a wide variety of organic solvents but were insoluble in water. The highest molecular weight poly(oxyvinylene)caprolactam polymer (0.07 dL/g) was found to be insoluble in chloroform and only soluble in methanol and tetrahydrofuran on heating. Further work on preparing high molecular weight polymers by reaction of acyl lactams with different substituents is under way.

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Registry No. **4a**, 43170-60-1; **4b**, 98303-90-3; **4b** (homopolymer), 98303-91-4; **4c**, 98303-85-6; **4c** (homopolymer), 98303-89-0; **4d**, 98303-92-5; **4d** (homopolymer), 98303-93-6; **4e**, 101697-80-7; **4e** (homopolymer), 101697-81-8; **4f**, 1888-91-1; **5a**, 101712-14-5; **5b**, 101712-15-6; **5c**, 101712-16-7; **5d**, 101712-17-8; **6a**, 101697-82-9; **6a** (homopolymer), 101697-83-0; **6b**, 101697-84-1; **6b** (homopolymer), 101697-85-2; $ClCH_2COCl$, 79-04-9; 2-pyrrolidone, 616-45-5.

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Synthesis and Characterization of Poly(methyl 2-decanamidopropenoate) [Poly(*N*-decanoyldehydroalanine methyl ester)]: A Novel Comb Polymer Derived from a Difunctional Monomer

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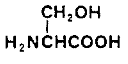
ABSTRACT: The synthesis of the difunctional vinyl monomer methyl 2-decanamidopropenoate [*N*-decanoyldehydroalanine methyl ester] was accomplished by using two general routes starting with D,L-serine (2-amino-3-hydroxypropanoic acid). The amino acid was methyl esterified, N-acylated, and dehydrated with a mild carbodiimide procedure. Alternatively, the hydroxy ester was converted to the chloride, N-acylated, and dehydrochlorinated with base to form the monomer. Characterization of the monomer included ^{13}C FT-NMR, FT-IR, and GC/MS. Radical polymerization [AIBN] in isomeric hexanes resulted in clear, high molecular weight polymers. Solution properties were studied in THF at 25 °C and included dilute solution viscometry, low-angle laser light scattering and size-exclusion chromatography. Intrinsic viscosities ranged from 0.36 to 8.79 dL/g, with $\bar{M}_w$ between 1×10^5 and 15.2×10^6. The Mark–Houwink constants K and a were calculated to be 2.63×10^{-4} and 0.63, respectively ([η] in dL/g, 0.1–2.63 million $\bar{M}_w$). Polymer configuration was examined by ^{13}C NMR and appeared to be essentially atactic. Wide-angle X-ray spectroscopy of a thin film indicated side-chain order typical of comblike polymers.

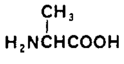
Introduction

Dehydroalanine (Dha), the vinyl analogue of alanine (Ala), is a substituent of many naturally occurring peptides which exhibit antibiotic properties. These antibacterial polypeptides have been isolated from numerous sources and contain as many as eight dehydroalanine residues. This fact, coupled with the search for new synthetic antibiotics, generated much interest in the preparation of peptides containing biologically active dehydroalanine residues. A review of dehydroamino acids, including dehydroalanine-containing peptides, appeared in 1979.[1]



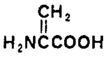
$H_2N\overset{CH_2OH}{\overset{|}{C}}HCOOH$

Ser



$H_2N\overset{CH_3}{\overset{|}{C}}HCOOH$

Ala



$H_2N\overset{CH_2}{\overset{||}{C}}COOH$

Dha

Many synthetic methods have been established for the introduction of the dehydroalanine residue into peptides. Indirect routes include base-catalyzed elimination reactions on substituted residues of *N*-hydroxy-,[2] *N*-chloro-,[3] and 3-chloroalanine,[4,5,6] ester elimination from 2-acetoxyamino acids,[7] and tosyl esters of serine (Ser)[8] and threonine,[9] and Hofmann elimination from 2,3-diamino acids.[10] Other methods have recently been reported and include direct elimination from cysteine using silver carbonate[11] and the dehydration of serine residues using isoureas,[12] carbodiimides,[13] and a triphenylphosphine–azidodicarboxylate complex.[14] Simpler analogues have been prepared by the direct condensation of pyruvic acid with various amides to produce N-substituted derivatives of dehydroalanine.[15,16] In fact, *N*-acetyldehydroalanine [2-acetamidoacrylic acid] is currently available commercially.[17]

Synthetic polymers have been prepared from various N-substituted derivatives of dehydroalanine and are the subject of numerous patents and publications. British (1946)[18] and US (1949)[19] patents describe the bulk and solution polymerization of *N*-acetyldehydroalanine methyl ester [methyl 2-acetamidoacrylate] to produce a clear, water-soluble homopolymer. Copolymers with acrylonitrile, methyl methacrylate, and styrene were also described.

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