the cation hydration shell,[16] would account for the observed order $Ca^{2+} > K^+ > Na^+$. Further, Daoust and Hade,[21] in investigating the effect of cation size on heats of dilution of polystyrene sulfonate, found that the degree of *site* binding in that case was $Ca^{2+} > K^+ > Na^+$. We conclude site binding is a significant factor in counterion binding to κ-carrageenan but not with λ-carrageenan.

The observation that at the highest operating frequency $\Delta\alpha/f^2 \neq 0$ means that a further relaxation process occurs at even higher frequencies since, in the interpretation of eq 1, $\Delta\alpha/f^2$ should equal zero when all of the processes have relaxed. This further relaxation process has an extremely weak amplitude, indicating that more than one step occurs in the cation condensation phenomenon.

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References and Notes

(1) T. J. Podlas and P. Ander, *Macromolecules*, **3**, 154 (1970).
(2) G. Pass, G. O. Phillips, and D. J. Wedlock, *Macromolecules*, **10**, 197 (1977).
(3) R. Fernandez-Prini, E. Baumgartner, S. Libermann, and A. E. Lagos, *J. Phys. Chem.*, **73**, 1420 (1969).
(4) B. N. Preston, J. McK. Snowden, and K. T. Houghton, *Biopolymers*, **11**, 1645 (1972).
(5) J. D. Wells, *Proc. R. Soc. London, Ser. B*, **183**, 399 (1973).
(6) G. S. Manning, *J. Chem. Phys.*, **51**, 934 (1969).
(7) F. Eggers, *Acoustics*, **19**, 323 (1968).
(8) R. A. Pethrick and E. Wyn-Jones, *Ultrasonics*, **10**, 228 (1972).
(9) G. Atkinson, E. Baumgartner, and R. Fernandez-Prini, *J. Acoust. Soc. Am.*, **93**, 6436 (1971).
(10) R. Zana and C. Tondre, *Biophys. Chem.*, **1**, 367 (1974).
(11) R. A. Pethrick, *J. Macromol. Sci., Part C*, **9**, 91 (1973).
(12) M. Eigen and K. Tamm, *Electrochemistry*, **66**, 107 (1962).
(13) I. Satake, M. Fukuda, T. Ohta, K. Nakamura, N. Fujita, A. Yamauchi, and H. Kimizuka, *J. Polym. Sci., Polym. Phys. Ed.*, **10**, 2343 (1972).
(14) R. Zana, C. Tondre, M. Rinaudo, and M. Milas, *J. Chim. Phys. Phys.-Chim. Biol.*, **68**, 1258 (1971).
(15) C. Tondre and R. Zana, *J. Phys. Chem.*, **76**, 3451 (1972).
(16) S. Arnott and W. E. Scott, *J. Mol. Biol.*, **90**, 253 (1974).
(17) T. C. M. Dea, A. A. McKinnon, and D. A. Rees, *J. Mol. Biol.*, **68**, 153 (1972).
(18) D. B. Smith and W. H. Cook, *Arch. Biochem. Biophys.*, **45**, 232 (1953).
(19) M. Glicksmann, "Gum Technology in the Food Industry", Academic Press, New York, N.Y., 1969.
(20) G. Pass, G. O. Phillips, and D. J. Wedlock, *J. Chem. Soc., Perkin Trans. 2*, 1229 (1977).
(21) H. Daoust and A. Hade, *Macromolecules*, **9**, 608 (1976).

Linear Poly(*N*-alkylethylenimine)s

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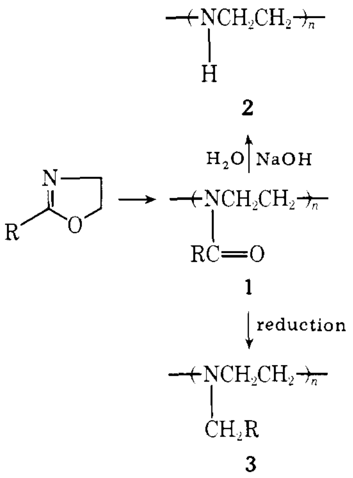
Poly(*N*-alkylethylenimine)s may be prepared by the ring-opening polymerization of *N*-alkylethylenimines.[1] The polymerization of *N*-alkylethylenimines, however, normally is accompanied by side reactions such as a reaction between the growing species and the amino group of the produced polymer chain and usually does not yield poly(*N*-alkylethylenimine)s having clear-cut structures in quantitative yield.[2] In some cases cyclic oligomers are also produced. Production of polymer and/or oligomer depends upon the monomer structure, the nature of initiator, and the polymerization conditions.[2]

In this paper we wish to report a new method of the preparation of linear poly(*N*-alkylethylenimine)s. Previously we reported the preparation of linear, crystalline polyethylenimine **2** by the alkaline hydrolysis of poly(*N*-formylethylenimine) **1** (R = H) which is obtained by the isomerization polymerization of unsubstituted 2-oxazoline.[3] Reductions of poly(*N*-acylethylenimine)s **1** are expected to give poly(*N*-alkylethylenimine)s **3**. The present paper describes the results, in which $LiAlH_4$ and AlH_3 were used as reducing agents.



R = H, alkyl, aryl

Experimental Section

Reagents. 2-Oxazoline was prepared and purified as reported previously.[4] 2-Propyl-2-oxazoline and 2-phenyl-2-oxazoline were prepared according to the literature.[5] Commercial reagents of 2-methyl-2-oxazoline (Aldrich Co.) and all solvents were dried and distilled under nitrogen. $LiAlH_4$ was commercial reagent and was used without further purification. AlH_3 was prepared according to the method of Yoon and Brown.[6]

Polymerization. The polymerizations of 2-oxazolines were carried out in acetonitrile using ethyl trifluoromethansulfonate as an initiator at room temperature 100 °C under nitrogen. Polymers obtained were purified by reprecipitation (chloroform solvent–ethyl ether nonsolvent) and subjected to a molecular weight determination by vapor pressure osmometer (Hitach Perkin-Elmer Model 115).

Reduction with $LiAlH_4$. A typical experiment (No. 3) proceeded as follows. Poly(*N*-acetylethylenimine) ($\overline{M}_n$ = 7600), 1.0 g (11.8 mmol), was dissolved in 19 mL of CH_2Cl_2. $LiAlH_4$, 0.34 g (9.0 mmol), in ethyl ether, 2.5 mL, was added to the solution. The mixture was stirred at 40 °C for 68 h under nitrogen. The reaction was stopped by the addition of 0.63 mL of water. The organic layer was filtered and the reduced polymer was obtained by the evaporation of the filtrate (0.36 g, 43%).

Reduction with AlH_3. A typical experiment (No. 5) was performed as follows. Poly(*N*-acetylethylenimine) ($\overline{M}_n$ = 4480), 0.5 g (5.9 mmol), was dissolved in 39 mL of CH_2Cl_2. To this solution, 5.2 mL of AlH_3–THF solution (AlH_3 7.08 mmol) was added at 0 °C under nitrogen. After stirring for 6 h, the reaction mixture was hydrolyzed with 5 mL of water and 1 g of NaOH in 30 mL of water was added. The organic layer was separated and the aqueous layer was extracted twice with CH_2Cl_2. The combined CH_2Cl_2 solution was filtered and evaporated to dryness under vacuum, polymer yield 0.25 g (59%). The product poly(*N*-ethylethylenimine) was converted into HCl salt with an excess of diluted hydrochloric acid and the HCl salt was reprecipitated from the aqueous solution with addition of ethanol. The HCl salt was dried at 70 °C in vacuo and subjected to elemental analysis. Anal. Calcd for $(C_4H_9N{\cdot}HCl)_n$: C, 44.66; H, 9.37; N, 13.02. Found: C, 44.02; H, 9.74; N, 12.95.

Reduction of Poly(*N*-formylethylenimine). A mixture of 0.50 g (7 mmol) of poly(*N*-formylethylenimine), 1.1 mL (25 mmol) of 85% formic acid, and 2.3 mL (28 mmol) of 37% aqueous formaldehyde solution was heated at 100 °C under nitrogen. After 68 h the reaction mixture was cooled and 2.5 mL of concentrated hydrochloric acid was added. Heating at 100 °C was continued for another 5 h. Then, water and formic acid were distilled off at 50 °C under reduced pressure. The residue was dissolved in a small portion of water, made strongly basic with sodium hydroxide, and extracted with CH_2Cl_2. The CH_2Cl_2 solution was evaporated to give 0.23 g (58%) of polymer. The elemental analysis of the product was performed with its HCl salt as described above. Anal. Calcd for $(C_3H_7N{\cdot}HCl)_n$: C, 38.52; H, 8.62; N, 14.97. Found: C, 38.14; H, 8.83; H, 14.41.

Purification of Reduced Polymers. Poly(*N*-benzylethylenimine) was purified by reprecipitation by pouring its CH_2Cl_2 solution into *n*-hexane. The other polymers did not precipitate well in *n*-hexane.

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Table I
Reduction of Poly(*N*-acylethylenimine)s 1 with Metal Hydrides[a]

		Reaction conditions				Polymer structure by NMR analysis (unit (%))			$\overline{M}_n$[c]	
No.	R of 1	Hydride/ >NCOR	Temp, °C	Time, h	Yield, %	—N— | CH_2R	—N— | H	—N— | RC=O	Calcd[d]	Found
1	Me	0.62	r.t.	96	25	83	0	17		
2	Me	0.90	40	44	50	100	0	0	2300	2200
3	Me	0.76	40	68	43	100	0	0	6300	5500
4	Ph	0.66	r.t.	140	59	59	26	15	3700	4600
5	Me	1.20	0	6	59	100	0	0	3740	3750
6	Me	1.20	r.t.	45	30	79	0	21		
7	*n*-Pr	2.00	0	24	94	100	0	0	2000	1820
8	Ph	1.16	0	24		28	0	72		
9	Ph	3.65	0	24	98	100	0	0	4200	3900
10	Ph	2.91	r.t.	70	64	42	0	58		
11	H	1.40	r.t.	310		0	0	100		
12[b]	H		100	68	58	100	0	0		

[a] No. 1–4: $LiAlH_4$ in CH_2Cl_2/Et_2O. No. 5–11: AlH_3 in CH_2Cl_2/THF. [b] Reduction with $HCO_2H/HCOH$ in H_2O. [c] Determined by vapor pressure osmometry in $CHCl_3$ solvent at 35 °C. [d] Based on the molecular weight of the starting poly(*N*-acylethylenimine) and on the product polymer structure.

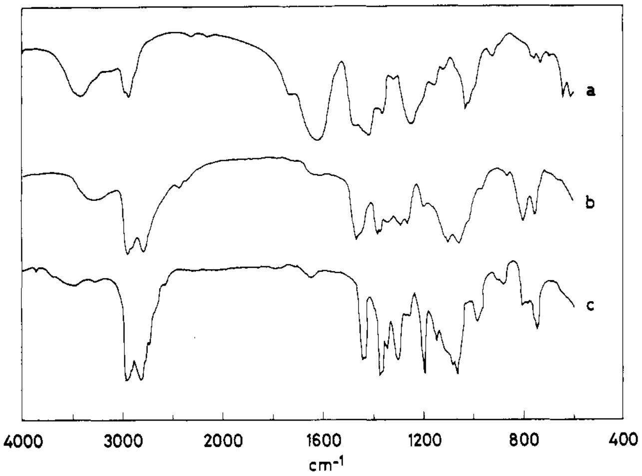

Figure 1. The IR spectra: (a) poly(*N*-acetylethylenimine); (b) poly(*N*-ethylethylenimine); (c) *N,N,N′,N′*-tetraethylethylendiamine.

Therefore, they were converted to HCl salts with an excess of diluted hydrochloric acid and the HCl salts were reprecipitated from their aqueous solution with ethanol. The precipitated salts were neutralized with aqueous sodium hydroxide. The polyamines liberated containing sodium chloride were dried under vacuum. Then the polyamines were extracted with CH_2Cl_2. The CH_2Cl_2 solutions of polyamines were filtered or centrifuged and evaporated to dryness in vacuo.

Results and Discussion

Reduction with Metal Hydrides. In the reduction of amides, ethyl ether or THF is generally used as solvent. Poly(*N*-acylethylenimine)s are not soluble in these solvents. Therefore, the mixture of CH_2Cl_2 and ethyl ether (or THF) was used in the present study. The results are shown in Table I. Both $LiAlH_4$ and AlH_3 reduced poly(*N*-acetylethylenimine) to poly(*N*-ethylethylenimine) with high selectivities. The reduction of poly(*N*-benzoylethylenimine) with $LiAlH_4$ produced a considerable amount of ethylenimine unit (No. 4, Table I). This is due to the *N*-benzyl group cleavage of the product polymer by $LiAlH_4$.[7] The N–C bond cleavage of the polymer main chain, however, did not occur as shown by the molecular weight of the reduced polymer. The $\overline{M}_n$ of the reduced polymer was even a little larger than the calculated value for the structure determined by NMR. This is probably caused by the loss of low molecular weight fraction by the reprecipitation with *n*-hexane. AlH_3 gave a better result even in the reduction of poly(*N*-benzoylethylenimine) carried out at 0 °C (No. 9, Table I). In this case, a large excess of AlH_3 was required. The reduction with AlH_3 at room temperature did not give good results, probably due to the side reaction between AlH_3 and the solvent.

In the case of R = Me, the isolated yield was low. This is owing to the higher solubility of the product polymer in the aqueous layer in the separation procedure. The longer N-substituted alkyl group gave the higher isolated yield because of its larger hydrophobic nature.

The selectivity of the reduction was calculated from ^1H NMR spectrum. For example, in experiment No. 5, only two peaks were observed, δ 1.00 (t, 3 H, CH_3) and 2.48 ppm (m, 6 H, CH_2), indicating 100% reduction. In Figure 1, the IR spectrum of the product of experiment No. 5 (Figure 1b) is shown together with that of the starting polymer (Figure 1a). A band of $\nu_{C=O}$ at 1650 cm^{-1} in the starting polymer was diminished by the reduction. The similarity of the spectrum of Figure 1b to that of *N,N,N′,N′*-tetraethylethylenediamine (Figure 1c) is taken as a support for the structure of poly(*N*-ethylethylenimine).

Reduction of Poly(*N*-formylethylenimine). Poly(*N*-formylethylenimine) is not soluble in the usual organic solvents. Therefore, the polymer was not reduced in CH_2Cl_2–THF with AlH_3 (No. 11, Table I). Therefore, the Eschweiler-Clarke reaction[8] was applied (No. 12, Table I). The ^1H NMR spectrum of the product polymer in D_2O was quite compatible with the structure of poly(*N*-methylethylenimine). No peak assignable to the $-N(CHO)CH_2CH_2-$ unit was observed. Thus, the reduction was shown to be almost perfect.

References and Notes

(1) M. Hauser, *"Ring-Opening Polymerization"*, K. C. Frisch and S. L. Reegen, Ed., Marcel Dekker, New York and London, 1969, p 219.
(2) E. J. Goethals, *Adv. Polym. Sci.*, **23**, 103 (1977), and references therein.
(3) T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, **5**, 108 (1972).
(4) T. Saegusa, H. Ikeda, and H. Fujii, *Polym. J.*, **3**, 35 (1972).
(5) J. A. Frump, *Chem. Rev.*, **71**, 483 (1971).
(6) N. M. Yoon and H. C. Brown, *J. Am. Chem. Soc.*, **90**, 2927 (1968).
(7) It was reported that $LiAlH_4$ reduction of *N,N*-diethylbenzamide produced benzyl alcohol in 13% yield at 0 °C but did not give the alcohol in refluxing ether. V. M. Mićović and M. L. Mihailović, *J. Org. Chem.*, **18**, 1190 (1953).
(8) S. R. Sandler and W. Karo, "Organic Functional Group Preparations", Academic Press, New York and London, 1968, p 345.