

Synthesis, X-ray Structure, and Polymerization of 1-Vinyl-3-cyanomethylimidazolium Chloride

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Received 29 July 2000; accepted 2 December 2000

ABSTRACT: A new monomer, 1-vinyl-3-cyanomethylimidazolium chloride (**1**), was synthesized via quaternization of 1-vinylimidazole with chloroacetonitrile. The monomer was characterized using ¹H- and ¹³C-NMR as well as Raman spectroscopic techniques; its crystal structure was studied by means of X-ray analysis. The radical polymerization of **1** in aqueous solution brought about the formation of a polyelectrolyte that retains cyano groups intact and possesses film-forming properties. The structure of the polymer was characterized by NMR and Raman spectroscopy. The high viscosity of aqueous solutions and chemical structure of the polymer obtained suggest its possible applications as a thickener and/or detergent additive. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 499–509, 2001

Key words: 1-vinyl-3-cyanomethylimidazolium chloride; molecular structure; radical polymerization

INTRODUCTION

Homo- and copolymers of *N*-vinylimidazole (NVI) and its derivatives have attracted considerable interest in recent years.^{1–3} Particular attention has been focused on (co)polymers of quaternized NVI derivatives because of a promising set of valuable properties being exhibited by these substances. A wide variety of potential applications of polymeric imidazolium salts has been reportedly claimed in numerous patents and research papers. The copolymers of NVI quaternized mostly with alkyl halides and/or sulfates or sulfonates were reported to be useful as water- and electrolyte-retaining agents,^{4–6} paper-sizing agents^{7–11}; flocculating

agents^{8,12–15}; emulsifiers,^{8,10} dispersants,^{16,17} and stabilizers¹⁸; binders^{8,10,11,19,20} and adhesives^{8,10,11,21,22} including those possessing bacteria- and mold-resistant properties²³; thickeners^{16,17,24}; oil-recovery additives^{12,14,15,21}; soil improvers²¹; antistatic agents,^{8,15,25} conductive resins,^{12,13} and molten salt polymer electrolytes that can be used in fuel cells²⁶; anticorrosive agents^{8,21}; ion exchangers^{25,27}; ester saponification catalysts^{28,29}; biocides^{25,30}; enzyme immobilization enhancers,³¹ hypocholesterolemic agents,^{27,32} and antiheparin agents.³³ Finally, the copolymers containing *N*-vinylimidazolium moieties were shown to have great potential in cosmetics (e.g., in hair and skin care products^{12,14,15,21}) and detergents,^{21,22} particularly as dye-transfer inhibitors.^{34,35}

Modern detergents contain complex mixtures of additives performing various special functions during the washing process (e.g., dye transfer and salt incrustation inhibition, bleach activation,

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Journal of Applied Polymer Science, Vol. 82, 499–509 (2001)
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Table I Effect of the Nature and Concentration of the Solvent on Yield of the Product

Solvent	Concentration (%)	Crude Yield (%)	Recrystallization ^a	Isolated Yield (%)
None	0	49	+	35
Acetone	10	32	–	32
	30	13	–	13
	50	6	–	6
	10	33	–	33
Ethyl acetate	30	15	–	15
	50	7	–	7
	10	33	–	33
THF	30	17	–	17
	50	8	–	8
	10	35	+	17
Toluene ^b	30	19	+	7
	50	11	–	11
	10	39	+	12
Dioxane	30	23	–	23
	50	10	–	10
	10	38	+	17
Methylene chloride	30	18	–	21
	50	11	–	11

^a From a 2 : 1 v/v mixture of ethyl acetate with methanol.

^b Technical grade.

softening, etc.). Therefore, to develop efficient detergents, one should try to create multifunctional agents by imparting as many useful functions as possible into common additives.

Taking into account the above-mentioned observations along with the fact that quaternary ammonium salts containing cyanomethyl groups were recently reported to be promising substances for application as activators in peroxide-bleaching processes,^{36–42} it was reasonable to assume that polymeric *N*-vinylimidazolium salt bearing a cyanomethyl grouping at position (3) might hold promise as a multifunctional detergent additive, performing both dye transfer-inhibiting and bleach-activating functions. The present study reports on the synthesis, X-ray structure, and polymerization of a new monomer, 1-vinyl-3-cyanomethylimidazolium chloride.

EXPERIMENTAL

Materials and Methods

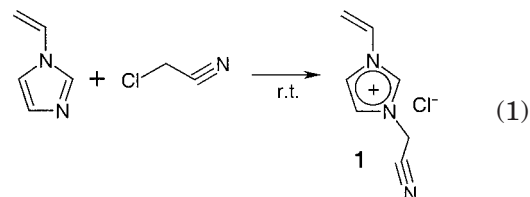
1-Vinylimidazole (*N*-vinylimidazole, BASF AG, Germany) and chloroacetonitrile (Fluka Chemie, Buchs, Switzerland) were distilled prior to use.

2,2'-Azobis(2-methylpropionamide) dihydrochloride (V-50; Wako Pure Chemicals, Tokyo, Japan) and solvents were used as received.

FT-Raman and NMR spectra were recorded on Bruker IFS 88 and Bruker DPX 360 spectrometers (Bruker Instruments, Billerica, MA), respectively. The X-ray structural study was performed on a Siemens P4 diffractometer (Cu K_α radiation, λ = 154.178 pm, graphite monochromator, θ/2θ scan mode; Siemens Medical Systems, South Iselin, NJ).

Synthesis of 1-Vinyl-3-cyanomethylimidazolium Chloride

1-Vinyl-3-cyanomethylimidazolium chloride (**1**) was synthesized via quaternization of *N*-vinylimidazole with chloroacetonitrile:



To a 100-mL flask, equipped with a magnetic stirring bar, were added 28.8 g (0.3 mol) of *N*-

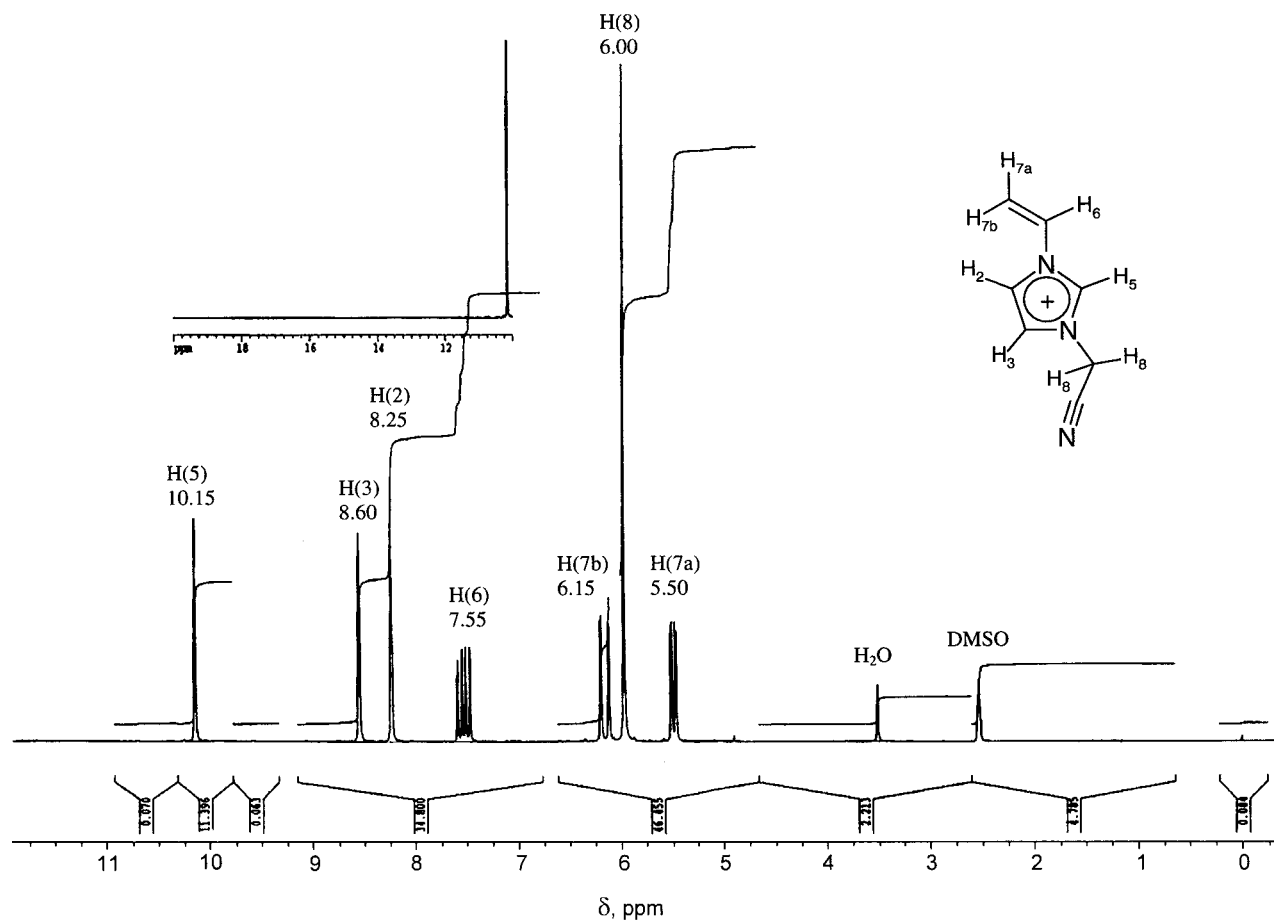


Figure 1 ^1H -NMR spectrum of **1** in $\text{DMSO-}d_6$.

vinylimidazole and 22.7 g (0.3 mol) of chloroacetonitrile with or without solvent (see Table I). The mixture was stirred at ambient temperature for a while and left standing over 2 days. The formation of crystals as needles or prisms was observed within a few hours. The crystalline product was filtered off and washed with the same solvent to afford **1** in a 6–39 yield, depending on concentration and the purity of the solvent (Table I).

1-Vinyl-3-cyanomethylimidazolium chloride (**1**), $\text{C}_7\text{H}_8\text{N}_3\text{Cl}$, $M = 169.61$, m.p. = 160°C (dec.). Calcd (%): C, 49.56; H, 4.72; N, 24.78; Cl, 20.94. Found: C, 49.6; H, 4.8; N, 24.9; Cl, 20.9. ^1H -NMR (in $\text{DMSO-}d_6$), δ (ppm): 10.15 (s, 1H), 8.60 (t, 1H), 8.25 (t, 1H), 7.55 (dd, 1H), 6.15 (dd, 1H), 6.00 (s, 2H), 5.50 (dd, 1H). ^{13}C -NMR (in D_2O), δ (ppm): 137.71, 130.59, 125.75, 122.98, 116.25, 113.36, 39.90. FT-Raman: 2257 cm^{-1} (CN).

Polymerization of 1-Vinyl-3-cyanomethylimidazolium Chloride

Radical polymerization of **1** was performed in an aqueous solution using V-50 [2,2'-azobis(2-meth-

ylpropionamide dihydrochloride)] as an initiator. In a typical procedure a 100-mL three-neck flask equipped with a reflux condenser, magnetic stirring bar, and thermometer was charged with 3 g of **1**, 0.01 g of V-50, and 10 mL of water, and flushed with nitrogen. The mixture was heated at 75°C for 3 h. Two additional portions of V-50 (0.01 g each) were added at 1-h intervals. Normally, the final product was an extremely viscous ("semiliquid") pale yellow mass that could subsequently be diluted with water and precipitated into acetone or methanol.

RESULTS AND DISCUSSION

Monomer Synthesis and Characterization

The NMR spectra are in full agreement with the expected structure of **1**. The ^1H - and ^{13}C -NMR spectra along with their peak assignments are shown in Figures 1 and 2, respectively.

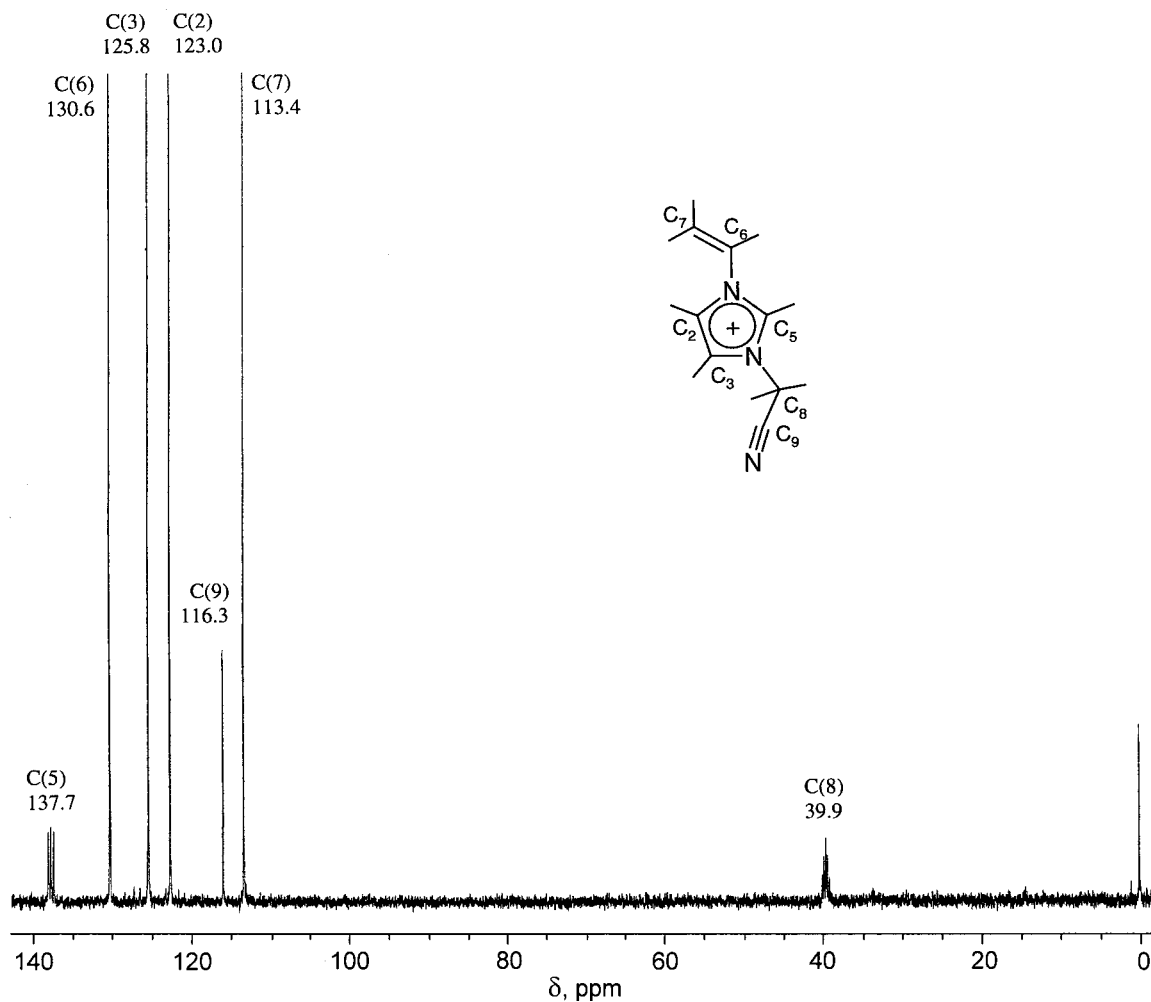


Figure 2 ^{13}C -NMR spectrum of **1** in D_2O .

The presence of the CN group in the salt **1** is clearly demonstrated by the Raman spectrum. The strong and sharp peak at 2257 cm^{-1} (Fig. 3) is characteristic for stretching vibrations of cyano groups. Surprisingly, the FTIR spectrum exhibited just a very weak absorption at 2260 cm^{-1} .

The purity of the product and, thus, the necessity of carrying out its recrystallization depend on the nature and concentration of the solvent. Generally, dioxane and methylene chloride gave the best isolated yields, whereas those obtained in acetone and tetrahydrofuran (THF) were somewhat lower. It should be noted that the purity of the solvent markedly affects both the quality and the yield of the ultimate crystalline product. For example, the quaternization reaction carried out in a 70% solution in technical-grade acetone

brings about the formation of the target compound contaminated with brown-colored side products in a 16% yield. When the reaction was conducted in a 50% solution, no crystalline product was formed.

When necessary, the product can be recrystallized, for instance, from a 2 : 1 v/v mixture of ethyl acetate with methanol, respectively, to afford colorless crystals of 1-vinyl-3-cyanomethylimidazolium chloride as needles or prisms. In this case, however, substantial losses of the product occurred, probably as a result of its partial oligomerization, and the recrystallization yield did not exceed 70% (normally 50–60%). The introduction of a small crystal of **1** (or few crystals) as a seed (nucleation centers) into the solution facilitates the formation of larger crystals.

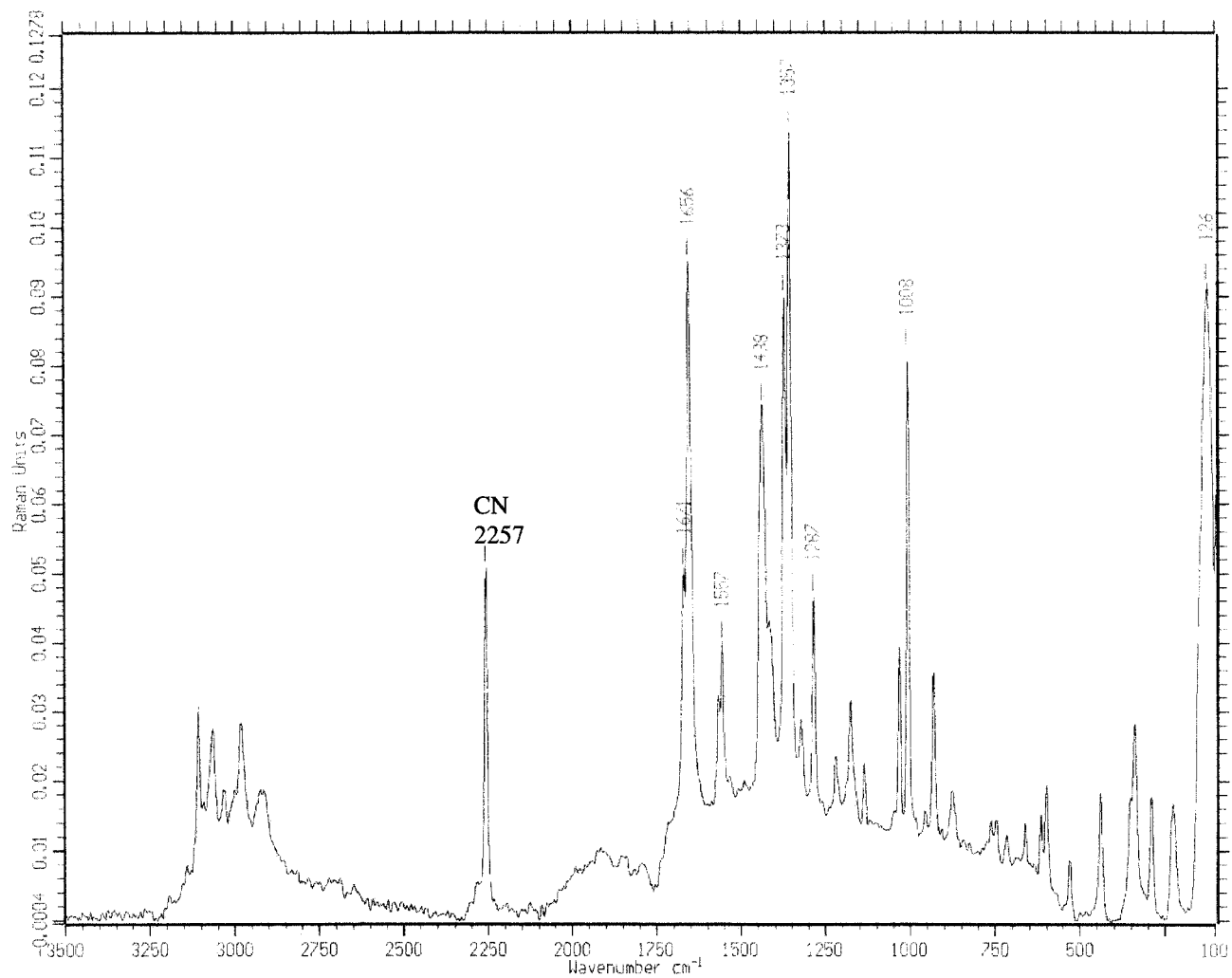


Figure 3 FT-Raman spectrum of 1.

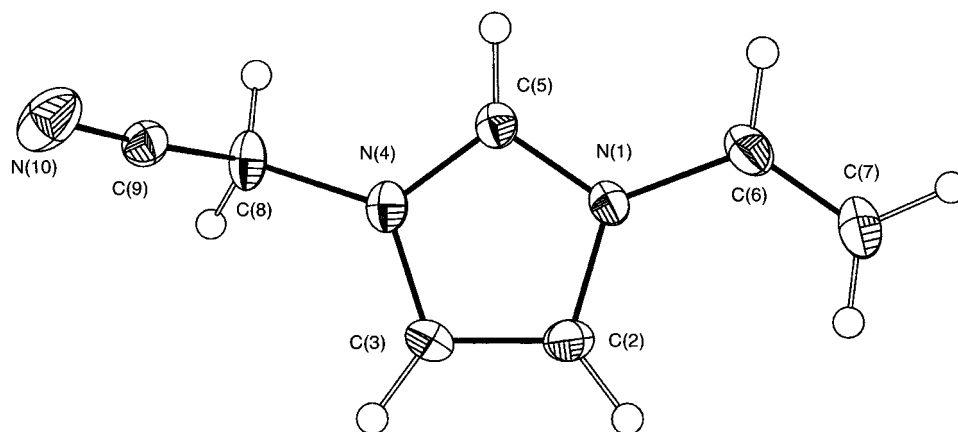


Figure 4 Molecular structure of 1 in crystal.

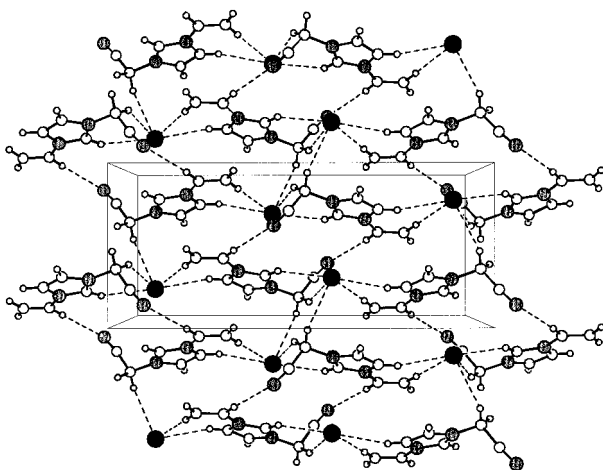


Figure 5 Crystal structure of salt **1** shown in the projection onto the *ab* plane. Main hydrogen bonds are shown as dashed lines; black circles denote chlorine; gray circles, nitrogen; large open circles, carbon; and smaller open circles, hydrogen atoms.

Molecular and Crystal Structure of 1-Vinyl-3-cyanomethylimidazolium Chloride

Surprisingly, the literature search revealed that **1**, a seemingly simple compound, has not been reported to date. It was therefore quite reasonable to study its molecular and crystal structure using X-ray diffraction analysis.

The unit cell parameters and intensities of 1065 independent reflections were measured at 203 ± 2 K within the $4.27 \leq 2\theta \leq 56.06$ range from a single crystal of $0.25 \times 0.25 \times 0.25$ mm in size. Some 1065 independent reflections with $I \geq 2\sigma(I)$ were included in the final calculations.

Table II Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{pm}^2 \times 10^{-1}$) in Structure **1**^a

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^b
Cl	1032 (1)	4175 (1)	2093 (1)	29 (1)
N(1)	22 (1)	6778 (1)	1690 (3)	23 (1)
C(2)	-888 (2)	7110 (1)	2300 (3)	28 (1)
C(3)	-1465 (2)	6532 (1)	2983 (3)	28 (1)
N(4)	-907 (2)	5859 (1)	2791 (3)	23 (1)
C(5)	-17 (2)	6018 (1)	1989 (3)	23 (1)
C(6)	877 (2)	7162 (1)	867 (4)	30 (1)
C(7)	973 (2)	7916 (2)	811 (4)	33 (1)
C(8)	-1207 (2)	5092 (1)	3464 (3)	28 (1)
C(9)	-1835 (2)	4650 (1)	2177 (3)	25 (1)
N(10)	-2290 (2)	4247 (1)	1250 (3)	38 (1)

^a Standard deviations are shown in parentheses.

^b *U*(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

The structure of **1** was solved by direct methods and refined by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms.⁴³ The location of the H atoms was determined from the difference Fourier synthesis and refined by the least-squares method.⁴³ The divergence factors for all observed reflections and for those with $I \geq 2\sigma(I)$ were found to be $R = 0.0385$; $R_w = 0.1009$ and $R = 0.0353$; $R_w = 0.0977$, respectively. The goodness of fit on F^2 was 1.118.

The crystals of the salt **1** are orthorhombic: $a = 1295.7 \pm 0.2$ pm, $b = 1725.6 \pm 0.2$ pm, $c = 733.92 \pm 0.10$ pm, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 1.6409 \pm 0.0004$ nm³, $Z = 8$, density d_{calc}

Table III Bond Lengths *d* and Angles ω in Molecule **1**

Bond	<i>d</i> ^a (pm)	Angle	ω ^a (°)
N(1)—C(5)	133.0 (3)	C(5)—N(1)—C(2)	108.83 (19)
N(1)—C(2)	138.6 (3)	C(5)—N(1)—C(6)	123.90 (19)
N(1)—C(6)	142.6 (3)	C(2)—N(1)—C(6)	127.27 (19)
C(2)—C(3)	134.4 (3)	C(3)—C(2)—N(1)	106.6 (2)
C(3)—N(4)	137.4 (3)	C(2)—C(3)—N(4)	107.2 (2)
N(4)—C(5)	132.4 (3)	C(5)—N(4)—C(3)	109.23 (19)
N(4)—C(8)	146.6 (3)	C(5)—N(4)—C(8)	124.6 (2)
C(6)—C(7)	130.7 (4)	C(3)—N(4)—C(8)	126.1 (2)
C(8)—C(9)	146.2 (3)	N(1)—C(5)—N(4)	108.1 (2)
C(9)—N(10)	113.8 (3)	C(7)—C(6)—N(1)	123.3 (2)
		C(9)—C(8)—N(4)	113.6 (2)
		N(10)—C(9)—C(8)	173.7 (2)

^a Standard deviations are shown in parentheses.

Table IV Anisotropic Displacement Parameters ($\text{pm}^2 \times 10^{-1}$) in Structure 1^a

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl	33 (1)	20 (1)	33 (1)	-2 (1)	-2 (1)	0 (1)
N(1)	27 (1)	16 (1)	26 (1)	-2 (1)	2 (1)	-3 (1)
C(2)	29 (1)	18 (1)	38 (1)	-3 (1)	0 (1)	3 (1)
C(3)	25 (1)	22 (1)	37 (2)	-1 (1)	3 (1)	2 (1)
N(4)	31 (1)	16 (1)	24 (1)	-1 (1)	-2 (1)	-6 (1)
C(5)	28 (1)	18 (1)	24 (1)	-3 (1)	0 (1)	-3 (1)
C(6)	30 (1)	28 (1)	33 (1)	-1 (1)	7 (1)	-4 (1)
C(7)	38 (1)	28 (2)	34 (1)	1 (1)	4 (1)	-11 (1)
C(8)	37 (1)	20 (1)	27 (1)	4 (1)	-1 (1)	-10 (1)
C(9)	28 (1)	16 (1)	31 (1)	2 (1)	-1 (1)	2 (1)
N(10)	46 (1)	20 (1)	47 (2)	-5 (1)	-16 (1)	3 (1)

^a The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + \dots + 2hka^{*}b^{*}U^{12}]$. Standard deviations for U^{ij} tensor values are shown in parentheses.

= 1.373 g/cm³ (for C₇H₈ClN₃, $M = 169.61$), space group *Pccn*.

The X-ray structure of molecule 1 and its packing in crystal are shown in Figures 4 and 5, respectively. Atomic coordinates, displacement parameters, bond lengths, and angles in 1-vinyl-3-cyanomethylimidazolium chloride are presented in Tables II through VI.

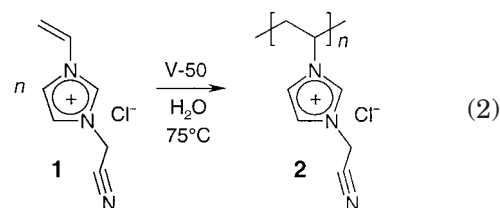
Polymerization of 1-Vinyl-3-cyanomethylimidazolium Chloride

The polymerization of 1 outlined in eq. (2) occurs readily and relatively fast. However, the molecular weight and, possibly, the yield depend strongly on the concentration of the monomer. The best results (highest viscosities) were obtained in a 20 to 25 wt % concentration range.

Table V Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($\text{pm}^2 \times 10^{-1}$)

	x	y	z	$U(\text{eq})^a$
H(2)	-1067	7638	2247	32 (7)
H(3)	-2127	6578	3495	39 (7)
H(5)	498	5657	1683	30 (6)
H(6)	1399	6858	338	51 (8)
H(7A)	461	8233	1331	43 (5)
H(7B)	1552	8141	252	43 (5)
H(8A)	-581	4795	3742	43 (5)
H(8B)	-1594	5155	4602	43 (5)

^a Standard deviations are shown in parentheses.



The formation of insoluble partially crosslinked gels was observed at higher concentrations. At concentrations lower than 20 wt % only oligomeric products exhibiting low viscosities were formed.

An attempt to measure intrinsic viscosity in an aqueous NaCl solution failed because the polymer

Table VI Torsion Angles φ in Structure 1

Angle	φ^a (°)
C(5)—N(1)—C(2)—C(3)	0.5 (3)
C(6)—N(1)—C(2)—C(3)	-179.6 (2)
N(1)—C(2)—C(3)—N(4)	0.2 (3)
C(2)—C(3)—N(4)—C(5)	-0.9 (3)
C(2)—C(3)—N(4)—C(8)	175.5 (2)
C(2)—N(1)—C(5)—N(4)	-1.1 (2)
C(6)—N(1)—C(5)—N(4)	179.05 (19)
C(3)—N(4)—C(5)—N(1)	1.2 (2)
C(8)—N(4)—C(5)—N(1)	-175.2 (2)
C(5)—N(1)—C(6)—C(7)	-170.0 (2)
C(2)—N(1)—C(6)—C(7)	10.1 (4)
C(5)—N(4)—C(8)—C(9)	-96.0 (3)
C(3)—N(4)—C(8)—C(9)	88.2 (3)
N(4)—C(8)—C(9)—N(10)	154 (2)

^a Standard deviations are shown in parentheses.

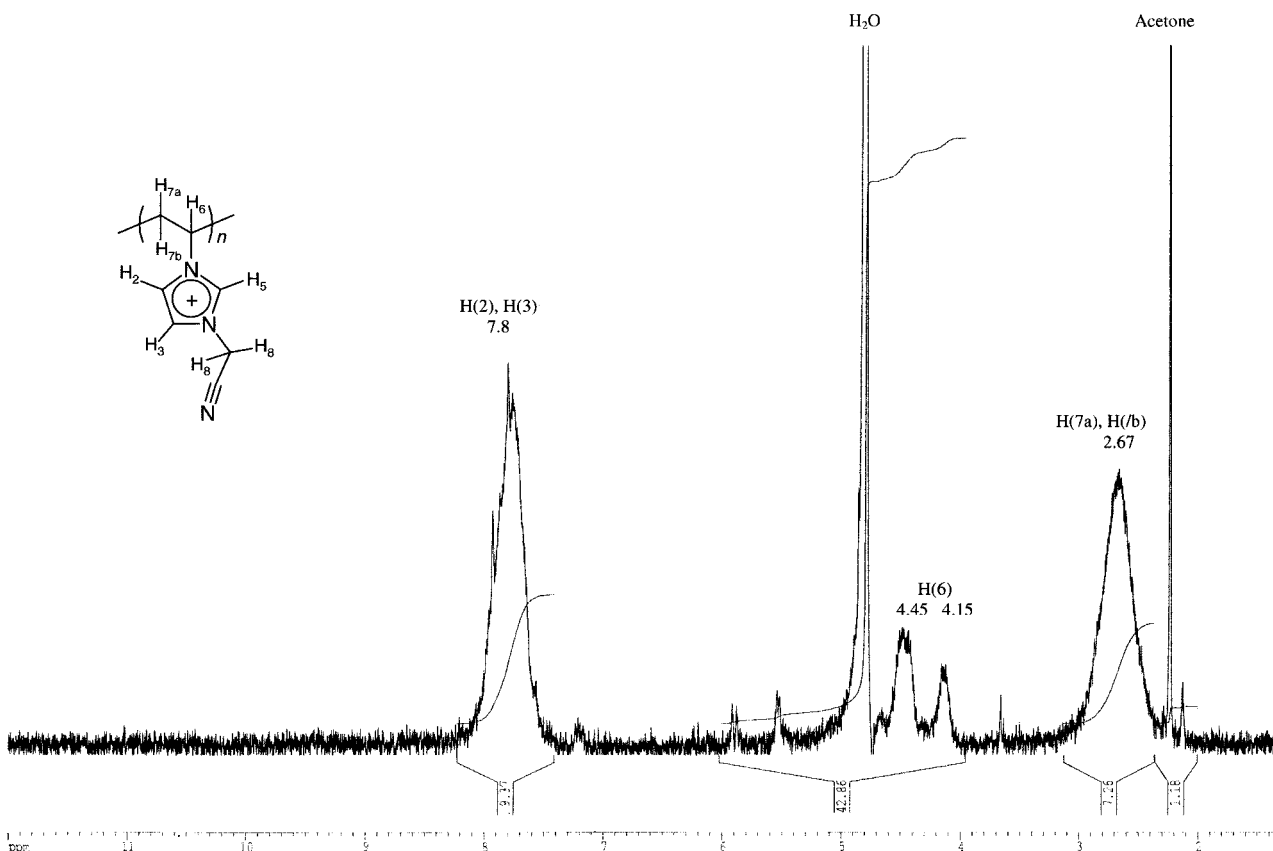


Figure 6 ^1H -NMR spectrum of polymer **2** in D_2O .

2 is not soluble in this solution. The addition of NaCl to the aqueous solution of **2** caused precipitation of the polymer. The intrinsic viscosity

measured in pure water was found to be 36.8 dL/g. This result, however, does not allow one to correctly estimate the molecular weight of **2** be-

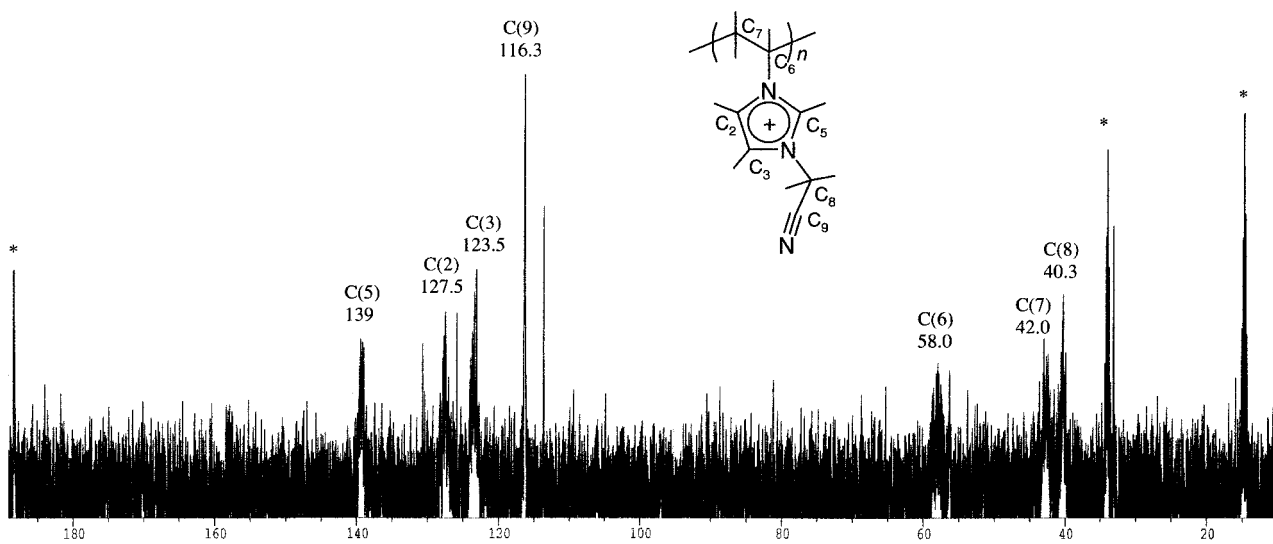


Figure 7 ^{13}C -NMR spectrum of polymer **2** in D_2O . Asterisk indicates peaks of sodium 2-trimethylsilylpropionate used as an internal standard.

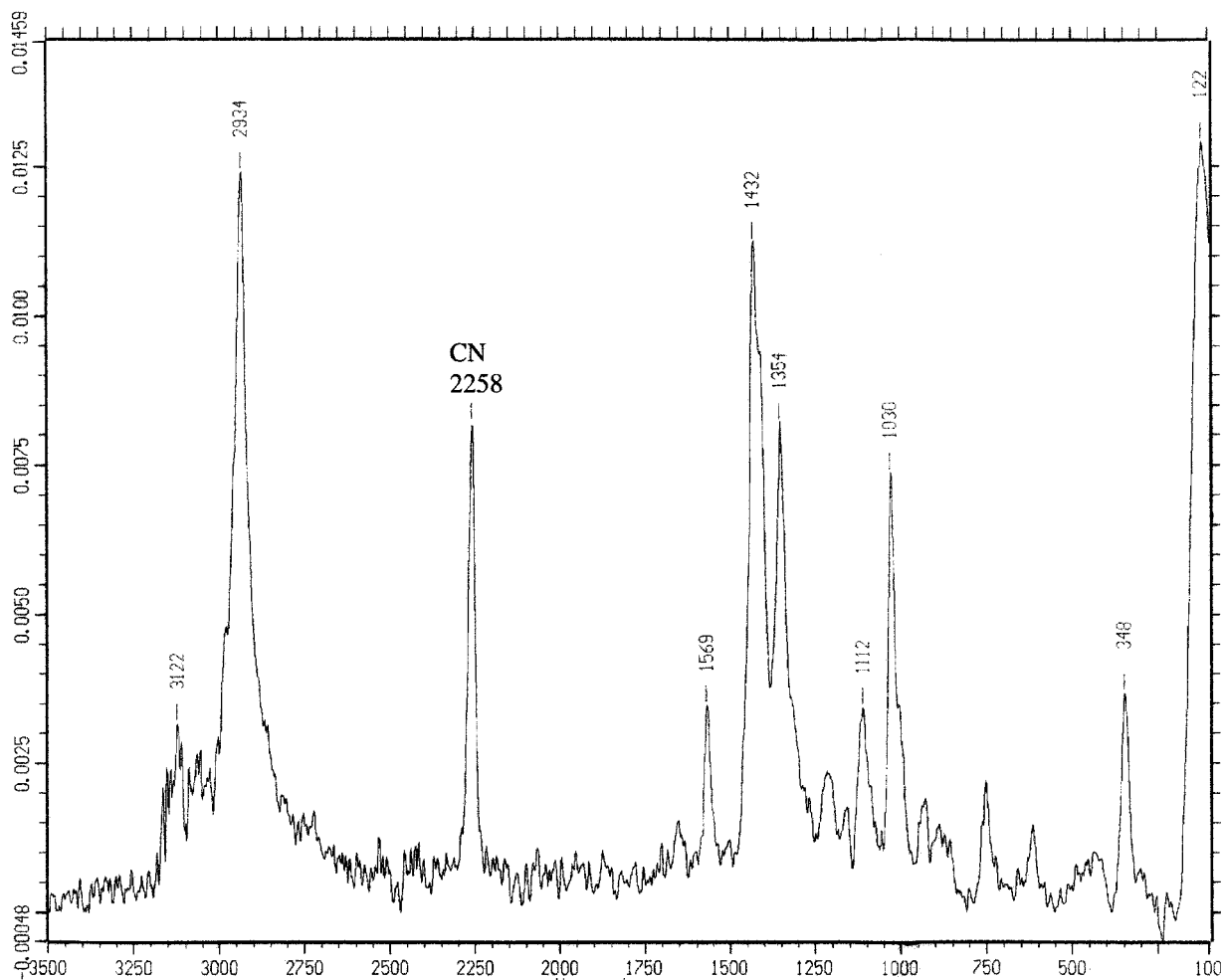


Figure 8 FT-Raman spectrum of polymer 2.

cause of its polyelectrolytic nature. Using a membrane osmometry technique, the molecular weight was found to be $M_n = 120,000$ g/mol.

The yield of the product precipitated into acetone was always beyond 100% because both polymer and monomer **1** are insoluble in acetone, and it was difficult to properly dry the product from water. The precipitation into methanol, which is a good solvent for the monomer, normally afforded the product as a fine white powder in about 80% yield.

The structure of the product was confirmed by NMR spectra, which are consistent with conjectured formula **2** in eq. (2). The ^1H -NMR spectrum (Fig. 6) exhibits a set of broadened peaks attributable to protons H(7a,7b) at 2.67 ppm, H(6) at 4.15 and 4.45 ppm (possible stereoisomers), as well as H(2) and H(3) both at 7.8 ppm. The protons H(8) are not detectable in the spectrum. Appar-

ently, they can contribute to the large peak of water near 4.8 ppm or may not be visible as a result of the tentative hydrogen-deuterium exchange. The latter also goes for the H(5) proton. Two small peaks at 5.65 and 5.95 ppm are attributable to protons H(7a,7b) in the monomer.

The ^{13}C -NMR spectrum (Fig. 7) shows peaks at 40.3, 42.0, 58.0, 116.3, 123.5, 127.5, and 139 ppm, attributable to the carbon atoms C(8), C(7), C(6), C(9), C(3), C(2), and C(5), respectively.

The Raman spectrum demonstrates a strong and sharp line at 2258 cm^{-1} (Fig. 8), suggesting that the cyano group of the starting monomer remains intact during polymerization.

CONCLUSIONS

We have demonstrated the possibility, in principle, of synthesizing polymeric imidazolium salt

bearing the cyanomethyl grouping as a quaternizing substituent. A new monomer, 1-vinyl-3-cyanomethylimidazolium chloride, was synthesized and polymerized in aqueous solution, affording a water-soluble, high molecular weight polymer in high yield. Very high viscosity observed in moderately diluted (~ 30%) aqueous solutions of **2** suggests the existence of extensive intermolecular hydrogen bonding. This conjecture is substantiated by the presence of intermolecular hydrogen bonds in the crystals of monomer **1** (Fig. 5). Therefore, poly(1-vinyl-3-cyanomethylimidazolium chloride) can be useful as a thickener for aqueous solutions and dispersions. Furthermore, a particular chemical structure allows one to speculate that homo- and copolymers of 1-vinyl-3-cyanomethylimidazolium chloride may turn out promising additives for detergents as dye-transfer inhibitors and/or as peroxide-bleaching activators. The investigation is presently under way.

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