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Polycationic Salts V [1]. ^{15}N NMR Spectra of Amines, Ammonium Salt Monomers, and Polymers of Styrene Based Trialkylammonium Salts[a]

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Summary. ^{15}N NMR spectroscopy was found to be essential for the detailed characterization of tertiary amines, vinylbenzylammonium salts, and polymers derived from these compounds. It proved important for the characterization of low 2-ionene oligomers and vinylbenzylammonium salts derived thereof as well. The polymers of these novel monomers were also characterized and identified.

Keywords. ^{15}N NMR spectroscopy; Tertiary amines; Quaternary ammonium salts; 2-Ionene oligomers; Polycationic salts.

Introduction

The characterization of monomeric chemical compounds and polymers derived from them has been increasingly dependent on NMR spectroscopy [2,3]. ^{1}H and ^{13}N NMR spectroscopy satisfied most needs. Other NMR spectroscopic disciplines are used whenever it is necessary or essential. ^{15}N NMR spectroscopy has become increasingly desirabile for the characterization of nitrogen containing compounds, such as amines and ammonium compounds.

The carbon-13 isotope suitable for NMR spectroscopy has an abundance of 1.1%, nitrogen isotope ^{15}N has one of 0.37%. Whereas ^{13}C NMR spectroscopy has become a routine method, ^{15}N NMR spectroscopy at natural abundance is still relatively rare [3–5], in particular for non-protonated N, and is used only when unavoidable. It usually requires the accumulation of many thousands of acquisitions which means a demand of many hours or even days for obtaining a good spectrum.

Techniques have been developped that allow to cut these extensive acquisition times to manageable time periods, including the addition of ferric chloride to

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[a] Dedicated to Prof. Dr. *Karl Schlögl* on the occasion of his 75th birthday

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overcome the *Overhauser* effect [6]. It was our objective to collect and analyze ^{15}N NMR spectra of a number of tertiary amines, ammonium salts, polymerizable ammonium salts, and their polymers [7]. We also attempted to attain a ^{15}N NMR spectrum of a lightly crosslinked polymers, free of monomer or oligomers.

Results and Discussion

^{1}H NMR and ^{13}C NMR spectroscopy was found to be of limited value for the determination of the structure the vinylbenzylammonium salts [8–11] and their polymers and of 2-ionene oligomers. Vinylbenzylammonium salts [12] as well as their polymers have been synthesized previously. However, ^{15}N NMR spectroscopy proved to be an invaluable tool due to its power of clearly identifying the various amino- and/or ammonium groups.

Tertiary amines and ammonium salts

The first phase of this characterization was to identify simple tertiary amines and ammonium salts. Since ^{15}N chemical shifts extend over a range of 1000 ppm, more than five times the width of the chemical shift values of ^{13}C and one hundred times that of the chemical shift values of ^{1}H, a much greater structural discrimination can be achieved with this nucleus. This feature enabled us to distinguish between fine structures that ^{1}H and ^{13}C NMR spectroscopy were unable to resolve.

Tertiary amines were initially investigated during our preliminary investigation to determine the effect of the *n*-alkyl substituent on tertiary amines. Part of the work consists of reinvestigations under our experimental conditions. The amines were

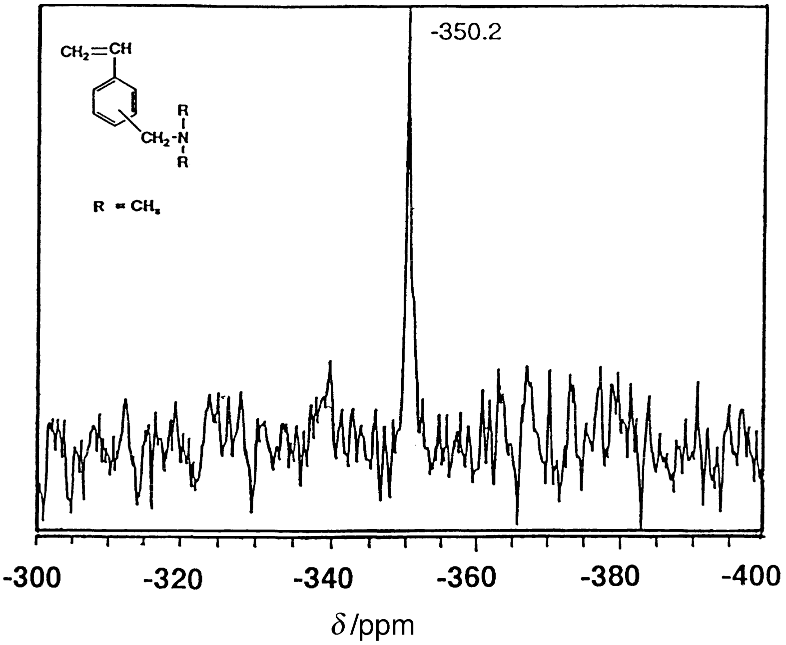

Fig. 1. ^{15}N NMR spectrum of vinylbenzyldimethylamine

Table 1. ^{15}N NMR chemical shift values for tertiary amines

	Chemical shift (ppm)	Literature value (ppm)	$FeCl_3 \cdot 6H_2O$ (mg)
Trimethylamine (10.0 *M* in H_2O)	−331.7	−332.0 [3]	–
2 (neat)	−340.9	–	–
3 (10.0 *M* in H_2O)	−350.5	–	–
4 (neat)	−356.8	–	–
5	−356.9	–	–
6 (10.0 *M* in MeOH)	−355.2	–	–
7 (neat)	−357.9	–	–
8 (4.0 *M* in MeOH)	−370.5	–	20
9 (5.0 *M* in MeOH)	−350.2	–	20
10 (neat)	−360.5	–	–

triethylamine (**1**), tri-*n*-butylamine (**2**), N,N-dimethylethylamine (**3**), N,N-dimethyl-*n*-octylamine (**4**), N,N-dimethyl-*n*-dodecylamine (**5**), N,N-dimethylamino-ethanol (**6**), N,N,N′,N′-tetramethylethylenediamine (**7**), 1,4-diazobicyclo[2.2.2]octane (**8**), vinylbenzyldimethylamine (**9**) (Fig. 1), and 2-dimethylaminoethyl methacrylate (**10**) (Table 1).

Table 1 shows the ^{15}N NMR chemical shift values of some of the tertiary amines. **8** has the most pronounced shielding effect of all compounds investigated with a δ value of −370.5 ppm.

10 also has a strong shielding effect due to its *n*-alkyl group and the carboxamide group, producing a ^{15}N NMR chemical shift value of −360.5 ppm. Simple tertiary amines, such as **4**–**7** showed chemical shifts characteristic for *n*-alkyl substituted amines. Their ^{15}N chemical shift values are all located in the region of −356.0 to −358.0 ppm. The tertiary amines displaying the highest deshielding effect of the nitrogen atom were **1**, **2**, **3**, and **9** which all have ^{15}N chemical shift values in the range of −331.0 ppm to −350.0 ppm. The effect of the *n*-alkyl substituents varies most between compounds **1** and **2**. The shorter *n*-alkyl chain in **1** deshields the N atom by more than 9 ppm as compared to **2**. In addition to *n*-alkyl substituents, aryl units can influence the ^{15}N chemical shift of a tertiary amine, resulting in a shift value of −350.2 ppm for **9**.

The aromatic amine N-methylimidazole was measured neat or in highly concentrated aqueous, methanol, or chloroform solutions with molarities of 10 or greater. Table 2 shows the corresponding chemical shifts values.

The ^{15}N chemical shift values obtained for N-methylimidazole are similar to those reported for other heterocyclic tertiary amines [6]. The ^{15}N chemical shift values of the nitrogen atom in position 1 of N-methylimidazole [14] are essentially the same in the three solvents, but the nitrogen atom in position 3 of the imidazole ring is substantially shifted in water and methanol, possibly due to some hydrogen bonding.

Tetraalkyammonium salts were chosen to study the possible influence of the counterion on the ^{15}N chemical shift values of the ammonium nitrogen.

Table 2. ^{15}N NMR chemical shift values of N-Methylimidazole

	Chemical shift (ppm)	Literature value (ppm)
Neat	−218.7 (N1)	–
	−125.5 (N3)	
H_2O	−217.1 (N1)	–
	−134.0 (N3)	
MeOH	−218.1 (N1)	–
	−127.8 (N3)	
$CHCl_3$ [16]	−219.9 (N1)	−221.3 (N1)
	−121.9 (N3)	−125.5 (N3)

Table 3. ^{15}N NMR chemical shift values of tetra-*n*-alkylammonium halide salts

	Chemical shift (ppm)	Literature value (ppm)	$FeCl_3 \cdot 6H_2O$ (mg)
$MeNO_2$ (neat)	0.0	0.0	–
H_2NCHO (neat)	−267.8	−267.8 [4]	–
NMe_4Cl (3.0 *M* in H_2O)	−337.1	−336.7 [5]	20
NMe_4Br (3.0 *M* in H_2O)	−337.0	–	20
NEt_4Cl (10.0 *M* in H_2O)	−316.5	–	20
NEt_4Br (6.0 *M* in H_2O)	−316.7	–	20
NEt_4l (0.5 *M* in H_2O)	−316.6	–	20

Tetramethylammonium chloride and bromide as well as tetraethylammonium chloride, iodide, and bromide were chosen because of their high water solubility. The ^{15}N NMR chemical shifts values revealed that the counterion is of no significant effect; the type of *n*-alkyl substituents, however showed a substantial influence (Table 3). The ethyl groups of the tetraethylammonium chloride, bromide, and iodide salts showed an upfield shift of about 21 ppm, indicating a deshielding effect for the N-ethyl groups as compared to the N-methyl groups.

Vinylbenzyltrialkylammonium chlorides

The products of the reaction of vinylbenzyl chloride with tertiary amines were also characterized by ^{15}N NMR spectroscopy to identify the influence of counter ions or alkyl substituents on the ^{15}N NMR shift values of the ammonium compounds. These studies revealed that the type of alkyl groups had a profound influence on the ^{15}N NMR shifts, similar to simple tertiary amines and tetra-*n*-alkyl ammonium salts. Vinylbenzyltri-*n*-alkyl ammonium chlorides synthesized previously [1, 8–12] were examined first with respect to the influence of the alkyl and benzyl

Table 4. ^{15}N NMR shift values of vinylbenzyltri-*n*-alkyl ammonium chloride monomers ($FeCl_3 \cdot 6H_2O$, 20 mg)

	Chemical shift (ppm)
11	−330.0
12	−312.9
13	−329.0
14	−313.6
15	−324.2
16	−313.0
17	−324.5
18	−324.5
19	−196.8, −208.6
20	−323.9

substituents on the nitrogen atom. Solvent effects were also considered but did not play a significant role for the chemical shift of the compounds.

First, benzyltrimethylammonium chloride (**11**) and benzyltriethylammonium chloride (**12**) were investigated and found to have chemical shift values of −330.0 and −312.9 ppm. Vinylbenzyltri-*n*-alkylammonium chloride monomers were investigated further. Vinylbenzyltrimethylammonium chloride (**13**) had a chemical shift value similar to **11**, the δ-value of vinylbenzyltriethylammonium chloride (**14**) was similar to that of **12** (Table 4).

The ^{15}N NMR spectra of vinylbenzyltrimethylammonium chloride (**13**, Fig. 2), vinylbenzyltriethylammonium chloride (**14**, Fig. 3), vinylbenzyldimethylethylam-

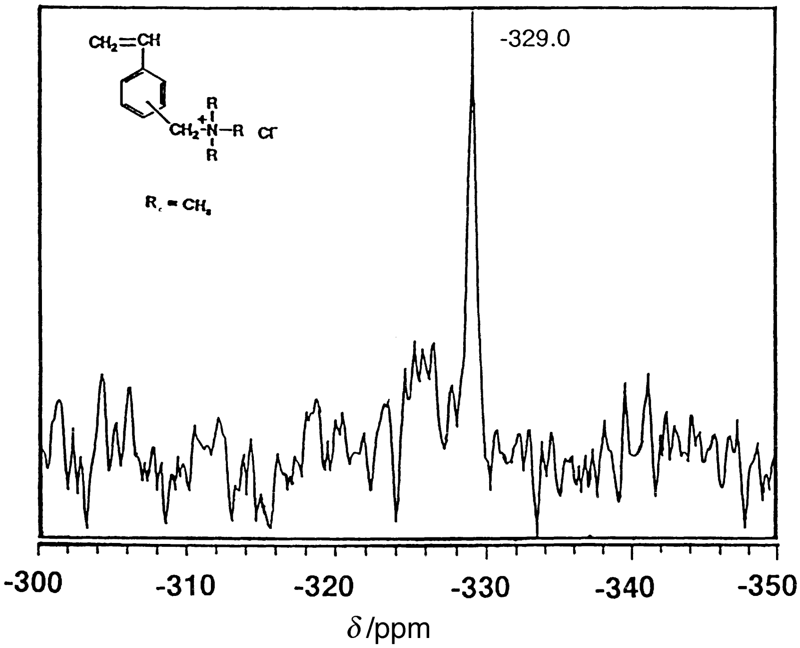

Fig. 2. ^{15}N NMR spectrum of vinylbenzyltrimethylammonium chloride

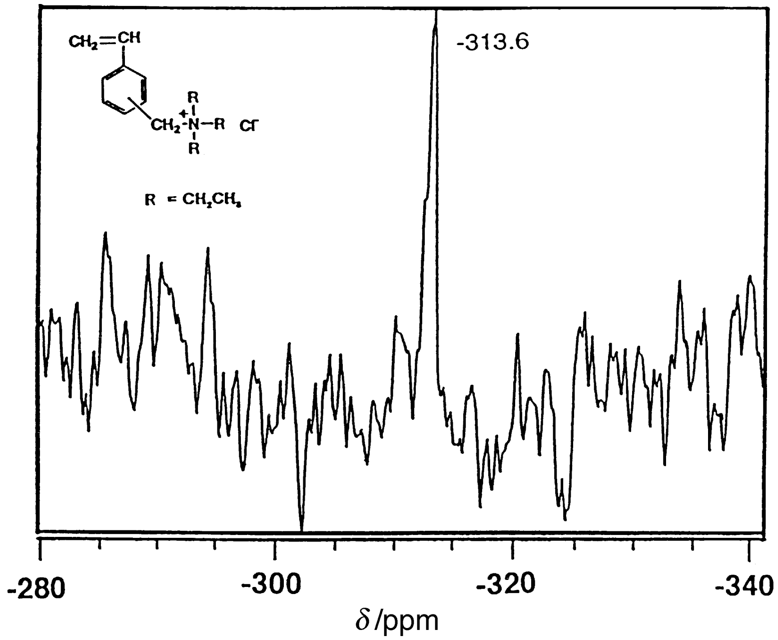

Fig. 3. ^{15}N NMR spectrum of vinylbenzyltriethylammonium chloride

monium chloride (**15**), vinylbenzyltri-*n*-butylammonium chloride (**16**), vinylbenzyldimethyloctylammonium chloride (**17**), vinylbenzyldimethyl-*n*-dodecylammonium chloride (**18**), and vinylbenzyl-N-methylimidazolium chloride (**19**) were measured. **14** and **16** were the most deshielded ones of the vinylbenzyltri-*n*-alkylammonium chlorides, appearing at −313.6 and −313.0 ppm due to the influence of the ethyl and *n*-butyl groups attached to the nitrogen atom. **13**, **15**, **17**, and **18** were the most shielded compounds because of the influence of the methyl substituent. In all cases, a trimethyl and/or a di-*n*-methyl group are attached to the nitrogen atom. Their influence causes a shielding effect of up to 16 ppm. The most shielded compound **13** resonates at −329.0 ppm. **17** and **18** are slightly deshielded by about 4.5 ppm, appearing at −324.5 ppm because of the influence of one long aliphatic group, and **15** is found at −324.2 ppm. N,N-Divinylbenzyl-N,N,N′,N′-tetramethylethylenediammonium dichloride (**20**) gave a value of −323.9 ppm, deshielded by approximately 6.0 ppm from **13**.

In each case, the spectra were examined for a possible solvent effect. **17** and **18** were measured in methanol (5.0 *M*) because of their lower solubility in water. **13** was examined in both water and methanol (5.0 *M*), giving an insignificant chemical shift difference (−329.2/−329.0 ppm).

Compound **19** with two nitrogen atoms in the molecule was also investigated; its ^{15}N chemical shift values are −208.7 and −195.8 ppm. The identification of these peaks was carried out by first preparing the 1,3-dimethyl-imidazolium iodide [6] and measuring its ^{15}N NMR spectrum. In this case, the N1 and N3 nitrogen atoms are equivalent and give one peak at −210.4 ppm. When the counter ions were changed, there was only an insignificant difference between iodide and chloride (1.7 ppm) For **19** the N1 nitrogen appeared at −195.8 ppm, whereas the N3 nitrogen was found at −208.7 ppm, shielded from the benzylic nitrogen atom by 13 ppm.

Polyvinylbenzyltrialkylammonium chlorides

Polymers prepared from the corresponding vinylbenzyltri-*n*-alkylammonium chloride monomers yielded several new pieces of information from their ^{15}N NMR spectra (Table 5). The polymers examined were poly(vinylbenzyltrimethylammonium chloride) (**21** Fig. 4), poly(vinylbenzyltriethylammonium chloride (**22**), poly(vinylbenzyldimethylethylammonium chloride) (**23**), poly(vinylbenzyltri-*n*-butylammonium chloride (**24**), poly(vinylbenzyldimethyloctylammonium chloride) (**25**), poly(vinylbenzyldimethyl-*n*-dodecylammonium chloride) (**26**), and poly(vinylbenzyl-N-methylimidazolium chloride) (**27**). The experiments to determine their exact ^{15}N chemical shifts required concentrated solutions of the polymers. Several of

Table 5. ^{15}N NMR chemical shift values of poly(vinylbenzyltri-*n*-alkylammonium chloride)

	Chemical shift (ppm)	$FeCl_3 \cdot 6H_2O$ (mg)
21	−329.2	20
22	−313.6	20
23	−324.5	20
24	−312.5	–
25	−324.2	–
26	−324.5	–
27	−196.0 (N1) −209.0 (N3)	–

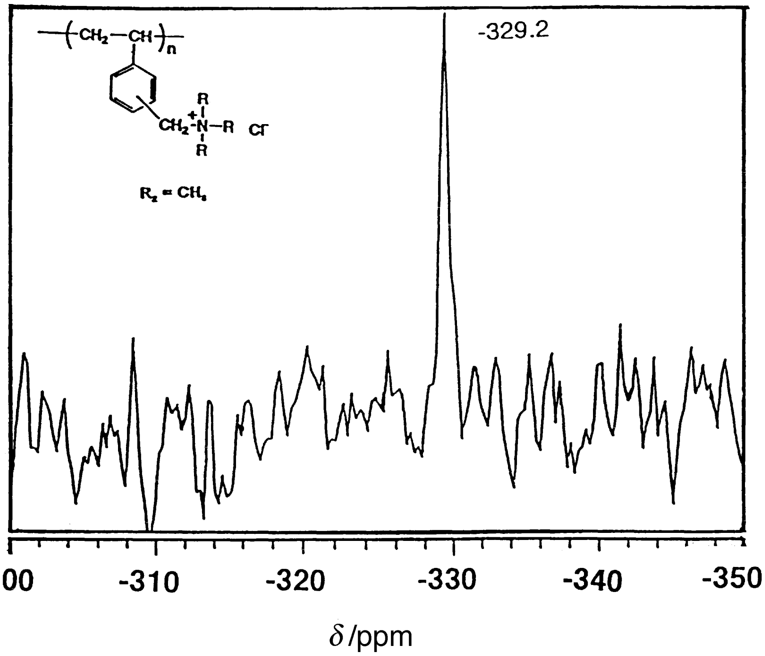

Fig. 4. ^{15}N NMR spectrum of poly(vinylbenzyltrimethylammonium chloride)

the polymers were readily water soluble and could be measured in concentrations of 1.0 *M* and slightly above. The monomers were measured in concentrations of 5.0 *M* and above for both aqueous and non aqueous solutions; acquisition times for these samples were in the order of 12 hours. The aqueous solutions prepared for **21** (2.0 *M*), **22** (1.0 *M*), and **23** (1.0 *M*) required acquisition times of 24 to 36 hours. The polymer spectra were quite similar to those of the monomers with the expected slight broadning usually associated with polymer samples.

Other polymers were measured in methanol. **25**, **26**, and **27** all (1.0 *M*) showed no difference in their ^{15}N chemical shifts values as compared to the monomers. **24** (1.0 *M*) in dichloromethane had a broader line width than the other polymers due to gelation in the NMR tube and required 200000 scans (72 h).

Copolymers were also investigated by ^{15}N NMR spectroscopy. First, a 1:1 aqueous mixture of homopolymers of **21** and **22** were investigated and gave ^{15}N values of −330.0 and −313.5 ppm, respectively. A 1:1 copolymer of **21** and **22** showed the same values. Also a copolymer of **21** and **23** gave the chemical shift values of the two homopolymers. Three copolymers were then investigated: **21/22** (−329.9 and −313.5 ppm), **21/23** at (−330.4 and −324.9 ppm), and **23/22** (−313.6 and −330.4 ppm). The chemical shift values obtained demonstrated that the copolymers could be investigated accurately by ^{15}N spectroscopy and that the monomer composition can be estimated. It was also shown that polymer samples with molecular masses of more than 10^6 Daltons can give reliable ^{15}N NMR spectra.

2-Ionene oligomers, vinylbenzyl-2-ionenes, and polymers

Our ultimate objective was to attach the 2-ionene oligomer $H_2N\text{-}CH_2CH_2N^+Me_3Cl^-$ to vinylbenzylchloride, polymerize the vinylbenzylammonium salts [9,12], and characterize the monomers and polymers by ^{15}N NMR spectroscopy. ^{15}N NMR identification of the 2-ionene oligomers unimer, dimer, and trimer were possible, and tertiary amino and ammonium nitrogens could be easily distinguished. ^{15}N enrichment was found not to be necessary because of the high water solubility of these compounds (concentrations of 10.0 *M* were possible).

The key and starting compound for the ionomer series was N,N,N′,N′-tetramethylethylene diamine with a single ^{15}N NMR peak at 357.9 ppm (Fig. 5). Ethylene *bis*(trimethylammonium iodide) (**28**) had a chemical shift value of −331.5 ppm, ethylene *bis*-(dimethylethylammonium bromide) one of −326.7 ppm because the ethyl group has the tendency of shifting to lower values. N,N,N′N′,-Tetramethyl-1,4-azacyclohexane dichloride has a shift value of −334.9 ppm. It is a very important compound because it can occur as side product in all 2-ionene studies.

Ethyl 2-ionene bromide showed two peaks at −327.0 and −356.4 ppm. The value at −356.4 ppm was identified as the dimethylamino nitrogen, shielded by 29.4 ppm with respect to the dimethylethyl ammonium nitrogen at −327.0 ppm. Methyl 2-ionene iodide (Fig. 6) also afforded two peaks at −331.2 and −357.1 ppm, the signal at −331.2 ppm belonging to the trimethylammonium nitrogen and the resonance at −357.1 ppm being attributed to the dimethylamino nitrogen atom.

2-Bromoethyl-2-ionene bromide had chemical shifts of −326.5 and −324.1 ppm. The peak at −326.5 ppm is due to the dimethylethylammonium nitrogen, the dimethylbromoethylene ammonium group is observed at −324.1 ppm. 2-Chloro-2-

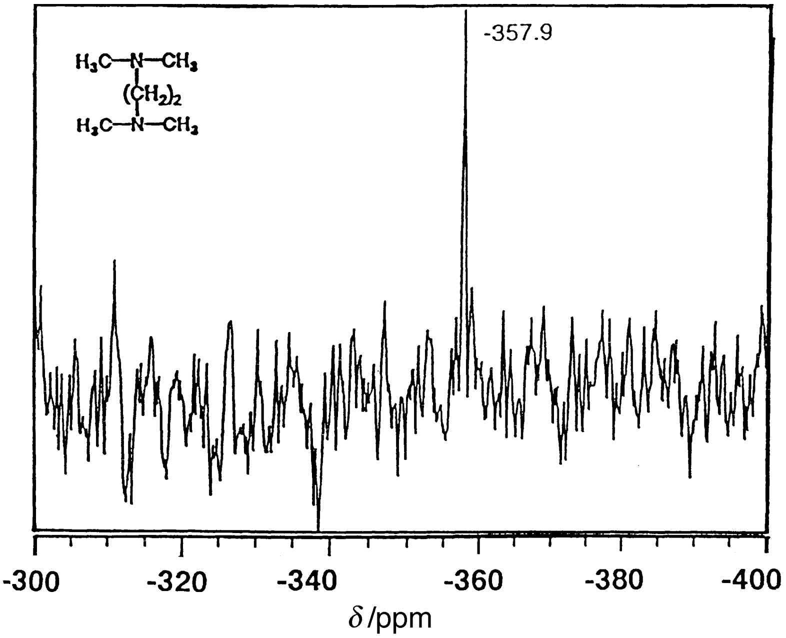

Fig. 5. ^{15}N NMR spectrum of N,N,N′,N′-tetramethylethylene diamine

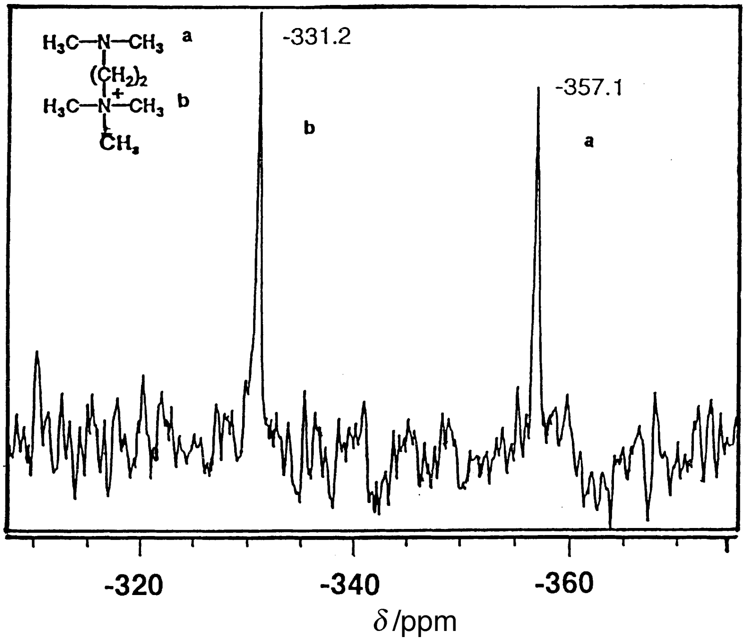

Fig. 6. ^{15}N NMR spectrum of 2-ionene iodide oligomer

ionene chloride ($ClCH_2CH_2N^+Me_2EtCl^-$) showed a single peak at −325.5 ppm (Table 6).

The ^{15}N NMR spectrum of the expected 2,2-ionene chloride showed 4 peaks at −325.3, −332.6, −346.0, and −347.3 ppm. In the expected 2,2,2-ionene bromide

Table 6. ^{15}N NMR chemical shift values of 2-ionene and related compounds (δ/ppm)

	-NMe$_2$		-NMe$_2$Et		-NMe$_3$
A-A	−357.9				
Et*A*-*A*Et 2Br$^-$					−326.7
Me*A*-*A*Me 2I$^-$					−331.5
-*A*-*A*- 2Br$^-$					−334.9
Br-A-AMe Br$^-$	−356.1				−327.0
A-*A*Me l$^-$	−357.1				−331.2
A-*A*Et Br$^-$	−356.4		−327.0		
Et*A*-*A*Et 2Br$^-$			−326.7		
Cl-*A*Me Cl$^-$				−325.5	
Br-*A*-AEt 2Br$^-$		−324.1		−326.5	

A = -N(CH$_3$)$_2$; *A* = -N$^+$(CH$_3$)$_2$-; - = -CH$_2$CH$_2$-; Me = -CH$_3$; Et = -CH$_2$CH$_3$

Table 7. ^{15}N NMR chemical shift values of vinylbenzyl-2-ionenes and their polymers

	-NMe$_2$		N(alk)$_3$		-NMe$_2$Et		-NMe$_3$
VBzAM	−350.2						
VBz*A*Me Cl$^-$							−329.0
PVBz*A*Me Cl$^-$							−329.2
VBz*A*Et Cl$^-$					−324.2		
PVBz*A*Et Cl$^-$					−324.5		
VBz*A*Bu Cl$^-$		313.0					
PVBz*A*Bu Cl$^-$			312.5				
VBz*A*-A Cl$^-$	356.5					−324.1	
VBz*A*-*A*Et 2Br$^-$				−323.9		−326.0	
VBz*A*-*A*Et 2Cl$^-$				−324.5		−327.2	
PVBz*A*-*A*Et 2Cl$^-$				324.7			−327.4
VBz*A*-*A*Me 2I$^-$				−324.5			−332.2
Copolymers:							
VBz*A*Me/VBz*A*Et					324.9		−330.4
VBz*A*Et$_3$/VBz*A*Et				−313.6	−324.7		

A = -N(CH$_3$)$_2$; *A* = -N$^+$(CH$_3$)$_2$-; - = -CH$_2$CH$_2$-; P = Poly-; Me = -CH$_3$; Et = -CH$_2$CH$_3$; alk = -*n*-alkyl; Bz = -C$_6$H$_4$CH$_2$-; Bu = -*n*-CH$_2$CH$_2$CH$_2$CH$_3$

there were 5 peaks −326.2, −331.4, −351.0, −354.1, and −357.6 ppm), undoubtedly pointing to starting material and, possibly, to side reaction products.

Vinylbenzyl-2-ionene oligomers of styrene were also characterized by ^{15}N NMR spectroscopy. Vinylbenzyl-2-ionene bromide showed two peaks at −323.9 and −326.0 ppm. The chemical shift at −326.0 ppm originated from the dimethyethylammonium group on the nitrogen atom deshielded from the benzyl group by 2.1 ppm relative to the peak at −323.9 ppm. Vinylbenzyl-2-ionene iodide had two peaks at −324.5 and −332.2 ppm, respectively. The peak at −332.2 ppm was due to the trimethylammonium nitrogen atom associated with the iodide counterion, and the peak at −324.5 ppm to the benzylic ammonium nitrogen (Table 7).

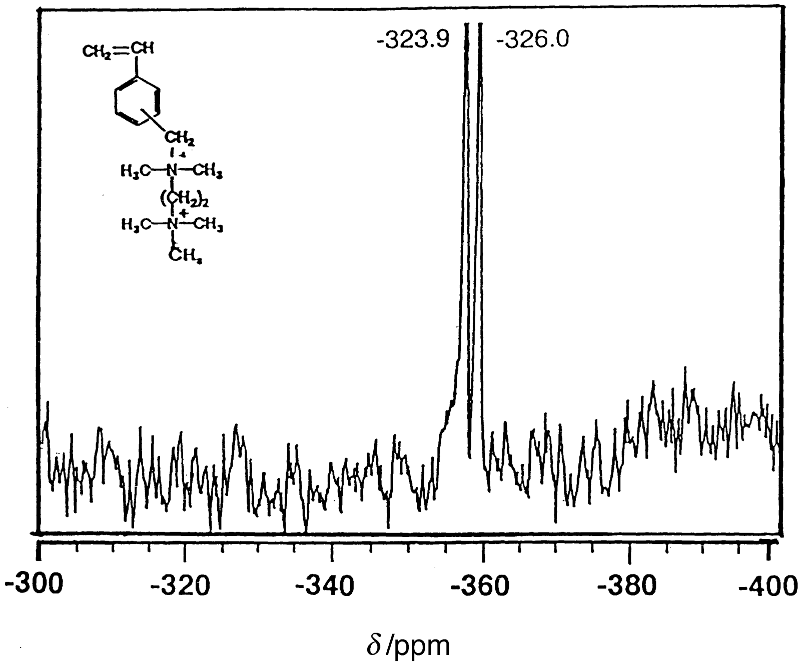

Fig. 7. ^{15}N NMR spectrum of vinylbenzyl-2-ionene bromide

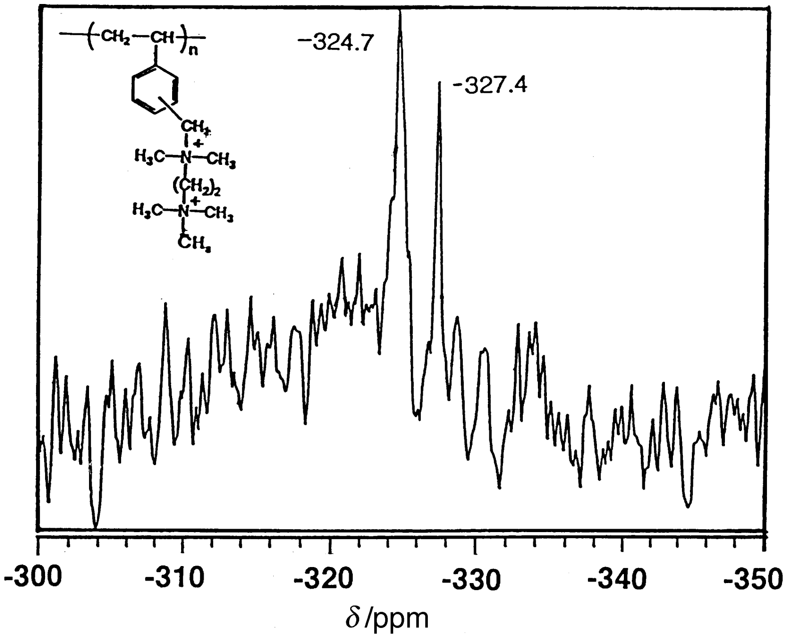

Fig. 8. ^{15}N NMR spectrum of poly(vinylbenzyl-2-ionene) chloride

The polymers based on these vinylbenzylethyl-2-ionene chlorides (Fig. 7) showed similar results based on their nitrogen substituents rather than the counterion. Poly-(vinylbenzyl-2-ionene chloride) had two peaks at −324.9 and −327.5 ppm (Fig. 8). The polymer from vinylbenzyl-2-ionene iodide had two peaks at −324.6 and −332.7 ppm.

Table 8. ^{15}N NMR chemical shift values of 2-Ionene oligomers ($FeCl_3 \cdot 6H_2O$, 20 mg)

	Chemical shift (ppm)
2-Ionene bromide (10.0 *M* in H_2O)	−327.0, −356.4
2-Ionene iodide (10.0 *M* in H_2O)	−331.2, −357.1
2-Bromo-2-ionene bromide (10.0 *M* in H_2O)	−324.1, −326.5
2-Chloro-0-ionene chloride (10.0 *M* in H_2O)	−325.5
2,2-Ionene chloride (10.0 *M* in H_2O)	−325.3, −332.6 −346.0, −347.3
2,2,2-Ionene bromide (10.0 *M* in H_2O)	−326.2, −331.4, −351.0, −354.1, −357.6

Acrylic monomers and polymers were also characterized by ^{15}N NMR spectroscopy. Methacrylatoethyltrimethylammonium chloride showed one peak at −332.6 ppm, identified as the trimethylammonium nitrogen atom. The polymer of this compound also had one peak at −332.8 ppm. Both monomer and polymer of methacrylamidopropyltrimethylammonium chloride (**29**) had two peaks each. The peaks of the monomer oppeared at −262.4 and −332.8 ppm and were attributed to the amido nitrogen and the trimethylammonium chloride nitrogen. The amide peak at −262.4 ppm was deshielded 68.4 ppm. The polymer exhibited similar peaks at −262.2 and −332.7 ppm.

Experimental

The ^{15}N NMR spectra were measured using a GE 300 MHz NMR spectrometer with an observation frequency of 30.45 MHz for ^{15}N. The non-decoupled ^{15}N NMR spectra were calibrated against external formamide (−267.8 ppm) and are referenced to the delta (δ) scale with nitromethane set to zero [13,14]. Previous standardizations used liquid ammonia (−381.9 ppm) [14]. Following the general practice, chemical shift values that are more shielded than the reference are given negative signs and those less shelded will have a positive sign. This means that most ^{15}N values are negative. Sample tube diameter: 10 mm; temperature: ambient; spinning condition: 15 Hz; RF pulse length: 10 μs (45°). The addition of the paramagnetic reagent ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 20 mg) helped to shorten the acquisition times for several compounds because it decreased the Nuclear *Overhauser* Effect (NOE) [6].

Most tetraalkylammonium salts used in this work [1,7,9,12] were readily soluble in water. Aqueous solutions of 3.0 *M* and above for the tetra-*n*-alkylammonium halide salts were not uncommon. Solution preparation in aqueous and methanolic reagents yielded similar results for obtained chemical shift data of these salts. The acquisition times of these solutions were about 1 h. N-Alkyl substituents on the nitrogen atom exerted the most important effect on the chemical shift of amines and ammonium salts. Other factors showed were of less influence on either the acquisition times and/or on the chemical shift values.

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