Detection of end-groups and estimation of molecular weights of polyiminoalkenes by ^{13}C n.m.r. spectroscopy

S. Guhaniyogi, K. J. Ivin and E. D. Lillie
Department of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG, UK
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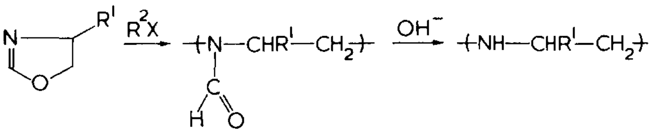
Linear polyiminoalkenes $R^2\text{-}[NHCHR^1CH_2]_nX$, ($R^1$ = H, CH_3, C_2H_5), were prepared by alkaline hydrolysis of the *N*-formyl precursors, which had been obtained by the polymerization of oxazoline, 4-methyloxazoline and 4-ethyloxazoline, respectively, using methyl iodide, ethyl iodide or dimethyl sulphate as initiator. When the initiator concentration was 5–20 mol % of the initial monomer concentration, the ^{13}C n.m.r. spectra showed minor peaks which could be assigned to carbon atoms in the two end units, R^2 being CH_3 or C_2H_5 according to the initiator, and X being OH. This confirms the mechanism in which the attack on the oxazoline molecule occurs at the nitrogen atom, with subsequent opening of the O—CH_2 bond. For R^1 = C_2H_5 the end-group X was successfully converted to Cl by reaction with thionyl chloride.

Values of *n* determined by v.p.o. were in the range 5–20 and similar values were obtained from ^{13}C n.m.r. peak intensities using the ratio of the average main peak intensity to the average end-group peak intensity. A correlation was also noted with the ratio of the initial monomer and initiator concentrations; after allowance for yield an initiator efficiency of the order of 50–100% may be deduced.

INTRODUCTION

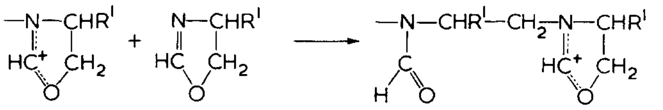
Linear polyiminoalkenes, III, may be obtained by the hydrolysis of their *N*-formyl derivatives II, prepared by the isomerization polymerization of oxazoline or its derivatives I,[1,2] and we have shown[3] that the ^{13}C n.m.r. spectrum of acidified atactic IIIb exhibits splitting for all three carbon atoms, the chemical shifts being sensitive to dyad or triad structure.



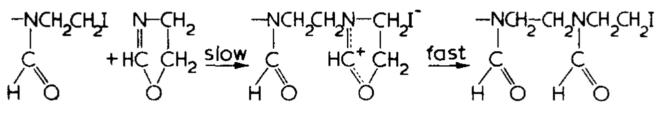
(Ia, b, c) (IIa, b, c) (IIIa, b, c)

a, R^1=H; b, R^1=CH_3; c, R^1=C_2H_5
R^2X=CH_3I, C_2H_5I or $(CH_3)_2SO_4$

The mechanism of polymerization of I using dimethyl sulphate as initiator is thought to proceed via an oxazolinium ion[4]:



but with alkyl iodides as initiator a covalent intermediate has been proposed[5] from kinetic and n.m.r. evidence (for R^1 = H).



In either case we can expect the ultimate end-group structure in the polyimine III to be $R^2\text{-}[NHCHR^1CH_2]_nX$ where R^2 = CH_3 or C_2H_5 depending on the initiator, and X = OH as a result of the final hydrolysis step.

In the present work in which *n* was usually less than 20, the ^{13}C n.m.r. peaks arising from the two end-groups are shown to be consistent with this structure. The assignments were made by comparison of the spectra with each other and with model compounds, and for IIIc it was found possible to convert the OH end-group cleanly to Cl.

EXPERIMENTAL

Preparation of monomers

The preparations of Ia and Ib have been described elsewhere[1,2]. The preparation of Ic was carried out in the same way starting from 2-aminobutan-1-ol (DL or L). After final fractionation in a spinning band column Ic had b.p. 120°–121°C. ^{13}C n.m.r. shifts (solvent $CDCl_3$): $\underline{C}H_3$ 10.01, $CH_3\underline{C}H_2$ 28.73, $\underline{C}HEt$ 67.00, $\underline{C}H_2O$ 70.77, $\underline{C}H{=}N$ 154.29 ppm, relative to TMS.

Initiators

Dimethyl sulphate was distilled under reduced pressure in a nitrogen atmosphere. Methyl and ethyl iodides were distilled over silver powder and collected over clean copper coils.

Solvents

Dimethylformamide (DMF) was dried over KOH pellets and distilled. Acetonitrile was distilled in a nitrogen atmosphere and stored over molecular sieves 4A.

Table 1 Polymerization conditions and yields for I → II. Degree of polymerization (n) of hydrolysed products III, as determined by v.p.o.

Monomer		Concentration of initiator[a]	Solvent[b]	Temperature[c] (°C)	Yield[d] (%)	$\frac{[M] \times \text{yield}^e}{[I] \times 100}$	n^f	Code[g] for III
Ia		5% CH_3I	DMF	100	49	9.8	28	PIE1[i]
		10% CH_3I	DMF	110	54	5.4	24	PIE2[i]
		20% CH_3I	DMF	110	50	2.5	–	PIE3[j]
		6.4% C_2H_5I	MeCN	100	54	8.4	22	PIE4[k]
1b	(±)	5.8% CH_3I	MeCN	105	27	4.7	5.3	PIP1
	(±)	10.9% CH_3I	MeCN	105	75	6.9	10.5	PIP2
	(±)	21% CH_3I	DMF	110	71	3.4	–	PIP3
	(–)	20% CH_3I	DMF	120	81	4.0	10.7	PIP4
	(±)	10.5% C_2H_5I	MeCN	110	89	8.5	11.7	PIP5
	(±)	18% C_2H_5I	MeCN	110	80	4.4	7.0	PIP6
Ic	(±)	5.1% CH_3I	MeCN	110	25	4.9	4.6	PIB1
	(±)	10.4% CH_3I	DMF	110	69	6.6	7.6	PIB2[h]
	(±)	20% CH_3I	DMF	110	60	3.0	7.0	PIB3
	(±)	7.5% C_2H_5I	MeCN	110	80	10.7	13.4	PIB4
	(±)	12.5% C_2H_5I	MeCN	105	80	6.4	10.3	PIB5
	(±)	6.3% $(CH_3)_2SO_4$	DMF	120	55	8.7	8.7	PIB6
	(–)	17% CH_3I	DMF	110	74	4.3	7.3	PIB7

[a] Concentration in mol % relative to monomer. [b] Weight of solvent was generally twice that of the monomer. [c] 40 h at this temperature. [d] Yield based on total weight of monomer and initiator. [e] [M] /[I] = ratio of initial monomer and initiator concentrations. [f] Molecular weight divided by that of repeat unit. [g] PIE = polyiminoethylene; PIP = polyiminopropene; PIB = polyiminobut-1-ene. [h] Soluble extract from hydrolysis (a small proportion was insoluble). [i] Product of hydrolysis of soluble part of IIa. [j] Product of hydrolysis of total polymer IIa. [k] Product of hydrolysis of insoluble part of IIa

Polymerization conditions

Details are shown in *Table 1*. With the iodides as initiators the use of a solvent was found to improve the yield. A solvent of the initiator was added to the monomer in an ampoule at 0°C. After several freeze–thaw cycles under vacuum the ampoule was sealed. It was then held at 105°–120°C for the period indicated in *Table 1*. The polymerizations of Ib and Ic were homogeneous and the polymers were recovered by precipitation in ether followed by two or three dissolutions and reprecipitations before drying under vacuum. With 5–10 mol % alkyl iodide the polymerization of Ia was partly heterogeneous.

Hydrolysis of II to III

1 g of IIa was heated with 0.9 g NaOH in 10 cm^3 water at 95°C for 12 h. The solution was cooled to room temperature and the precipitated IIIa centrifuged and washed repeatedly with water, and finally dried in vacuum to yield a white crystalline solid.

IIb and IIc (1 g) were dissolved in 0.9 g NaOH in 10 cm^3 water + 10 cm^3 methanol and heated in a sealed tube at 130°–150°C for 5–7 days. IIIb and IIIc were recovered by extraction with chloroform, drying with anhydrous Na_2SO_4 and evaporation of the chloroform to yield the product as a thick brown syrup.

Conversion of hydroxide end-group in IIIc to chloride end-group

The conversion of aminoalcohols to aminochlorides has been described by Raiziss and Clemence[6]. Dry HCl was bubbled through a solution of 1 g IIIc in 50 cm^3 chloroform until the polyamine hydrochloride was precipitated. HCl was passed through the solution for a further 2 h and then 4 g $SOCl_2$ was added dropwise over a period of 1 h. After refluxing the mixture for 30 min, the excess $SOCl_2$, HCl and chloroform were removed under reduced pressure, leaving the product. ^{13}C n.m.r. spectra indicated that conversion was complete. Similar attempts to convert IIIa and IIIb were only partly successful.

N.m.r. spectra

The ^{13}C spectra were recorded in the pulsed Fourier transform mode using a Bruker WH90 spectrometer operating at 22.63 MHz with a deuterium lock, the protons being decoupled by broad-band irradiation. The pulse length was usually 6 μsec, the delay time between pulses 0.68 sec, and the sweep width 6024 Hz. Solutions were made as strong as possible in D_2O (usually 20–30%) and contained an excess of HCl together with one or two drops of dioxane to provide an internal reference (taken as 69.15 ppm relative to internal TMS). The sample temperature was usually 60°C and the number of pulses was between 5000 and 120000. Peak areas obtained from the computer print-out were sufficiently accurate for the present exploratory investigation.

Molecular weights

Molecular weights of the polyimines IIIb and IIIc were determined by vapour pressure osmometry (Mechrolab V.P. Osmometer Model 301A) (v.p.o.) at 37°C using chloroform as solvent; for IIIa methanol was used as solvent. Concentrations were in the range 8–14 mg/cm^3 and each measurement was made in triplicate.

RESULTS AND DISCUSSION

Main peaks and model compounds

The spectra for the three polyiminoalkenes, having various end-groups, are shown in *Figures 1–3*. We have preferred to give these as stick diagrams for several reasons. First, the height of the sticks can be drawn proportional to the peak area given by the print-out. Second, spectra obtained at different sweep widths can be reduced to a common scale. Third it was found that one or two peaks were peculiar to polymers made in acetonitrile while occasionally an additional very small unidentifiable peak or peaks would appear in one spectrum only, apparently due to impurities; therefore only those peaks are shown in

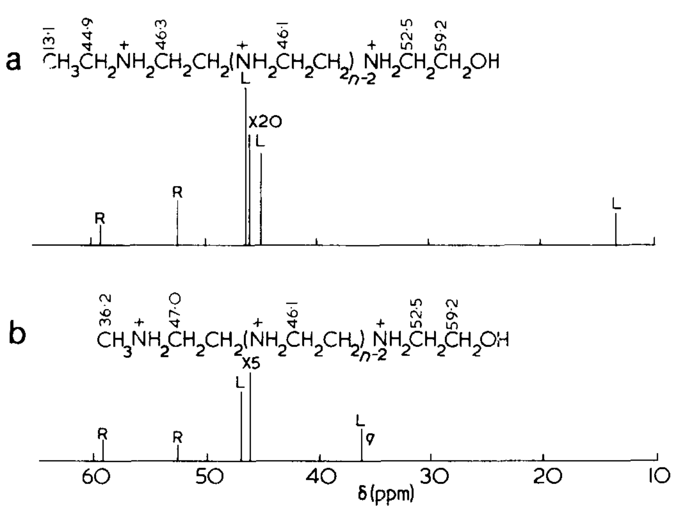


Figure 1 $^{13}C-\{^1H\}$ n.m.r. spectrum of polyiminoethylene. Solvent, acidified D_2O. Peak positions relative to dioxane 69.15 ppm. (a) Sample PIE4 (*Table 1*); (b) sample PIE3. Main peaks shown at 1/20 and 1/5 actual intensity as indicated. *q* denotes quarter in off-resonance spectrum. L and R denote peaks assigned to left- and right-hand ends of molecule as written

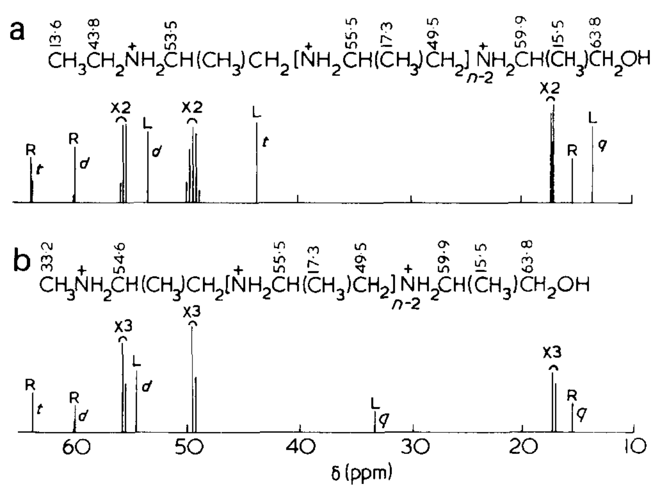


Figure 2 $^{13}C-\{^1H\}$ n.m.r. spectrum of polyiminopropene. Solvent, acidified D_2O. (a) Sample PIP6 (*Table 1*); (b) sample PIP2. Main peaks shown at 1/2 and 1/3 actual intensity as indicated. *q, t, d* denote quartet, triplet, doublet in off-resonance spectrum. L and R denote peaks assigned to left- and right-hand ends of molecule as written

Figures 1–3 whose positions are common to all polymers having a given end-group and repeat unit structure.

The low intensity of the minor peaks sometimes made it difficult to identify the number of attached protons from off-resonance spectra, especially when the peaks were adjacent to major peaks; those successfully identified are indicated.

The following model compounds were used to assist the assignments. The published values[7] for the chemical shifts of these compounds in aqueous acid solution have been converted to a scale on which dioxane has the value 69.15 ppm relative to internal TMS.

IV	$\overset{+}{N}H_3\overset{a}{C}H_2\overset{b}{C}H_2OH$	*a*	44.1
		b	60.3
V	$\overset{+}{N}H_3\overset{a}{C}H_2\overset{b}{C}H_2Cl$	*a*	43.3
		b	43.8
VI	$\overset{a}{C}H_3\overset{b}{C}H_2\overset{c}{C}H_2\overset{d}{C}H_2OH$	*a*	13.9
		b	19.4
		c	35.3
		d	61.7
VII	$\overset{a}{C}H_3\overset{b}{C}H_2\overset{c}{C}H_2\overset{d}{C}H_2Cl$	*a*	13.4
		b	20.4
		c	35.2
		d	44.6
VIII	$(\overset{a}{C}H_3\overset{+}{N}H_2\overset{b}{C}H_2)_2$	*a*	36.2
		b	47.0
IX	$(\overset{a}{C}H_3\overset{c}{C}H_2\overset{+}{N}H_2\overset{b}{C}H_2)_2$	*a*	13.7
		b	45.4
		c	46.3
X	$\overset{+}{N}H_3\overset{b}{C}H(\overset{a}{C}H_3)\overset{c}{C}H_2OH$	*a*	17.2
		b	52.1
		c	65.3
XI	$\overset{d}{C}H_3\overset{+}{N}H_2\overset{e}{C}H(\overset{b}{C}H_3)\overset{c}{C}H_2\overset{a}{C}H_3$	*a*	11.7
		b	17.6
		c	28.0
		d	32.6
		e	57.4

The observed main peak positions in III were as follows:

IIIa	$-\overset{+}{N}H_2\overset{a}{C}H_2CH_2-$	*a*	46.1
IIIb	$-\overset{+}{N}H_2\overset{c}{C}H(\overset{a}{C}H_3)\overset{b}{C}H_2-$	*a*	17.0 (r), 17.3 (m)
		b	49.3 mm), 49.5 (mr, rm), 49.7 (rr)
		c	55.4 (m), 55.6 (r)
IIIc	$-\overset{+}{N}H_2\overset{d}{C}H(\overset{b}{C}H_2\overset{a}{C}H_3)\overset{c}{C}H_2-$	*a*	11.4
		b	24.2
		c	48.0
		d	61.1

The dyad and triad assignments for IIIb were made previously[3]; there were no clear indications of any substantial variations of tacticity with initiator. The spectra of polymers of IIIc made from racemic and optically active monomer did not differ significantly; one concludes that either the polymer made from racemic monomer is isotactic, or, more likely, that the chemical shifts are insensitive to tacticity. The following substitution shifts may be noted.

IIIa/*a* → IIIb/*c*	$\alpha + \delta = 9.4$
IIIa/*a* → IIIb/*b*	$\beta + \gamma = 3.4$
IIIb/*a* → IIIc/*b*	$\alpha = 7.1$
IIIb/*c* → IIIc/*d*	$\beta = 5.6$
IIIb/*b* → IIIc/*c*	$\gamma + \delta = -1.4$

From this limited set of data we obtain $\alpha = 7.1$, $\beta = 5.6$, $\gamma = -2.2$, $\delta = 1.5 \pm 0.8$ ppm in reasonable agreement

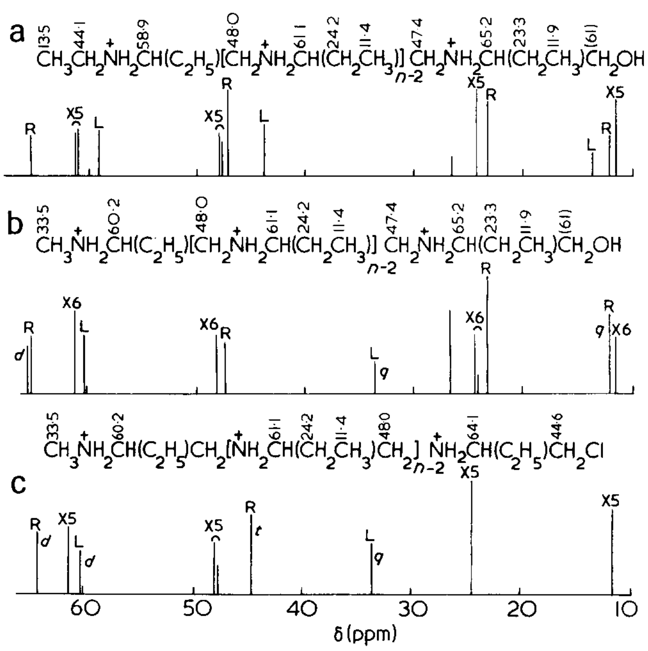


Figure 3 $^{13}C-\{^1H\}$ n.m.r. spectrum of polyiminobut-1-ene. Solvent, acidified D_2O. (a) Sample PIB5; (b) sample PIB1; (c) sample PIB3 converted to chloride end-group (PIB3'). Symbols as in *Figure 2*

(generally within ±1.0 ppm) with values which may be derived from the model compounds. These parameters are useful in checking the relative positions of peaks due to end-groups (see below).

Polyiminoethylene

In *Figures 1a* and *1b* the two peaks labelled R are common to both spectra and may be ascribed to the right-hand, or termination, end of the molecules, i.e. $-\overset{+}{N}H_2CH_2CH_2OH$. The 59.2 ppm peak is assigned to $\underline{C}H_2OH$ by comparison with IVb, $(60.3 + \gamma + \delta)$ ppm, while that at 52.5 ppm is assigned to $\underline{C}H_2CH_2OH$ even though it occurs somewhat more downfield from the position expected from IVa, $(44.1 + \beta + \gamma + \delta)$ ppm.

The two peaks labelled L in *Figure 1b* do not appear in *Figure 1a* and may be ascribed to the left-hand, or initiation, end of the molecule, i.e. $CH_3\overset{+}{N}H_2CH_2-$. The 36.2 ppm peak is assigned to $\underline{C}H_3$ by comparison with VIIIa, confirmed by the off-resonance spectrum. The peak at 47.0 ppm is assigned to $CH_3\overset{+}{N}H_2\underline{C}H_2-$ by comparison with VIIIb.

The three peaks labelled L in *Figure 1a* may likewise be ascribed to $CH_3CH_2\overset{+}{N}H_2CH_2-$. The 13.1 ppm peak is assigned to $\underline{C}H_3$ by comparison with IXa. The assignment of the other two peaks is uncertain but it seems probable that the peak at 44.9 ppm is to be assigned to $CH_3\underline{C}H_2$ by comparison with the corresponding peak in *Figure 1b*, $(36.2 + \alpha)$ ppm, and the peak at 46.3 ppm to $CH_3CH_2\overset{+}{N}H_2\underline{C}H_2$, again by comparison with the corresponding peak in *Figure 1b*, $(47.0 + \gamma)$ ppm.

Polyiminopropene

In *Figures 2a* and *2b* the three peaks labelled R are common to both spectra and may be ascribed to the right-hand, or termination, end of the molecules, i.e. $-\overset{+}{N}H_2CH(CH_3)CH_2OH$. The detailed assignments were made by means of off-resonance spectra: 59.9 ppm, $\underline{C}H$; 15.5 ppm, $\underline{C}H_3$; amd 63.8 ppm, $\underline{C}H_2$. The assignments are confirmed by comparison with the appropriate lines labelled R in *Figures 1a* and *1b*: $\underline{C}H$, $(52.5 + \alpha)$ ppm; $\underline{C}H_2$, $(59.2 + \beta)$ ppm. They are further supported by comparisons with Xb, $\underline{C}H$, $(52.1 + \beta + \gamma + \delta)$ ppm; Xa, $\underline{C}H_3$, $(17.2 + \gamma + \delta)$ ppm; Xc, $\underline{C}H_2$, $(65.3 + \gamma + \delta)$ ppm.

The two peaks labelled L in *Figure 2b* do not appear in *Figure 2a* and may be ascribed to two of the carbons in the initiation end unit, i.e. $CH_3\overset{+}{N}H_2\underline{C}H(CH_3)CH_2-$. The peak at 33.2 ppm is assigned to $\underline{C}H_3\overset{+}{N}H_2$ from the off-resonance spectrum and by comparison with XId, 32.6 ppm. The peak at 54.6 ppm is assigned to $\underline{C}H$ from the off-resonance spectrum and by comparison with VIIIb, $(47.0 + \alpha)$ ppm. The other methyl carbon (γ to the end methyl) differs from the main methyl carbons only by a δ effect and evidently this is too small to be resolved; likewise for $\underline{C}H_2$.

The three peaks labelled L in *Figure 2a* may likewise be ascribed to three of the carbons in $CH_3CH_2NH_2CH(CH_3)CH_2$-. The 13.6 ppm peak is assigned to $\underline{C}H_3CH_2$ from the off-resonance spectrum and by comparison with IXa, $(13.7 + \delta)$ ppm. The 43.8 ppm peak is assigned to $CH_3\underline{C}H_2$ from the off-resonance spectrum and by comparison with IXc, $(46.3 + \gamma + \delta)$ ppm. The peak at 53.5 ppm is assigned to $\underline{C}H$ from the off-resonance spectrum and by comparison with IXb, $(45.4 + \alpha)$ ppm.

Of all the spectra taken for this polymer, that represented in *Figure 2a* was the best resolved, showing more fine structure for the main peaks than that previously reported[3]. While this is probably caused by tacticity effects this requires confirmation with polymers of higher molecular weight so as to eliminate other possible explanations in terms of short chain oligomer etc. In our earlier work[8] the samples of IIb had been made using 1–3% dimethyl sulphate as initiator which, on hydrolysis gave IIIb in which the spectra of the end-groups were not noticed because of the higher molecular weights. Re-examination of these spectra showed that in favourable cases (high signal/noise ratio) some of the end-group peaks of *Figure 2b* could just be detected.

Polyiminobut-1-ene

In *Figures 3a* and *3b* the four peaks labelled R are common to both spectra and may be ascribed to four carbons in the right-hand, or termination, end of the molecules, i.e. $-CH_2\overset{+}{N}H_2CH(\underline{C}H_2CH_3)CH_2OH$. The peak at 47.4 ppm is assigned to $\underline{C}H_2\overset{+}{N}H_2$ from its proximity to the main $\underline{C}H_2$ peak at 48.1 ppm, from which its position should differ only by a δ effect. The peak at 65.3 ppm is assigned to $\underline{C}H$ from the off-resonance spectrum and by comparison with the corresponding peak in *Figure 2b*, $(59.9 + \beta)$ ppm. The 23.3 ppm peak is assigned to $\underline{C}H_2CH_3$ by comparison with the corresponding peak in *Figure 2b*, $(15.5 + \alpha)$ ppm. The peak at 11.9 ppm is assigned to $CH_2\underline{C}H_3$ from the off-resonance spectrum and by comparison with XIb, 11.7 ppm. The peak for CH_2OH may be predicted from *Figure 2b* to occur at $(63.8 + \gamma)$ ppm, i.e. at 62 ± 1 ppm, and is evidently obscured by the main $\underline{C}H$ peak at 61.1 ppm. The additional $\underline{C}H$ peak at 65.1 ppm in *Figure 3b* is more likely to be due to the presence of very short chain oligomer rather than to a tacticity effect since the latter is not resolved in the main $\underline{C}H$ peak (61.1 ppm) in *Figure 3b*, whereas it is in *Figure 3a*.

The two peaks labelled L in *Figure 3b* do not appear in *Figure 3a* but do so in *Figure 3c* and may be ascribed to two carbons in the left-hand, or initiation, end of the molecule, i.e. $CH_3\overset{+}{N}H_2CH(\underline{C}H_2CH_3)CH_2-$. The 33.5 ppm peak is assigned to $CH_3\overset{+}{N}H_2$ from the off-resonance spectrum, by comparison with VIIIa, $(36.2 + \gamma + \delta)$ ppm, and by comparison with the corresponding peak in *Figure 2b*, $(33.2 + \delta)$

Table 2 Degree of polymerization *n* of polyiminoalkenes estimated from ^{13}C n.m.r. intensities

	Main peak intensities[c,d]					End-group peak intensities[d,f] at positions indicated										*n*	
						Left-hand (ppm)					Right-hand (ppm)						
Polymer[a]	$\underline{C}H_2$	$\underline{C}HR^1$	$\underline{C}H_3$	$\underline{C}H_2$	Average	13.1	44.9		36.2	47.0			52.5	59.2	Average	n.m.r.[e]	v.p.o.[a]
PIE1	100 x 2				100				$\underline{0.7}$	7.3			4.5	$\underline{2.8}$	3.8	28	28
PIE2	100 x 2				100				$\underline{2.1}$	6.2			2.6	$\underline{2.1}$	3.3	32	24
PIE3	100 x 2				100				$\underline{13.6}$	31.2			7.7	$\underline{9.1}$	15.4	8.5	–
PIE4	100 x 2				100	$\underline{3.1}$	8.6						3.7	$\underline{1.8}$	4.3	25	22
						Left-hand (ppm)					Right-hand (ppm)						
						13.6	43.8	53.5	33.2	54.6		15.5	59.9	63.8			
PIP1	107	86	107		100				$\underline{11.1}$	23.4		16.4	11.5	$\underline{21.9}$	16.9	7.8	5.3
PIP2	107	94	99		100				$\underline{4.8}$	13.7		6.5	6.1	$\underline{8.7}$	8.0	14.6	10.5
PIP3	111	79	110		100				$\underline{13.4}$	18.6		6.2	15.8	$\underline{12.4}$	13.3	9.5	10.7
PIP3	110	100	90		100				$\underline{13.2}$	17.8		9.6	9.0	$\underline{13.6}$	12.6	9.9	10.7
PIP4	102	103	95		100				$\underline{3.8}$	16.5		4.6	4.6	$\underline{5.8}$	7.1	16.1	10.7
PIP5	105	91	104		100	$\underline{7.8}$	9.1	8.8				3.4	7.3	$\underline{8.2}$	7.4	15.4	11.7
PIP6	105	82	113		100	$\underline{17.6}$	18.4	16.5				9.9	12.7	$\underline{10.4}$	15.1	8.6	7.0
						Left-hand (ppm)					Right-hand (ppm)						
						13.5	44.1	58.9	33.5	60.2	47.4	11.9	23.3	65.3			
PIB1	85	117	82	116	100				$\underline{7.2}$	13.8	12.8	19.0	28.0	11.2	15.4	8.5	4.6
PIB2	98	114	83	105	100				$\underline{4.6}$	15.9	7.1	21.1	14.3	9.3	12.0	10.3	7.6
PIB3	89	90	109	113	100				$\underline{13.1}$	16.3		17.3	18.8	21.1	17.3	7.8	7.0
PIB3	81	109	101	108	100					12.5		24.0	25.4	12.6	20.9	6.8	7.0
PIB3′[b]	92	75	101	132	100				$\underline{12.6}$	10.0			14.0[g]	$\underline{18.2}$[h]	13.8	9.3	7.0[i]
PIB4	94	101	100	105	100	$\underline{5.8}$	6.8	4.8			12.6	10.8	16.1	8.9	9.4	12.6	13.4
PIB5	95	103	96	107	100	$\underline{6.1}$	12.1	10.2			20.5	11.0	18.5	9.6	12.6	10.0	10.3
PIB6	80	109	104	107	100				$\underline{4.0}$	11.5		10.1	14.4	8.6	9.7	12	8.7
PIB7	75	100	121	104	100				$\underline{7.2}$	16.7	9.4	8.6	11.8	10.2	10.7	9.3	7.3

[a] See *Table 1.* [b] See *Figure 3c*. [c] $\underline{C}H_2$ and $\underline{C}HR$ refer to the main chain; $\underline{C}H_3$ and $\underline{C}H_2$ to the side chain. Fine structure has been aggregated. [d] All peak intensities normalized to 100 for average main peak intensity. [e] n = 2 + (average main peak intensity)/(average end-group peak intensity). 2 added to allow for the two end-groups. [f] Intensities for carbon atoms at extreme ends of chains are underlined. [g] 64.1 ppm. [h] 44.6 ppm. [i] Value before conversion to chloride

ppm. The peak at 60.2 ppm is assigned to $\underline{C}H$ from the off-resonance spectrum and by comparison with the corresponding peak in *Figure 2b*, (54.6 + β) ppm. The unlabelled peak at 26.6 ppm is common to all three spectra and appears to be associated with one of the side-chain methylene carbons other than that in the right-hand end unit. This is somewhat surprising since a difference of 2.4 ppm from the main methylene side chain resonance would not have been expected.

The three peaks labelled L in *Figure 3a* do not appear in *Figures 3b* and *3c*, and may be ascribed to $CH_3CH_2\overset{+}{N}H_2CH{<}$. The peak at 13.5 ppm is assigned to $\underline{C}H_3$ by comparison with IXa, (13.7 + δ) ppm and with the corresponding peak in *Figure 2a*, 13.6 ppm. The peak at 44.1 ppm is assigned to $\underline{C}H_2$ by comparison with IXc, (46.3 + γ + δ) ppm, and by comparison with the corresponding peak in *Figure 3b*, (33.5 + α) ppm. The 58.9 ppm peak is assigned to $\underline{C}H$ by comparison with the corresponding peaks in *Figure 3b*, (60.2 + γ) ppm and in *Figure 2a*, (52.3 + β) ppm.

In *Figure 3c* the absence of a peak at 65.2 ppm shows that conversion of hydroxide to chloride was complete. A new peak appears at 64.1 ppm, assigned to $\underline{C}HCH_2Cl$ from the off-resonance spectrum and by comparison of IVa with Va which shows that a small upfield shift, relative to the hydroxide, is to be expected. A second new peak at 44.6 ppm is assigned to $\underline{C}H_2Cl$ from the off-resonance spectrum and by comparison with the position of $\underline{C}H_2OH$ in *Figure 3b*, taking account of the difference between IVb and Vb. A shoulder at 11.7 ppm, on the side of the main $\underline{C}H_3$ peak, is assigned to $\overset{+}{N}H_2CH(CH_2\underline{C}H_3)CH_2Cl$. The peak at 23.3 ppm in *Figure 3b* has disappeared in *Figure 3c*, as expected, but has not been replaced by a new peak. Presumably the peak due to $\overset{+}{N}H_2CH(\underline{C}H_2CH_3)CH_2Cl$ has merged with the main peak at 24.2 ppm.

Comparison of molecular weights by v.p.o. and n.m.r.

Ideally all the main peaks would have the same intensity (ignoring fine structure due to tacticity) and all the peaks due to end-group carbons would also have the same intensity. In practice the main peaks varied in intensity by up to a factor of 2 and the end-group peaks by up to a factor of 4 in any given spectrum. There are several reasons for such variations. First the different carbon nuclei may exhibit different Nuclear Overhauser Enhancements (*NOE*), as well as different degrees of saturation if the delay time between pulses is less than five times any one of the spin–lattice relaxation times T_1. There is also the possibility of errors arising from the computer print-out programme, particularly for noisy spectra containing peaks close together. However, with the exception of the main peak in IIIa, we can take an average of 3 or 4 intensities for the main peaks, and an average of 4 to 7 intensities for the end-group peaks so that the ratio of the two averages should give at least a rough estimate of the degree of polymerization, in which the effects just described will, to some extent, cancel out. Carbon nuclei at the end of a chain always have longer relaxation times than those in the middle and are therefore more prone to saturation effects This probably explains the greater variation in the end-group peak intensities compared with those in the body of the chain. Such effects will tend to lead to an overestimate of the degree of polymerization when the delay time between pulses is short.

The observed n.m.r. intensities for the polymers listed in *Table 1* are shown in *Table 2*. The derived values of the degree of polymerization are in satisfactory agreement with those obtained by v.p.o., considering the approximations involved, and indicate that, with refinement of the operating conditions so as to eliminate *NOE* and T_1 effects, very reliable results could be obtained by ^{13}C n.m.r.

Finally we may note that the values of n obtained by v.p.o. are generally in excess of [M] x yield/[I] x 100 (see *Table 1*), although the difference tends to become smaller as one goes from Ia to Ib to Ic. This suggests a stepwise growth of the polymer chain but with relatively slow initiation by alkyl iodides and a fairly broad molecular weight distribution, particularly for the product from Ia.

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