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^{13}C-NMR Analysis of Amino and Hydroxyl Endgroups in Telechelic Poly(oxyethylene)s

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SUMMARY

α,ω-Diamino derivatives of poly(oxyethylene)s are suitable carriers for the coupling of oligo- and polysaccharide chains by means of amide linkages. The extent of the replacement of the hydroxyl groups of the poly(oxyethylene) by amino groups can be determined from ^{13}C-NMR analysis. Unequivocal identification of the CH_2NH_2 groups at δ=41.3-41.8 ppm and the CH_2OH groups at δ=61.5-61.7 ppm ($CDCl_3$, TMS as standard) offers rapid information about the degree of conversion and is applicable also for higher molecular weight products.

RESULTS AND DISCUSSION

A general procedure for the coupling of oligosaccharides to various carriers containing carboxyl groups or amino groups by amide linkages has been previously described (EMMERLING and PFANNEMÜLLER 1978). As an example for linear A-B-A block copolymers with "synthetic" B and "natural" A sequences of variable lengths, maltooligomers were linked to α,ω-diamino oligo(methylene)s, n=2-12, by means of their aldonic acid lactone endgroups (EMMERLING and PFANNEMÜLLER 1981). The maltooligosaccharides allow further elongation by enzymatic synthesis.

In extension of these studies we were interested in products containing oligo- or poly(oxyethylene) as B block. Therefore different procedures recommended for the replacement of hydroxyl endgroups by amino groups were examined (MUTTER 1978, GECKELER 1979, KERN et al. 1979). Analytical problems with the evaluation of the degree of conversion arose mainly because of the need of a method sensitive enough to differentiate between unreacted hydroxyl groups and the amino groups introduced. Elemental analysis and infrared spectroscopy no longer give reliable information for higher molecular weight poly(oxyethylene)s. ^{1}H-NMR spectroscopy, thoroughly investigated with highly purified samples and model substances, proved to be only suitable for the amino endgroups. With α-(2-aminoethyl)-ω-amino oligo(oxyethylene), n=5, the signals of amino groups are found at δ=1.50 ppm in $CDCl_3$ and at δ=1.25 ppm in benzene. The protons of the hydroxyl groups such as in α-hydro-ω-hydroxy oligo(oxyethylene), n=4, PEO 200, PEO 400 ect. cannot be detected. The signal at δ=2.08 ppm reported previously

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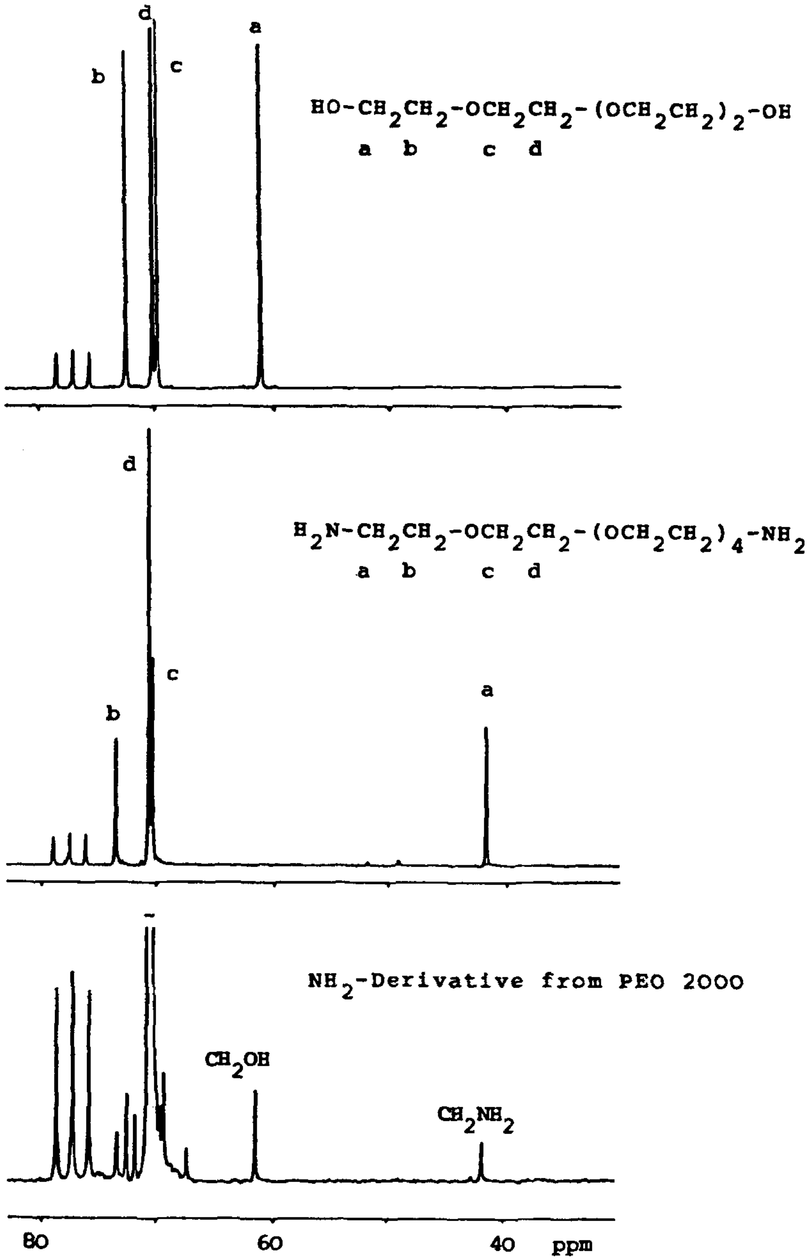

Fig.1: ^{13}C-NMR spectra of telechelic poly(oxyethylene)s
^{13}C frequency: 22.625 MHz; ^{1}H broadband decoupling;
solvent: $CDCl_3$; TMS = 0 ppm; temp. 295 K

TABLE 1: Assignments of chemical shifts δ (ppm) in ^{13}C-NMR spectra of reference substances and partially substituted amino derivatives of poly(oxyethylene).

	$X-CH_2CH_2-OCH_2CH_2-O\cdots$ a b c d X = OH		X = NH_2		Terminal NH_2 from relative ^{13}C intensities
	a	b	a	b	%
Reference substances:					
Ethanolamine	62.8		44.0		50
Diethyleneglycol-monobutylether	61.7	72.7			0
$H(OCH_2CH_2)_nOH$					
n=3	61.4	72.7			0
n=4	61.5	72.9			0
n=7	61.6	72.7			0
$H_2NCH_2CH_2(OCH_2CH_2)_nNH_2$					
n=5 a)			41.8	73.5	100
n=8 a)			41.8	73.5	100
Partially NH_2 terminated					
PEO 200 a)	61.2		41.3		90
PEO 2000 a)	61.5		41.8		35
PEO 2000 b)	61.7		41.5		46
PEO 6000 b)	61.6		41.3		18
PEO 6000 c)	61.5				0

a) (KERN et al. 1979); b) (MUTTER 1978); c) (GECKELER 1979)

(GECKELER 1979) is absent in $CDCl_3$ and in benzene. Obviously as a result of hydrogen bonding these protons have the same chemical shift as the bulk of the CH_2O-protons of the internal chain located at $\delta=3.6-3.7$ ppm ($CDCl_3$ and benzene). The protons of α-methylene groups bound to hydroxyl groups are located at $\delta=4.3$ ppm (triplet), those bound to amino groups at $\delta=2.7-2.8$ ppm (triplet). With increasing chain length (m.w.=400) integrals of these typical triplets are too insignificant to allow evaluation. Thus valuable information about the ratio of the hydroxyl to amino endgroups in partially substituted poly(oxyethylene)s cannot be derived from ^1H-NMR spectra.

Better results are obtained with ^{13}C-NMR spectroscopy. ^{13}C-NMR spectra of three representative samples are shown in Figure 1. The data are summarized in Table 1.

Using ethanolamine as reference CH_2OH groups are found at $\delta=61.8$ ppm, CH_2NH_2 groups at $\delta=44.0$ ppm ($CDCl_3$, TMS as standard). In all products based on oxyethylene subunits the signals from the terminal methylene groups (C_a) are slightly shifted to $\delta=61.5 \pm 0.2$ ppm and to $\delta=41.6 \pm 0.2$ ppm, respectively. Assignment of C_c and C_d is based on the observation of two separate signals at $\delta=70.2$ ppm (C_c) and at $\delta=70.6$ ppm (C_d) for α-hydro-ω-hydroxy oligo(oxyethylene), n=4, and as could be expected only one signal at $\delta=70.3$ ppm for the product with n=3. The lower field position of C_b at $\delta=72.7$ ppm and at $\delta=73.5$ ppm (hydroxyl or amino end, respectively) can be attributed to a steric effect. It is observed when two hydrogenated carbons are γ-gauche relative to each other (BREITMAIER and VOELTER 1978). The preference of the OCH_2-CH_2O subunit of poly(oxyethylene) for the gauche conformation has been previously reported (MATSUZAKI and ITO 1974, ABE and MARK 1976). No influence of terminal substituents on the signal position of C_c and C_d is found.

Since there is no difference between hydroxyl and amino endgroups in the number and distance of protons directly bound at C_a and most probably no major difference in the segment flexibility the influence of different relaxation times (T_1) has not to be taken into account. This can be seen from the 1:1 signal intensity ratio of aminoethanol as well as of α-amino-ω-hexanol. Similarly, a nuclear Overhauser effect will not contribute to falsification when comparing signal intensities of both endgroups (SCHAEFER and NATUSCH 1972). Thus the ^{13}C-NMR data of the amino derivatives listed in Table 1 should give a rough estimation of the degree of conversion. The products of preliminary experiments were obtained with different procedures applied for introduction of the amino groups (a: KERN et al. 1979; b: MUTTER 1978; c: GECKELER 1979). Methods a and c lead to chain elongation by an additional monomer unit per amino group. The reaction of the ditosyl esters of α,ω-dihydroxy poly(oxyethylene)s with the potassium salt of ethanolamine (KERN et al. 1979) proved to be more satisfactory. In the case of oligo(oxyethylene), n=4 and n=7 (a fraction of PEO 400, b.p. 200-220°C, 0.03 mbar) the signals of the hydroxyl groups in the products are completely absent. With these products starting material and the diamino derivatives could be purified by high vacuum distillation. The purity of the samples was confirmed by gas chromatography. Before further purification, in the products obtained by the same procedure from unfractionated PEO 200 and 2000 and in products prepared by the Gabriel synthesis (MUTTER 1978) variable amounts of unsubstituted hydroxyl groups are found. As shown from the spectrum of the amino derivative from PEO 2000[a)] (Figure 1) three peaks are observed in the range of C_b instead of only two for the different endgroups. This may arise from the obvious presence of side bands adjacent to the main signal of C_d.

The results show that ^{13}C-NMR provides rapid information about the degree of conversion. The method is especially useful for conversions with higher molecular weight poly(oxyethylene)s to optimize the reaction conditions and effectivity of the purification steps.

Further investigations on the coupling of oligosaccharide chains of variable length and on the properties of the three-block copolymers will be reported separately.

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