13C-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 13C-NMR analysis. Unequivocal identification of the CH2NH2 groups at δ=41.3-41.8 ppm and the CH2OH groups at δ=61.5-61.7 ppm (CDCl3, 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, maltooligos 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. 1H-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 CDCl3 and at δ=1.25 ppm in benzene. The protons of the hydroxyl groups such as in α-hydroxy-ω-hydroxy oligo(oxyethylene), n=4, PEO 200, PEO 400 ect. cannot be detected. The signal at δ=2.08 ppm reported previously...
Fig. 1: $^{13}$C-NMR spectra of telechelic poly(oxethylene)s

$^{13}$C frequency: 22.625 MHz; $^1$H broadband decoupling;
solvent: CDCl$_3$; TMS = 0 ppm; temp. 295 K