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Analysis

End Group Analysis of Commercial Poly(Ethylene Glycol) Monomethyl Ether's

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Summary.

Analysis of the hydroxyl content of a series of commercial poly(ethylene glycol)monomethyl ethers by means of 360 MHz ^{1}H NMR spectroscopy of the trichloroacetyl isocyanate modified polymers has shown that some compounds contain considerable amounts of poly(ethylene glycol).

Different suppliers of laboratory chemicals offer poly(ethylene glycol) monomethyl ether

$$CH_3-(O-CH_2-CH_2)_n-OH$$

with n varying from 8 to approx. 110. Such monofunctional poly(ethylene glycol)'s (PEG's) are the starting materials for the preparation of other semi-telechelic PEG's which in turn can be used to produce block- or graft-copolymers containing well defined PEG segments (HARRIS 1985, KENNEDY and HONGU 1985, GRAMAIN and FRÈRE 1986). For such purposes it is of primary importance that the polymers be pure semi-telechelics, e.i. that they do not contain any bifunctional (telechelic) PEG because this would lead to the formation of polyblocks and/or polymer networks. In the present communication we report on the end group analysis of a series of commercial PEG monomethyl ethers by means of 360 MHz ^{1}H NMR spectroscopy of the polymers after reaction with trichloroacetyl isocyanate (TAIC). This reagent transforms the hydroxyl end group into a trichloroacetyl urethane end group thereby causing a shift of approx. 1 ppm for the methylene protons in α position of the OH end group (GOODLETT 1965).

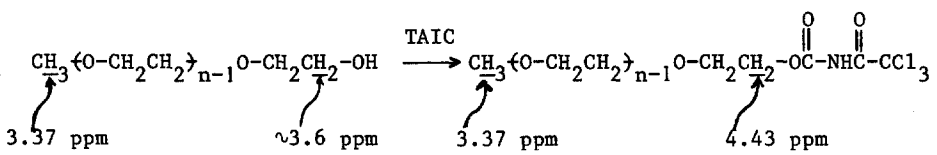

Fig. 1 shows the spectrum of a polymer with molar mass 750 g.mol^{-1}. The resolution power of the 360 MHz apparatus allows to differentiate the end standing methoxy protons from the methylene protons of the polymer chain. By integration of the methoxy peak and of the urethane methylene peak, the ratio of $[OH]/[OCH_3]$ can be determined. In case of a pure monomethyl ether this ratio should be 1. The accuracy of the method was checked by analysis of diethylene glycol monomethyl ether (PEG monomethyl ether with n = 2).

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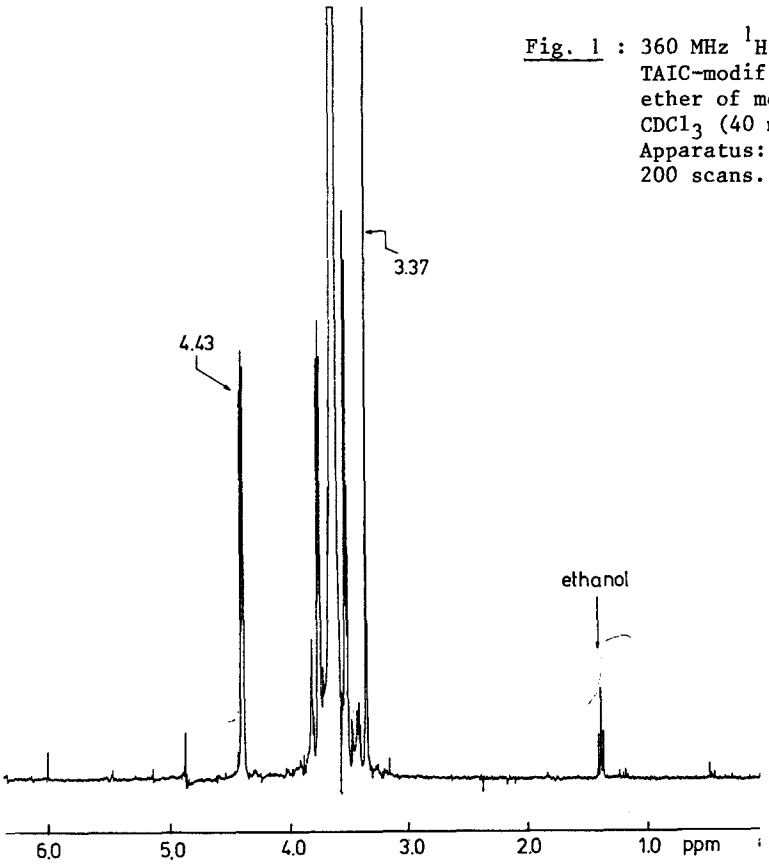

Fig. 1 : 360 MHz ^{1}H NMR spectrum of TAIC-modified PEG monomethyl ether of molar mass 750 in $CDCl_3$ (40 mg/ml). Apparatus: Bruker WH360, 200 scans.

Table 1 : End group analysis of commercial poly(ethylene glycol)monomethyl ether's.

Supplier	Molar mass ($g.mol^{-1}$)	$\overline{M}_n$ [a] $g.mol^{-1}$	$\frac{[OH]}{[OCH_3]}$	Average OH content [b] per mole
Aldrich	5000	4640	1.40	1.20
Aldrich	1900	1940	1.52	1.26
Sigma	750	640	1.08	1.04
Fluka	750	760	1.02	1.01
Polyscience	1900	1300	1.50	1.25
Polyscience	750	710	1.08	1.04
—	120 [c]	—	1.00	1.00

[a] determined by GPC, PL gel 10 μ Mix Å, eluent: $CHCl_3$, flow rate: 1 ml/min, detector: refractive index. Based on poly(propylene oxide)standards.

[b] after correction for ethanol present in $CDCl_3$ as stabilizer.

[c] diethyleneglycol monomethylether.

As shown in Table 1, the observed ratios are reasonably close to 1 for the polymer samples with molar mass 750 $g.mol^{-1}$. For the higher molar mass samples, however, ratios much higher than one were found which means that these polymers contain considerable amounts (up to 25%) of bifunctional PEG. The presence of this telechelic PEG in the alleged semi-telechelic one, may result in unexpected physical properties of the end products prepared from them.

References.

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