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Convenient method for the analysis of primary and secondary hydroxyl end groups in polyethers

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Summary

The content of primary and secondary hydroxyl end groups in polyethers is determined by means of 360 MHz ^{1}H NMR spectroscopy of the trichloroacetyl isocyanate modified polymers. For poly(ethylene oxide-co-propylene oxides) the NMR analysis allows a rapid analysis of the nature of the polyether end groups as well as the presence of other end groups resulting from side reaction.

Hydroxyl terminated polyethers (polyether polyols) find wide industrial application as starting materials for the preparation of polyurethanes. Copolymers based on ethylene oxide and propylene oxide may have primary and/or secondary hydroxyl end groups. The reactivity of the polyether polyols towards isocyanates is strongly dependent on the nature of the end groups. Hence, the analysis of the content of primary and secondary hydroxyl end groups is of primary importance.
The ratio of the concentrations of primary and secondary hydroxyl end group can be determined by ^{19}F NMR analysis of the trifluoro acetylated derivatives (WILLIAMS 1983), U.V.-spectroscopic analysis of the nitrite esters (CRUMMETT 1962) or by calorimetric determination of the secondary alcohols (CRITCHFIELD 1960) combined with total hydroxyl analysis (KRUGER 1982, FRITZ 1979, HILTON 1959, FALGOUX 1967). These methods all require relatively long analysis times.
The present communication describes a convenient alternative allowing a quick and accurate analysis. Its feasibility and accuracy will be tested on mixtures of poly(ethylene glycols (PEG) and poly(propylene glycols) (PPG) as well as on a commercial poly(ethylene glycol-co-propylene glycol) copolymer.
The method is based on a 360 MHz ^{1}H NMR spectroscopic analysis of the trichloroacetyl isocyanate (TAIC) modified polymers. Reaction of the alcohols end groups with trichloro acetyl isocyanate transforms the hydroxyls into the corresponding trichloroacetyl urethane derivatives, shifting the NMR signal for the methylene or methyn protons in α-position of the hydroxyl end group to 4.43 ppm, respectively to 5.12 ppm (GOODLETT 1965).

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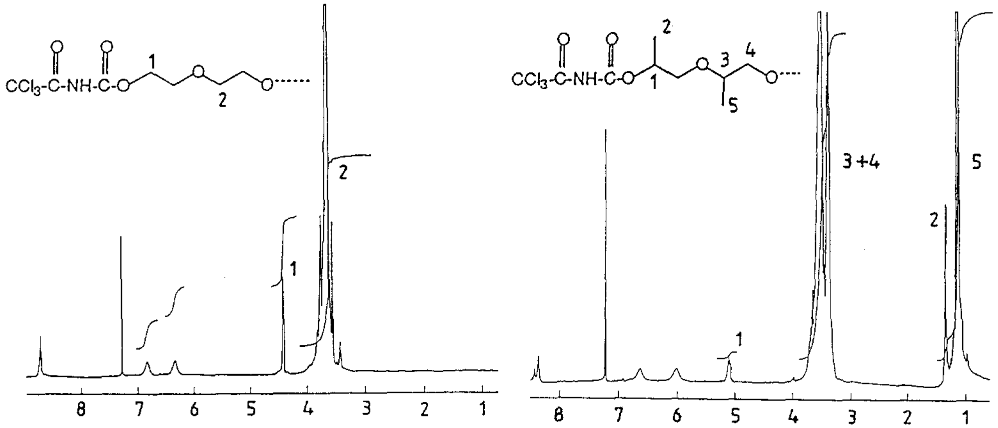


Fig. 1. 360 MHz ^{1}H NMR analysis of TAIC modified poly(oxyethylene) and poly(oxypropylene) (δ in ppm).

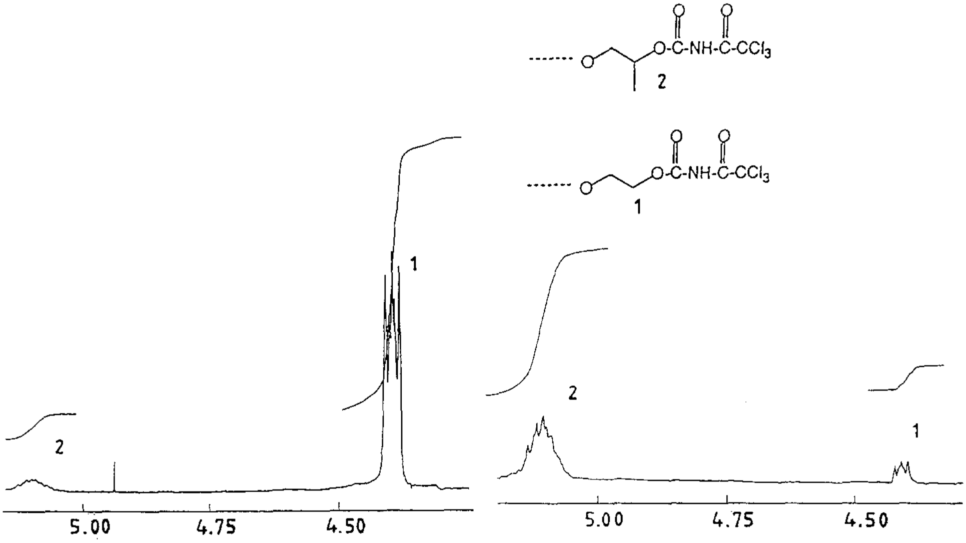
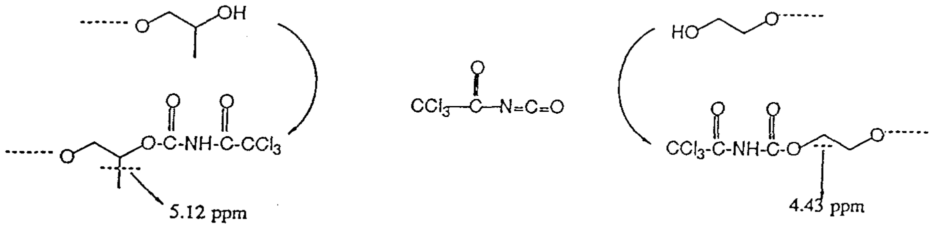


Fig. 2. The determination of the end group ratio secondary alcohol/primary alcohol; illustrated with the ratios P/S = 4.77 and P/S = 0.12.



The TAIC modification of primary alcohols has been used before in our laboratory to verify the functionality in poly(ethylene glycol)methylethers (DE VOS, 1986).
If both primary and secondary end groups are present, their ratio can be determined from the integration value of the respective signals. In order to evaluate the accuracy of this method mixtures of dry poly(ethylene glycol) (MW 2,000) and poly(propylene glycol)(MW 2,000) dissolved in $CDCl_3$ were treated with TAIC (50 µl/30 mg polymer) and analyzed by ^1H NMR.
Fig. 1 shows the NMR spectra of poly(ethylene glycol) and of poly(propylene glycol) treated with TAIC. Spectra for some polyether mixture of variable composition are given in Fig. 2. The results of the end group analysis for 5 different mixtures are summarized in Table 1.

Table 1. Determination of the ratio (prim. alcohol)/(sec. alcohol) in mixtures of PEG en PPG.

amount PEG (gram)	amount PPC (gram)	calculated ratio*	exp. ratio*
1.898	0.398	4.77	4.67
2.140	1.340	1.58	1.48
0.756	0.708	1.07	0.98
1.520	2.840	0.54	0.58
0.174	1.472	0.12	0.11

*) ratio expressed as the molar ratio of primary alcohols over secondary alcohols.

The data summarized in Table 1 indicates that for a molar ratio varying between 10 percent and 90 percent the presently described method allows end group analysis with a sufficient accuracy (within 5 à 8 %). This technic becomes less accurate if one type of end group is present in large excess or for polymers of higher molecular weight. The applicability of this method for analysing the end groups in commercial polyether polyols based on ethylene oxide propylene oxide copolymers is demonstrated in Fig. 2. A commercial polyether currently used in polyurethane manufacturing was analysed using the TAIC-method. As illustrated in Fig. 2 the ratio of the primary and secondary alcohols could be easily calculated. Moreover, the 360 MHz ^1H NMR analysis further demonstrated the presence of allyl end groups which may arise from side reaction during the production of the polyether. From one single NMR analysis the ratio of primary/secondary/allyl end groups was calculated being 5.2/4/1. It can be concluded that 360 MHz ^1H NMR spectroscopic analysis of TAIC-modified polyethers is a rapid and reliable method for the analysis of the end groups in polyether polyols.

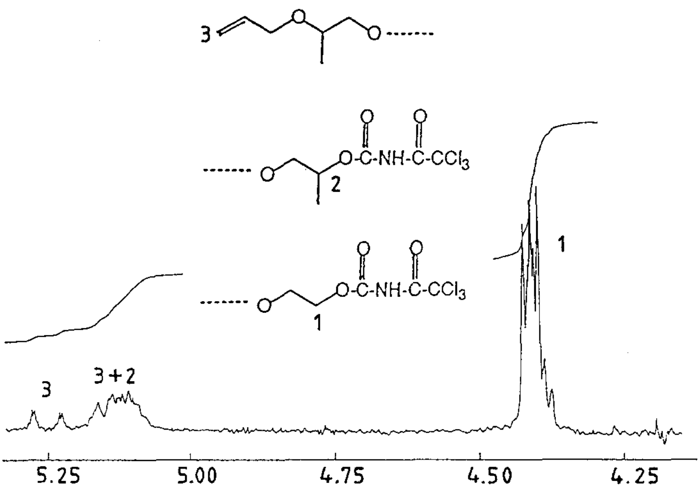


Fig. 3. 360 MHz ^{1} NMR analysis of a TAIC modified commercial poly(oxyethylene-oxypropylene) copolymer (δ in ppm).

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