Determination of Functionality and Functionality Distribution of Polyether Polyols by Quantitative ^{13}C NMR Spectroscopy

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SYNOPSIS

A method is described for the determination of the number average functionality and functionality distribution of polyether polyols based on the measured intensities of relevant end groups observed in ^{13}C NMR spectra. Longitudinal (T1) relaxation time measurements on glycerol-, trimethylolpropane-, and pentaerythritol-initiated copolymers of propylene oxide and ethylene oxide show that the slowest relaxing moiety that needs to be quantified is the vinyl $CH_2=$ group of the unsaturated side product of the propoxylation reaction. A chromium(III)-containing relaxation reagent allows the analysis to be speeded up by decreasing the relaxation times. The relative precision of the functionality measurement is ca. ±1%, while determinations of the mole percentage levels of species with different functionalities can be carried out with a precision better than ±3 mol %. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polyurethanes exhibit arguably the most varied range of applications of any polymeric material in the world today. Included in this range are products as diverse as rigid foams for insulation in refrigeration and construction, elastomers for shoe soles and sealants, and flexible foams for furniture and automotive seating.[1] This variation arises because of the possibilities for designing the chemical components that constitute the final polymer. Polyurethanes are formed typically from an isocyanate such as 4,4′-methylene-bis(*p*-phenyl isocyanate) [methylene diphenyl diisocyanate, MDI] and a polyfunctional hydroxy compound (polyol), together with a suitable package of catalyst(s), surfactant(s), and blowing agent(s). Thus, the physical properties of the product can be controlled by varying the compositions of isocyanate, polyol, and additives.

In flexible foam applications, the polyol is normally a polyether, formed by the base-catalysed addition polymerisation of ethylene oxide (EO) and propylene oxide (PO) onto a low molecular weight, polyfunctional alcohol such as 1,2,3-propantriol (glycerol). Important parameters of the polyol include the relative amounts of PO and EO, the structure of the polymer chains (block or random), the ratio of the primary and secondary hydroxyl end groups, and the relative amounts of species with different functionalities.

The functionality of polyether polyols can vary from that of the pure initiator because of the presence of water in the raw materials, leading to the formation of diols, and also from a side reaction during propoxylation that produces an allyl alcohol ion as the initiator of mono-hydroxy molecules (monofunctional with respect to isocyanate).

$$RO^- + H{-}CH_2{-}\underset{\backslash O /}{CH}{-}CH_2 \rightarrow$$

$$ROH + CH_2{=}CH{-}CH_2{-}O^-$$

The allyl groups can rearrange under certain conditions of temperature and pressure to give propenyl groups.

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Journal of Applied Polymer Science, Vol. 52, 1015–1022 (1994)
 CCC 0021-8995/94/081015-08

$$CH_2{=}CH{-}CH_2{-}O{-}R{-}OH \rightarrow$$
$$CH_3{-}CH{=}CH{-}O{-}R{-}OH.$$

(cis and trans isomers possible)

A plethora of analytical techniques and methods have been employed in the characterisation of polyether polyols. EO contents have been determined by cloud point tests[2] and by degradation of the alkoxide units followed by colorimetric[3] or gas chromatographic[4] quantification of the degradation products. Infrared[5] and near infrared[6] methods have also been used, but these rely on establishing a large set of calibration data.

As nuclear magnetic resonance (NMR) spectrometers became more widely available, direct determination of EO contents could be achieved with minimal sample preparation, the only significant drawback being the small interferences in the ^1H spectra caused by most of the initiators used by the polyol producers.[7,8]

End group analyses of polyethers have also been undertaken by NMR. ^1H methods rely on resolving the end groups from in-chain species either by derivatization[9,10] or by the use of chemical shift reagents.[11] The most widely used method for determining primary/secondary hydroxyl ratios in EO/PO polyethers, however, has been via ^{19}F NMR analysis of the trifluoroacetate ester derivatives.[12,13]

More recently, as ^{13}C NMR analysis became more straightforward because of the introduction of Fourier transform methods and increasing magnetic field strengths, much more information about the composition of polyether polyols could be acquired directly. Providing sufficient care is taken over the analysis, high quality data can be obtained on the nature of the initiator, the EO/PO ratio, and the primary/secondary hydroxyl ratio in a single analysis.[8,14,15] As the resolution of spectra increases with the use of superconducting-magnet-based instruments of higher field strength, even more detailed information on the structure of the polymer chains can be obtained.[16–18]

The functionality distribution is another parameter of great importance in the detailed characterisation of polyether polyols. The amount of unsaturated species formed during the production process can be determined by a wet chemical analysis based on the production of acetic acid from the reaction of the unsaturated bonds with mercuric acetate.[19] The amount of difunctional material present can be estimated from a knowledge of the water contents of the EO, PO, and initiator. Because the hydroxyl value of the polyether can be measured, the average functionality can be calculated, although the imprecisions of the individual measurements can lead to significant variation in the final calculated functionality value.

Direct methods of determining the weight average functionality of polyether polyols have been used in the past. These were based on theories of gelation[20,21] and included series of static reactions and titrations, but these have been found to be unsatisfactory because of inaccuracies in the result and the time-consuming, labor-intensive methods (unpublished data).

A great deal of information about the polyol composition can be obtained by the separation of species according to their functionality and molecular size,[22,23] although the problems associated with obtaining the critical conditions necessary for the liquid chromatographic separations means that such an approach cannot yet be considered as a routine method.

Described below are relaxation time measurements and reproducibility studies that show how ^{13}C NMR spectroscopy can be used to obtain reliable results on the number average functionality and functionality distribution of the polyether polyols used in the production of flexible polyurethane foams.

EXPERIMENTAL

All analyses were carried out on a GSX270 FT NMR spectrometer (Jeol, Japan), operating at a frequency of 67.8 MHz for ^{13}C with a dedicated ^{13}C high sensitivity probe, using 10 mm glass tubes spinning at ca. 15 Hz. Spectra were acquired using 64K data points covering a frequency width of 20 kHz.

Sample solutions for analysis were prepared from 4 g of the polyether and 1 g of deuteroacetone (Janssen Chimica, Geel, Belgium). Acetone was used in preference to chloroform because it causes no interference with the glycerol $\diagdown\!\!\diagup$CH— group signal nor with the methylene group of terminal PO groups on EO (i.e., $-O-CH_2-CH_2-O-\underline{C}H_2-CH \cdot CH_3-OH$). The sample solutions were not degassed as this is not practical for routine analyses in an industrial situation and because the objective was not to determine highly precise T1s but, rather, to establish optimum quantitative conditions for analysis. The central peak of the deuteroacetone multiplet was used as the chemical shift reference (δ = 29.8 ppm vs. TMS). The relaxation reagent used was chromium(III) acetylacetonate (Fluka AG, Buchs, Switzerland).

Four commercially available polyether polyols were used in this study:

polyol A a glycerol-initiated PO/EO block copolymer with ca. 15 wt % EO (OH value = 28 mg KOH/g) (two different batches)
polyol B a trimethylolpropane (TMP) initiated PO/EO random copolymer with ca. 76 wt % EO (OH value = 45 mg KOH/g)
polyol C a pentaerythritol (PE) initiated PO/EO block copolymer with ca. 12.5 wt % EO (OH value = 38 mg KOH/g)
polyol D a TMP initiated PO/EO block copolymer with ca. 10 wt % EO (OH value = 37 mg KOH/g).

Relaxation time (T1) measurements were made via an inversion recovery pulse sequence (90-*t*-180-*t*-Ac) with a repetition delay of 15 s. Proton broad band decoupling was only turned on during data acquisition to prevent buildup of NOE (inverse gated decoupling). Various values of *t* between 100 ms and 15 s were selected to cover the time interval during which the signals of interest pass through a null point equivalent to [ln 2 (T1)]. Two thousand scans were recorded for each step in the inversion recovery sequence.

Data processing of the relaxation time measurement spectra was carried out using the spectrometer software. After manual phase correction, reference setting, and peak selection for subsequent calculations on the fully relaxed spectrum (largest value of *t*), the other spectra in the series were processed automatically using the same conditions. The size of the peaks changes with the value of *t* according to the relationship $M_z = M_o (1 - 2e^{-t/T1})$ where M_o and M_z are, respectively, the z-axis magnetisation initially and at time *t*. From this relationship, the value of T1 for each of the selected peaks was calculated using the spectrometer software.

Quantitative spectra were acquired using repeated single 90° pulses (12.5 μs) with inverse gated decoupling and a pulse delay at least a factor of five times the longest relevant relaxation time as determined by the inversion recovery measurements. Again, 2000 scans were acquired for each spectrum. After Fourier transformation, manual phase correction and automatic drift correction were carried out. Peak areas were determined by computer integration of the processed spectrum. The positions of the integration blocks were stored and retrieved from computer files with the optimum values for the baseline offset and declination parameters of each block being determined manually to give flat integrals before and after each peak. In order to assess the level of variation caused by this manual operation, all data sets were processed independently by two of the authors.

RESULTS AND DISCUSSION

Relaxation Time Measurements

Using the inversion recovery pulse sequence and conditions described above, the relaxation times for all relevant groups in the polyols were determined. An example of the series of partially relaxed spectra produced is shown in Figure 1. The results for these analyses are summarized in Table I.

It is clear that the slowest relaxing carbon atoms of importance for the functionality and functionality distribution calculations are those of the unsaturated allyl group. However, because only one of these two signals needs to be quantified to determine the abundance of this moiety, it is the $-CH_2=$ group with a T1 of 1.6 s that is the limiting factor in the speed of analysis. It is normal practice to allow a repetition delay of 5T1 when carrying out quantitative analysis because this allows practically complete recovery. Thus, a repetition delay of 8 s would be optimum and 10 s would be on the safe side. The length of time for a complete analysis depends upon the level of unsaturated species and the desired S/N, but 2000 scans with a repetition delay of 10 s giving approximately 6 h total analysis time has proved to be acceptable. Instruments with stronger magnetic fields and more sensitive probes would be significantly faster.

One mechanism that can be extremely effective in bringing about relaxation is interaction with unpaired electrons.[24] The magnetic moment of the electron is about 1000 times greater than that of the proton[25] so in the presence of paramagnetic materials relaxation times can be greatly reduced.[26] Chromium(III) acetylacetonate [$Cr(acac)_3$] is a widely used relaxation reagent because it is paramagnetic, soluble in a range of common organic solvents, and does not affect the chemical shifts of resonance signals. In high concentrations, however, detrimental line broadening effects can occur. In order to assess the suitability of using such a relaxation reagent to reduce the analysis time, the effect of various concentrations of $Cr(acac)_3$ on both relaxation time and analytical results was investigated.

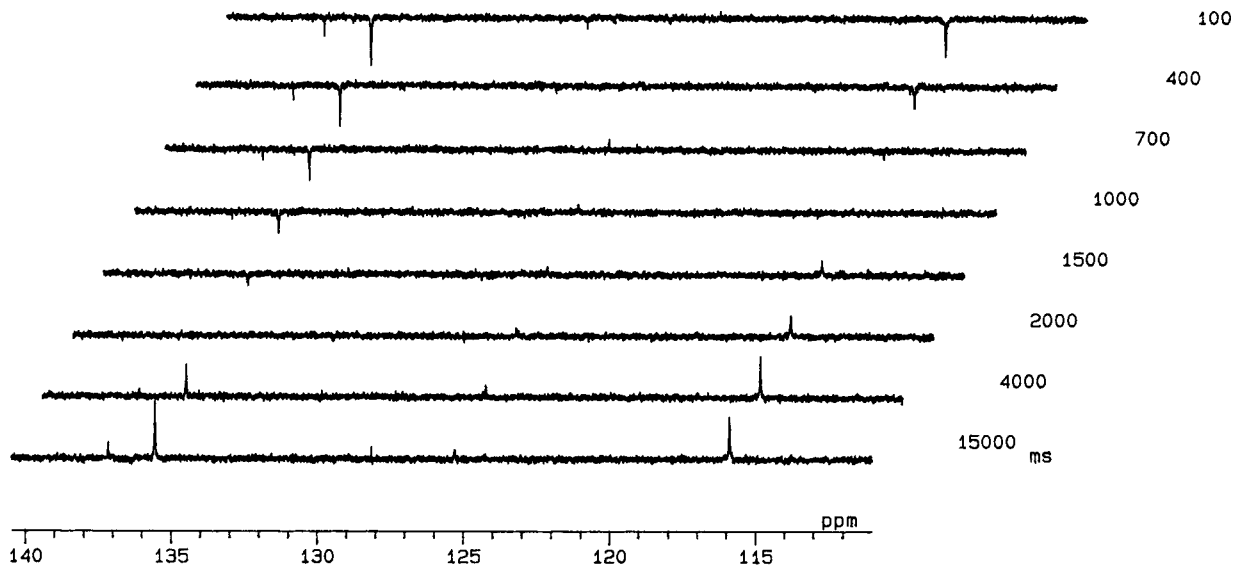

Figure 1 Series of partially relaxed spectra obtained to determine T1 relaxation times. The —CH= and CH_2= peaks at 135.5 and 116.1 ppm, respectively, are shown for each of the delays used in the inversion recovery pulse sequence.

Three solutions of polyol A were prepared with different amounts of the chromium acetylacetonate added. The relaxation times were measured as before. Comparison with the results obtained previously with no relaxation reagent show (Table II) that the required repetition delay can indeed be significantly reduced, in fact, by a factor of two. Higher levels of $Cr(acac)_3$ were not tested because minor changes in the measured ethylene oxide content of the polyol were already occurring because of line broadening and sacrificing the accuracy of the EO determination for decreased analysis time was not desired.

Functionality and Functionality Distribution Measurements

The number average functionality of a polymeric material is defined as the average number of functional groups per molecule. For the polyether polyols considered here, the functional groups in question are the hydroxyl end groups of the polyether chains. Thus, a polyol is a mixture of molecules with different numbers of hydroxyl groups, the exact composition depending upon the initiator, the level of contaminating water in the raw materials and the chemistry of the reaction that can produce the mo-

Table I Relaxation Time Measurements

	Group	Chemical Shift (ppm)	Relaxation Time (s)
CH_2=CH—CH_2—O—	Allyl =CH—	135.5	3.2
CH_2=CH—CH_2—O—	Allyl CH_2=	116.1	1.6
>CH—	Glycerol >CH—	78.6	< 0.4
O—CH_2—CH·Me—OH	Secondary —OH	66.5/65.6	1.1
O—CH_2—CH_2—OH	Primary —OH	61.3	0.9
C—$(CH_2—O—)_4$	PE quarternary	45.7	1.2
$CH_3—CH_2—C—(CH_2—O—)_3$	TMP quarternary	43.3	1.1
$CH_3—CH_2—C—(CH_2—O—)_3$	TMP methyl	7.7	0.8

All peaks from in-chain species gave relaxation times of less than 1 s.

Table II Relaxation Time Measurements for Polyol A

	$Cr(acac)_3$ Added (mg/g)	Relaxation Time (s)				
		CH=	CH_2=	Glycerol > CH—	> CHOH[a]	CH_2OH
Sample 1	0.00	3.2	1.6	< 0.4	~ 1.0	0.9
Sample 2	1.15	1.9	1.3	nd	~ 0.9	nd
Sample 3	2.73	1.0	nd	nd	~ 0.7	0.6
Sample 4	3.38	0.8	0.8	0.2	~ 0.6	0.5

nd, not determined.

[a] The secondary hydroxyl end group carbon signals were too small to give precise values, but the T1s have been estimated from the observed null signal times according to the relation T1 = t(null signal)/ln 2.

nohydroxyl by-product. Taking a glycerol-initiated polyol as an example, the number average functionality can be defined as:

$$F = \frac{\text{total number of hydroxyl end groups}}{\text{total number of molecules}}$$

$$= \frac{e}{m + d + t}$$

where F = number average functionality, e = total number of hydroxyl end groups, m = number of monofunctional molecules, d = number of difunctional molecules, t = number of trifunctional molecules. Because $e = m + 2d + 3t$, then $d = (e - m - 3t)/2$. In the ^{13}C NMR spectrum of glycerol-initiated polyether polyols, the peaks from the CH_2= group of the monofunctional species, the >CH— group of the glycerol and the —CH_2OH and >CH—OH of the primary and secondary hydroxyl end-groups can all be observed. Thus, with m, t, and e measured, the relative number of difunctional molecules can be calculated by difference and, hence, the overall number average functionality and functionality distribution of the polyol can be determined.

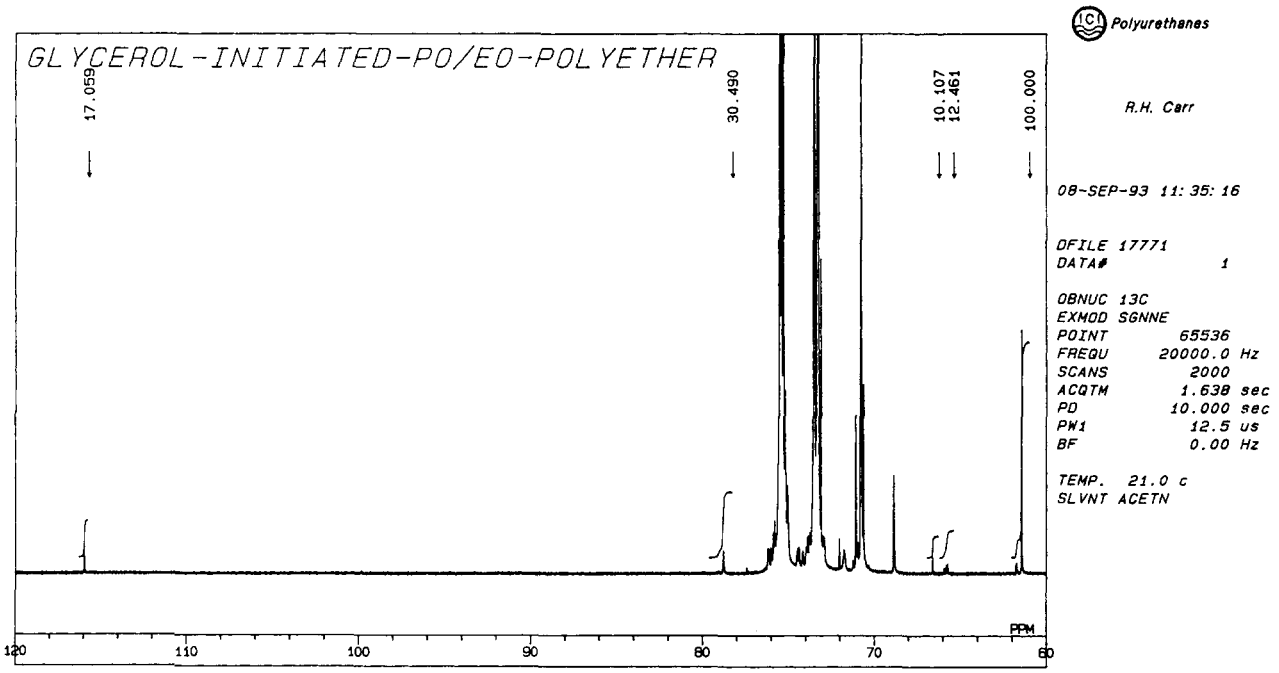

Figure 2 Part of the processed and integrated spectrum of one batch of polyol A.

Table III Functionality Measurements for Polyol A

Block	Chemical Shift (ppm)	Assignment		Integral
B1	115.7–116.3	Allyl	$CH_2=$	17.06
B2	78.3–79.6	Glycerol	> CH—	30.49
B3	66.2–66.9	POH	> CH—OH	10.11
B4	65.4–66.2	POH	> CH—OH	12.46
B5	60.9–62.0	EOH	$-CH_2OH$	100.00

Calculation

m = B1 = 17.06
t = B2 = 30.49
e = B3 + B4 + B5 = 122.6

Therefore

$d = (e - m - 3t)/2 = 7.02$
$F = e/(m + d + t) = 2.25$

Monofunc. species = $100m/(m + d + t)$ = 31.3 mol %
Difunc. species = $100d/(m + d + t)$ = 12.9 mol %
Trifunc. species = $100t/(m + d + t)$ = 55.9 mol %

Figure 2 shows part of the spectrum from a sample of a second batch of polyol A acquired and processed as described above (no Cr^{3+} reagent present). Peak assignments, integration values, and subsequent calculations are given in Table III to illustrate the way in which the results are produced.

The three solutions of polyol A used for the relaxation time measurements, together with one solution of the same batch of polyol A containing no relaxation reagent, were analysed quantitatively. In order to eliminate one variable, the repetition delay was kept as 10 s for each sample. The results from this limited data (Table IV) show reasonable agreement between the authors' data processing and acceptable consistency from sample to sample.

Five solutions of polyol D containing 3.3 mg/g of $Cr(acac)_3$ and five solutions without relaxation reagent were also analysed. Pulse delays of 5 and 10 s, respectively, were used for solutions with and without Cr^{3+}. The results are summarised in Table V. A two-factor Anova statistical analysis gives > 90% confidence that the determinations of mol % triol and overall functionality are not affected by the presence of relaxation reagent, but there is a dependence on the analyst carrying out the data processing. The determination of mono-ol content may be affected by the Cr^{3+}, but the resulting difference is less than that introduced by the manual data processing. Consistent sample preparation, either always with or always without relaxation reagent, would eliminate this possible variation, but avoiding the variations caused by manual data processing is not so straightforward. Greatly improved S/N would probably reduce the effect or even allow automatic integration, but this could only be achieved with longer analysis times while using $Cr(acac)_3$ or by using a more sensitive spectrometer. Generally, the precisions of the determinations are similar to those found for the glycerol-initiated polyol, with the relative precision of the functionality being < ±1%, while levels of mono-, di-, and trifunctional species can be determined to within a few mol %.

Table IV Functionality and Functionality Distribution Measurements for Polyol A

	Mol % Mono		Mol % Di		Mol % Tri		Functionality	
Sample	RHC	JH	RHC	JH	RHC	JH	RHC	JH
1	29.0	28.8	16.8	15.6	54.3	55.6	2.25	2.27
2	28.2	28.6	16.9	16.6	54.8	54.8	2.27	2.26
3	28.1	29.2	14.7	9.1	57.1	61.7	2.29	2.32
4	28.5	28.2	11.7	12.1	59.8	59.6	2.31	2.31
Mean	28.5	28.7	15.0	13.4	56.5	57.9	2.28	2.29
SD	0.4	0.4	2.4	3.4	2.5	3.3	0.03	0.03
Both Authors								
Mean	28.6		14.2		57.2		2.29	
SD	0.4		2.9		2.8		0.03	

Table V Functionality and Functionality Distribution Measurements for Polyol D

	Mol % Mono			Mol % Di			Mol % Tri			Functionality		
Sample	RHC	Both	JH	RHC	Both	JH	RHC	Both	JH	RHC	Both	JH
No Cr^{3+}												
1	24.10		24.50	10.60		11.90	65.30		63.50	2.41		2.39
2	24.50		24.40	12.20		9.00	63.30		66.70	2.39		2.42
3	22.10		24.40	14.50		9.90	63.30		65.70	2.41		2.41
4	24.10		23.80	9.00		10.20	66.90		66.00	2.43		2.42
5	23.10		24.20	12.60		10.50	64.30		65.30	2.41		2.41
With Cr^{3+}												
6	24.50		23.20	10.50		13.60	65.00		63.10	2.41		2.40
7	25.40		25.00	8.40		11.70	66.20		63.30	2.41		2.38
8	22.80		25.40	14.80		11.20	62.40		63.30	2.40		2.38
9	25.30		25.20	7.40		11.20	67.30		63.50	2.42		2.38
10	23.00		22.80	13.80		16.10	63.10		61.20	2.40		2.38
Mean (1–5)	23.58		24.26	11.78		10.30	64.62		65.44	2.41		2.41
SD (1–5)	0.98		0.28	2.08		1.06	1.52		1.20	0.01		0.01
Mean (1–5)		23.92			11.04			65.03			2.41	
SD (1–5)		0.77			1.74			1.36			0.01	
Mean (6–10)	24.20		24.32	10.98		12.76	64.80		62.88	2.41		2.38
SD (6–10)	1.24		1.22	3.25		2.11	2.06		0.95	0.01		0.01
Mean (6–10)		24.26			11.87			63.84			2.40	
SD (6–10)		1.16			2.75			1.82			0.02	
Mean (1–10)	23.89		24.29	11.38		11.53	64.71		64.16	2.41		2.40
SD (1–10)	1.10		0.84	2.61		2.04	1.71		1.69	0.01		0.02
Mean (1–10)		24.09			11.46			64.44			2.40	
SD (1–10)		1.00			2.35			1.72			0.02	

CONCLUSIONS

The results presented show that the described method can be used to determine the number average functionality and functionality distribution of these types of polyether polyols with a satisfactory precision and in an acceptable analysis time. The use of $Cr(acac)_3$ as a relaxation reagent allows faster pulse repetition, thereby generating equivalent data in a shorter overall analysis time. The method is generally applicable to any polyether where signals from the initiator can be identified and quantified and is now used routinely in this laboratory for analysis of a range of experimental and commercial products. For diols based on, for example, ethylene glycol or propylene glycol, where the initiator species cannot be distinguished from the polyether chain species, the functionality and functionality distribution can still be determined, although no differentiation can be made between diols from the initiator and diols from contaminating water.

This more detailed characterisation has already proved to be of value in assessing the consistency of commercial polyols and in investigating production processes. The method will undoubtedly form a cornerstone of research and development of these types of polyether polyols in the future.

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Received May 12, 1993
Accepted October 13, 1993