Designation: D4875 – 11

Standard Test Methods of Polyurethane Raw Materials: Determination of the Polymerized Ethylene Oxide Content of Polyether Polyols[1]

This standard is issued under the fixed designation D4875; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 *Test Method A*—Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR) measures polymerized ethylene oxide (EO) in ethylene oxide-propylene oxide polyethers used in flexible urethane foams and nonfoams. It is suitable for diols made from the commonly used initiators and containing EO percentages above five. For triols initiated with glycerin and trimethylol propane, an uncorrected EO value is obtained since both initiators have protons that contribute to the EO measurement.

1.2 *Test Method B*—Carbon-13 Nuclear Magnetic Resonance Spectroscopy (^{13}C NMR) measures the polymerized EO content of ethylene oxide-propylene oxide polyethers used in flexible urethane foams and nonfoams. It is suitable for diols and triols made from the commonly used initiators and containing EO percentages above five.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

NOTE 1—There is no known ISO equivalent to this standard.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D883 Terminology Relating to Plastics

E386 Practice for Data Presentation Relating to High-Resolution Nuclear Magnetic Resonance (NMR) Spectroscopy

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions*—Terminology in these test methods follows the standard terminology defined in Terminology D883 and Practice E386.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *heteric polyol, n*—a polyether polyol in which ethylene oxide and propylene oxide units are randomly arranged.

3.2.2 *initiator, n*—a substance with which ethylene oxide or propylene oxide reacts to form a polyether polyol.

3.2.2.1 *Discussion*—One initiator unit is incorporated into each polymer or oligomer molecule.

3.2.3 *EO capped polyol*—a polyol that contains a terminal block of ethylene oxide units

4. Summary of Test Methods

4.1 *Test Method A*—The ^{1}H NMR spectra of polyether polyols show two groups of resonance peaks corresponding to the methyl protons of propylene oxide (PO) and to the methylene and methine protons of EO and PO. The EO peak area is obtained by subtracting the area of the PO methyl peaks from the area of the methylene and methine peaks. Initiators other than glycols of EO and PO give systematic errors (see Note 2).

NOTE 2—The initiator error can be estimated by calculating the theoretical contribution of initiator protons to the EO and PO peak areas.

4.2 *Test Method B*—The ^{13}C NMR spectra of polyether polyols contain multiple resonances arising from initiator, EO, PO, EO/PO, sequencing, and end-group distribution. EO content can be determined relative to PO or relative to PO and triol initiator. In the former, the area of the EO peaks is ratioed to the total area of PO methylene and methine carbons. In the latter, the area of the EO peaks is ratioed to the total area of PO methylene and methine carbons and two initiator carbons. This test method describes the determination of EO relative to PO only.

[1] These test methods are under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.22 on Cellular Materials - Plastics and Elastomers.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

***A Summary of Changes section appears at the end of this standard**

5. Significance and Use

5.1 Measurements of EO content correlate with polyol reactivity (as related to primary hydroxyl content), linearity of foam rise, and the hydrophilicity of the polyol and final product.

5.2 Statistical data suggest that the ^{13}C NMR test method is the preferred method for measuring low levels (less than 10 %) of polymerized EO in polyols.

5.3 The ^{1}H and ^{13}C NMR test methods give different results which are highly correlated. The equation of the linear regression is:

$$\%EO_{proton} = 1.031\,(\%EO_{carbon-13}) + 0.883 \quad (1)$$

The standard deviation of the regression is 0.49 and the multiple R-square is 0.9990.

TEST METHOD A—HYDROGEN-1 NMR

6. Equipment

6.1 *NMR Continuous Wave (CW) or Fourier Transform (FT) Spectrometer,* with a ^{1}H resonance frequency of 60 MHz or higher.

6.2 *NMR Sample Tubes,* having an outside diameter of at least 5 mm.

7. Reagents and Materials

7.1 All reagents are to be ACS-certified or spectroscopic grade unless otherwise specified.

7.2 *Trifluoroacetic Acid.*

7.3 *Chloroform-d_1,* NMR-grade, containing tetramethylsilane as an internal standard.

8. Standard

8.1 This test method does not require standards. To evaluate the test method, standards can be prepared from commercially available poly(propylene oxide) and poly(ethylene oxide).

9. Preparation of Sample

9.1 Mix a few drops of polyol with deuterated chloroform to prepare 1 mL of an approximately 10 %[3] polyol solution. Add a drop of trifluoroacetic acid, mix well, and transfer to an NMR tube.

10. Instrument Preparation

10.1 The instrument settings given here are for a Varian EM-390 CW spectrometer, a Varian XL-100 FT spectrometer, and a Bruker AC 300 FT spectrometer. Instrument preparation can vary with the spectrometer. For a description of a particular spectrometer and suitable parameters, refer to the manufacturer's operating manual.

10.2 Typical Varian EM-390 console settings are as follows:

Lock	optional, TMS
Offset	0
Sweep width	5 ppm
Sweep time	2 min
Integration time	2 min
Rf Filter	open
RF power	0.05 mG

10.3 Typical Varian XL-100 console settings are as follows:

Lock	chloroform-d-1
Pulse angle	90°
Pulse delay	0
Spectral width	10 ppm
Acquisition time	4 s
Data points	8K
Number of transients	128

10.4 Typical Bruker 300 MHz console settings are as follows:

Lock	chloroform-d-1
Pulse angle	90°
Pulse delay	5 s
Spectral width	10 ppm
Acquisition time	5.3 s
Data points	32K
Number of transients	64

11. NMR Analysis

11.1 Place the NMR tube containing the polyol solution into the spectrometer probe and optimize the field homogeneity. For CW NMR, scan the spectrum from 5 to 0 ppm. Integrate the spectrum five times at a power level below that which causes saturation. See Figs. 1 and 2 for examples of polyol spectra with high and low EO concentrations, respectively.

11.2 For FT NMR, acquire the desired number of transients and transform the free induction decay signal to the frequency domain spectrum. Integrate the peaks as shown in Figs. 1 and 2.

11.3 Chemical shifts for the PO methyl proton resonances (area A) range from about 0.6-1.6 ppm and chemical shifts for the EO and PO methylene and methine proton resonances (area B) range from about 2.8-4.0 ppm

12. Calculation

12.1 Determine the areas of the PO methyl protons (area A) and the EO and PO methylene and methine protons (area B) from the integrals. Calculate the weight percent EO from the following equation:

$$EO = \frac{33 \times Z}{33 \times Z + 58} \times 100 \quad (2)$$

where:

Z = $(B/A) - 1$
33 = g EO/mole after weighting for the number of EO protons vs. PO protons, and
58 = g PO/mole.

13. Report

13.1 Report results to the nearest tenth percent EO.

14. Precision and Bias

14.1 Table 1 is based on a round robin conducted in 1981 in accordance with Practice E691, involving six polyol samples

[3] Highfield, FT spectrometers require less concentrated solutions. A 1 % solution is more appropriate for such spectrometers.

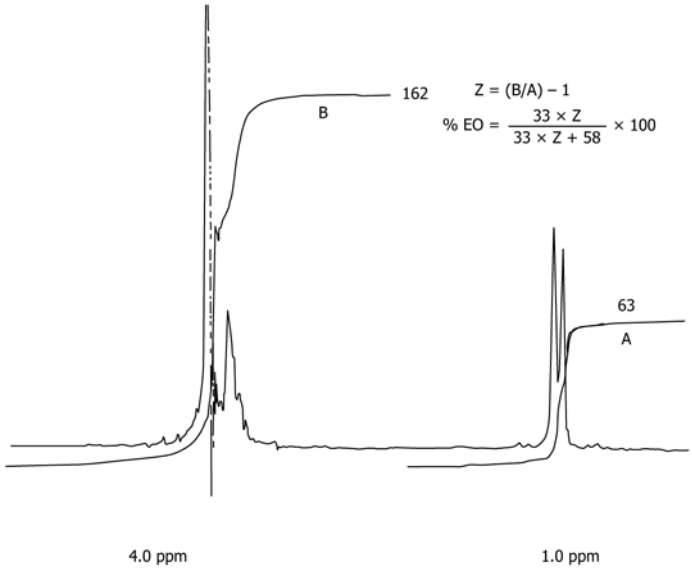

FIG. 1 ^{1}H NMR Spectrum of a Polyol Containing 45 % EO

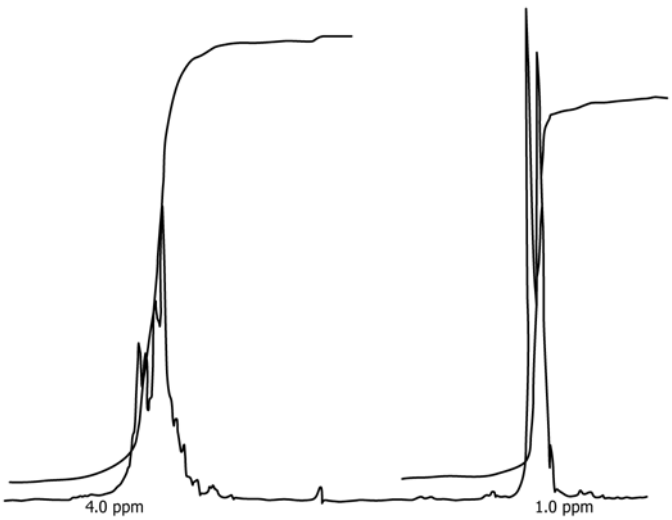

FIG. 2 ^{1}H NMR Spectrum of a Polyol Containing 8 % EO Uncorrected for Glycerin Initiator

TABLE 1 ^{1}H Method, % EO Content, for Eight Laboratories, Six Polyols

Sample	Mean	S_r	S_R	I_r	I_R
1	10.85	0.3207	1.045	0.898	2.926
2	16.40	0.3951	1.086	1.106	3.041
3	46.05	1.009	1.680	2.825	4.704
4	7.97	0.6809	1.557	1.907	4.360
5	13.61	0.5831	1.225	1.641	3.430
6	24.64	0.4496	0.5573	1.259	1.560

with EO content ranging from 6 to 45 weight % (see Table 2) tested by eight laboratories. For each polyol, all of the sampless were prepared at one source, but the individual specimens were prepared at the laboratories that tested them. Each test result was obtained from one individual NMR run. Each lab obtained two test results for each material on two separate days.

TABLE 2 Description of Samples Analyzed

Sample	Approximate Molecular Weight	Nominal Functionality	Polymerized EO Distribution	Approximate Weight, % EO
1	4000	diol	cap	10
2	2800	diol	cap	15
3	4000	diol	random/cap	45
4	3000	triol	random	6
5	3200	triol	random	10
6	6500	triol	cap	24

14.2 In Table 1, for the polyols indicated and for test results that are derived from testing two specimens of each polyol on each of two separate days:

14.2.1 S_r is the within-laboratory standard deviation of the average: $I_r = 2.83\ S_r$ (see 14.2.3 for application of I_r).

14.2.2 S_R is the between-laboratory standard deviation of the average; $I_R = 2.83\ S_R$ (see 14.2.4 for application of I_R).

14.2.3 *Repeatability*—In comparing two test results for the same polyol, obtained by the same operator using the same equipment on the same day, those test results are to be judged not equivalent if they differ by more than the I_r value for that polyol and condition.

14.2.4 *Reproducibility*—In comparing two test results for the same polyol, obtained by different operators using different equipment on different days, those test results are to be judged not equivalent if they differ by more than the I_R value for that polyol and condition. (This applies between different laboratories or between equipment within the same laboratory.)

14.2.5 Any judgment in accordance with 14.2.3 and 14.2.4 will have an approximate 95 % (0.95) probability of being correct.

14.2.6 Other polyols can give somewhat different results.

14.3 For further information on the methodology used in this section see Practice E691.

14.4 There are no recognized standards on which to base an estimate of bias for this test method.

14.5 Six CW spectrometers (60 and 90 MHz) were used in this study and two FT instruments (100 MHz). The participating companies were Dow, Union Carbide, Mobay, Texaco, Olin, Arco, and Upjohn.

TEST METHOD B—CARBON-13 NMR

15. Equipment

15.1 *Fourier-Transform NMR (FT-NMR) Spectrometer,* with carbon-13 capability. The spectrometer is to have a minimum signal-to-noise ratio of 70:1.

15.2 *NMR Sample Tubes,* with diameters of 5 mm or more.

16. Reagents

16.1 All reagents are to be spectroscopic grade deuterated solvents.

16.2 *Deuterated acetone,* NMR-grade, containing tetramethylsilane (TMS) as an internal standard.

17. Standards

17.1 This test method does not require standards. Standards prepared from poly(propylene oxide) and poly(ethylene oxide) can be used to approximate the spectrum of block copolymers. They are not suitable for heteric polyols.

18. Preparation of Sample

18.1 Mix 3 mL of polyol with 1 to 2 mL of deuterated acetone. Transfer an appropriate amount to an NMR tube.

19. Instrument Preparation

19.1 Prepare a decoupled carbon-13 experiment, selecting appropriate parameters to obtain quantitative intergration of the peaks.

19.2 The settings presented here apply to a Varian CFT-20 spectrometer and a Bruker AC 300 spectrometer. Instrument settings for other spectrometers vary. Consult the manufacturer's operating manual.

19.3 Typical Varian CFT-20 spectrometer parameters are as follows:

Lock	acetone d-6
Pulse angle	60°
Acquisition time	2 s
Pulse delay	0 s
Spectral width	2000 Hz
Data points	8K
FT transform	8K
Exponential weighting function	–0.8
H-1 decoupler	on

19.4 Typical Bruker AC 300 spectrometer parameters are as follows:

Lock	acetone d-6
Pulse angle	90°
Acquisition time	~2 s
Pulse delay	5 s
Spectral width	100 ppm
Data points	32K
H-1 decoupler	on, or gated decoupling

20. NMR Analysis

20.1 Place the NMR tube containing the sample solution into the spectrometer probe. After a stable lock is obtained, optimize the field homogeneity. Acquire a sufficient number of transients to obtain satisfactory signal to noise, usually 1000 to 2000. Transform the weighted free induction decay signal to the frequency domain spectrum. The PO methine and methylene carbon resonances range from 76.6 to 72.8 and 67.0 to 65.2 ppm (TMS reference). Chemical shifts for the EO peaks range from 72.6 to 68.3 and 62.0 to 61.0 ppm. See Figs. 3 and 4 for examples of EO capped polyols.

20.2 Integrate the PO methine and methylene carbons and the EO carbons as shown in Fig. 4.

21. Calculation

21.1 Determine the areas of the PO peaks (B' + C' – F, Fig. 4) and the areas of the EO peaks (B + C + F, Fig. 4). (See Note 3.) Calculate the PO to EO ratio from the following equation:

$$PO/EO = \frac{B' + C' - F}{B + C + F} \quad (3)$$

where:

B' = area of PO methylene and methine carbons,
B = area of EO carbons,
C' = area of PO terminal methine carbon,
C = total area of terminal EO carbons, and
F = area of terminal EO carbon of an EO block.

NOTE 3—Areas C and F are only significant in EO-capped polyols. Area F corrects for the beta carbon of a terminal EO block which resonates at 73.1 ppm and integrates as a PO carbon.

21.2 Determine the weight percent EO using the PO/EO ratio calculated in 21.1:

$$EO = \frac{44}{58(PO/EO) + 44} \times 100 \quad (4)$$

where:

44 = g EO/mole, and
58 = g PO/mole.

22. Report

22.1 Report data to nearest tenth percent EO.

23. Precision and Bias[4]

23.1 Table 3 is based on a round robin conducted in 1981 in accordance with Practice E691, involving six polyol samples with EO content ranging from 6 to 45 weight % (see Table 4) tested by eight laboratories. For each polyol, all of the samples were prepared at one source, but the individual specimens were prepared at the laboratories that tested them. Each test result was obtained from one individual NMR run. Each lab obtained two test results for each material on two separate days.

23.2 In Table 3, for the polyols indicated and for test results that are derived from testing two specimens of each polyol on each of two separate days:

23.2.1 S_r is the within-laboratory standard deviation of the average: $I_r = 2.83\ S_r$ (see 23.2.3 for application of I_r).

23.2.2 S_R is the between-laboratory standard deviation of the average; $I_R = 2.83\ S_R$ (see 23.2.4 for application of I_R).

[4] Supporting data are available from ASTM Headquarters. Request RR:D20-1148.

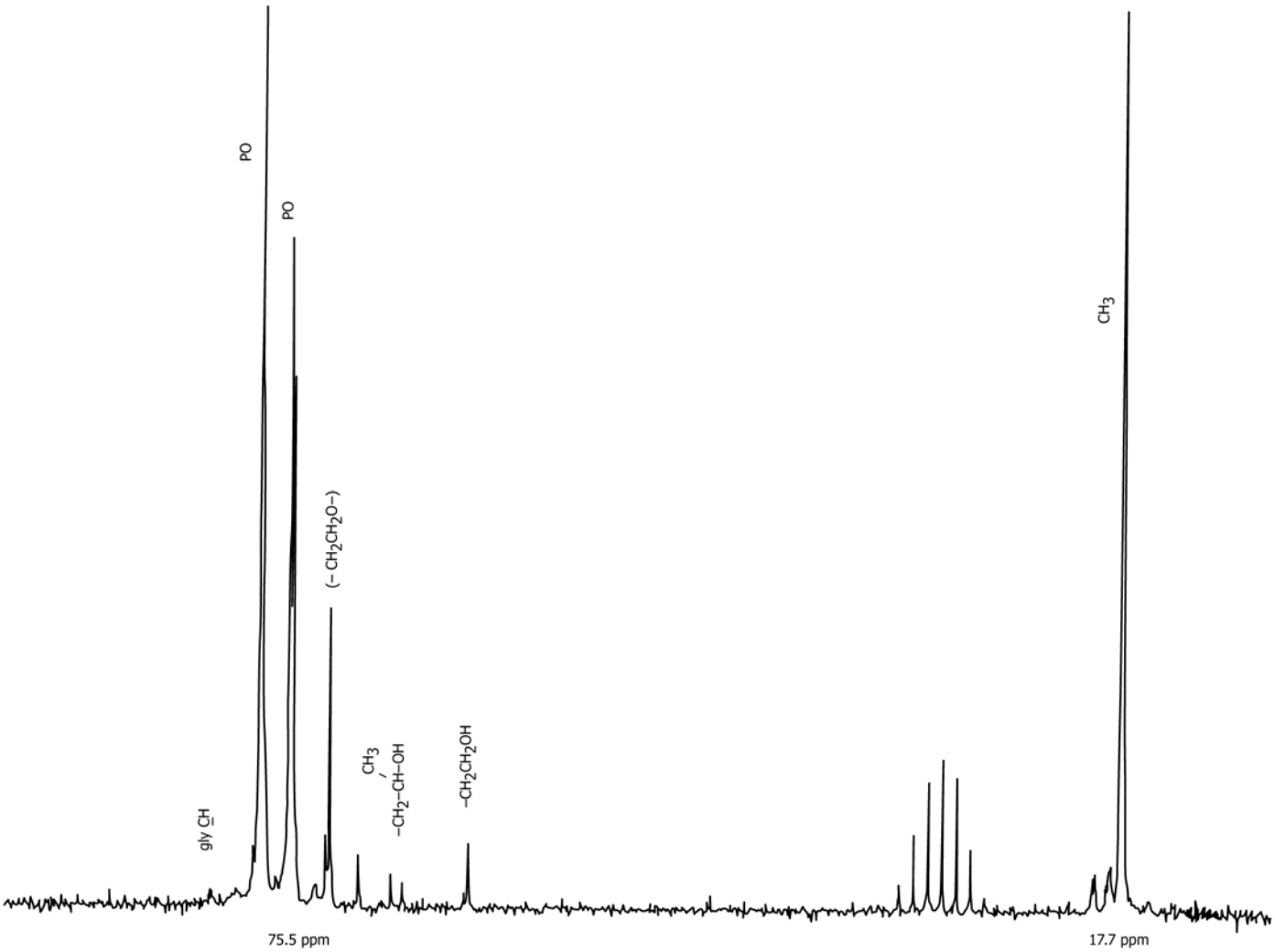

FIG. 3 ^{13}C NMR Spectrum of a Polyol With a 7 % EO Cap

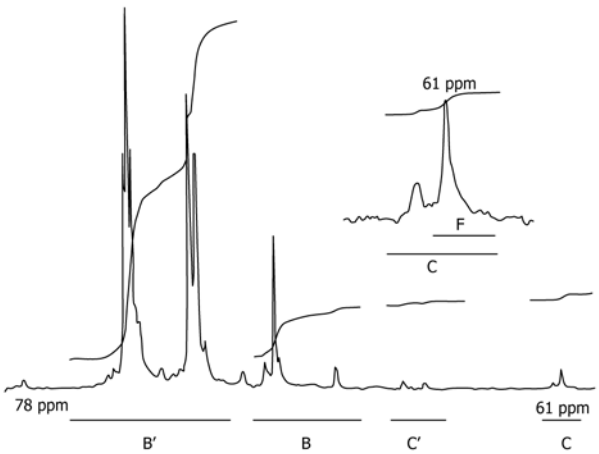

FIG. 4 ^{13}NMR Spectrum: Polyether Methylene and Methine Region, % EO = 10

TABLE 3 ^{13}C Method, % EO Content, for Eight Laboratories, Six Polyols

Sample	Mean	S_r	S_R	I_r	I_R
1	10.07	0.4630	1.255	1.296	3.514
2	14.61	0.4472	0.9880	1.252	2.766
3	43.54	0.8658	1.5689	2.424	4.393
4	6.51	0.2686	1.1223	0.752	3.142
5	12.52	0.3953	0.8873	1.107	2.484
6	23.57	0.3843	0.8549	1.076	1.394

23.2.3 *Repeatability*—In comparing two test results for the same polyol, obtained by the same operator using the same equipment on the same day, those test results are to be judged not equivalent if they differ by more than the I_r value for that polyol and condition.

23.2.4 *Reproducibility*—In comparing two test results for the same polyol, obtained by different operators using different equipment on different days, those test results are to be judged not equivalent if they differ by more than the I_R value for that polyol and condition. (This applies between different laboratories or between equipment within the same laboratory.)

23.2.5 Any judgment in accordance with 23.2.3 and 23.2.4 will have an approximate 95 % (0.95) probability of being correct.

TABLE 4 Description of Samples Analyzed

Sample	Approximate Molecular Weight	Nominal Functionality	Polymerized EO Distribution	Approximate Weight, % EO
1	4000	diol	cap	10
2	2800	diol	cap	15
3	4000	diol	random/cap	45
4	3000	triol	random	6
5	3200	triol	random	10
6	6500	triol	cap	24

23.2.6 Other polyols can give somewhat different results.

23.3 For further information on the methodology used in the section see Practice E691.

23.4 There are no recognized standards on which to base an estimate of bias for this test method.

23.5 The NMR spectrometers used in this study were three Varian CFT20's, two JEOL FX60's, a Varian XL100, a Bruker WP80, and a Bruker MW250. The participating companies were Dow, Union Carbide, Mobay, Texaco, Olin, Arco, Upjohn, and DuPont.

24. Keywords

24.1 EO polymer; EO/PO ratio; ethylene oxide; NMR; polyethers; polyols; polyurethane raw materials

SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this standard since the last issue, D4875 - 05, that may impact the use of this standard. (April 1, 2011)

(1) Corrected spelling error in 1.1.
(2) Added a statement about SI units (1.3) in accordance with D4968.
(3) Revised Note 1 to reflect the format (language and location) specified in D4968
(4) Added a definition for EO capped polyols in 3.2.3.
(5) Replaced the term alkoxide with EO and PO in 4.2 for clarity and added the term polyol for consistency.
(6) Removed duplicate spaces in 5.2, 5.3, 6.2, 23.2.3, and 23.2.4.
(7) Corrected a grammatical error in 6.1.
(8) Revised 10.2, 10.3, 10.4, 19.3, and 19.4 to include to complete names of the instruments referenced and to remove non-mandatory language.
(9) Added 11.3, which gives approximate chemical shift ranges of the resonances of interest to augment the figures provided.
(10) Changed percent to weight percent for clarity in 12.1.
(11) Corrected a typographical error in 15.1.