



# Standard Test Methods of Polyurethane Raw Materials: Determination of the Polymerized Ethylene Oxide Content of Polyether Polyols<sup>1</sup>

This standard is issued under the fixed designation D 4875; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope \*

1.1 *Test Method A*—Proton Nuclear Magnetic Resonance Spectroscopy ( $^1\text{H}$  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 greater than or equal to six. 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 (see Note 1).

1.2 *Test Method B*—Carbon-13 Nuclear Magnetic Resonance Spectroscopy ( $^{13}\text{C}$  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 greater than or equal to six.

NOTE 1—There are no equivalent ISO standards.

1.3 *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.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 883 Terminology Relating to Plastics<sup>2</sup>

E 180 Practice for Developing the Precision Data of ASTM Methods for Analysis and Testing of Industrial Chemicals<sup>3</sup>

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method<sup>4</sup>

## 3. Terminology

3.1 *Definitions*—Terminology in these test methods follows the standard terminology defined in Terminology D 883.

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D-20 on Plastics and are the direct responsibility of Subcommittee D20.22 on Cellular Plastics.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 08.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 15.05.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 14.02.

## 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *heteric polyol, n*—a poly ether 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.

## 4. Summary of Test Methods

4.1 *Test Method A*—The  $^1\text{H}$  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  $^{13}\text{C}$  NMR spectra of polyethers contain multiple resonances arising from initiator, alkoxide, alkoxide sequencing, and end-group distribution. EO content may 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 alkoxide methylene and methine carbons. In the latter, the area of the EO peaks is ratioed to the total area of alkoxide methylene and methine carbons and two initiator carbons. This test method describes the determination of EO relative to PO only.

## 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  $^{13}\text{C}$  NMR test method is the preferred method for measuring low levels (less than 10 %) of polymerized EO in polyols.

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

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

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

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 an <sup>1</sup>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 should be ACS certified or spectroscopic grade unless otherwise specified.

7.2 *Trifluoroacetic Acid*.

7.3 *Chloroform-d<sub>1</sub>*, 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 may 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 %<sup>5</sup> 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 and a Varian XL-100 FT spectrometer. Instrument preparation may vary with the spectrometer. For a description of a particular spectrometer and suitable parameters, refer to the manufacturer’s operating manual.

10.2 Typical 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 XL-100 console settings are as follows:

Lock	chloroform-d <sub>1</sub>
Pulse width	90°
Pulse delay	0
Spectra width	10 ppm
Aquisition time	4 sec
Data points	8K
Number of transients	128

**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 spectrum.

**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 integration curves. Calculate the percent EO from the following equation:

$$EO = \frac{33.1 \times Z}{33.1 \times Z + 58.1} \times 100 \tag{2}$$

where:

$$Z = (B/A) - 1$$

**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 E 691, involving six polyol samples with EO content ranging from 6 to 45 weight % (see Table 2) 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.

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<sub>r</sub>* is the within-laboratory standard deviation of the average; *I<sub>r</sub>* = 2.83 *S<sub>r</sub>* (see 14.2.3 for application of *I<sub>r</sub>*).

14.2.2 *S<sub>R</sub>* is the between-laboratory standard deviation of the average; *I<sub>R</sub>* = 2.83 *S<sub>R</sub>* (see 14.2.4 for application of *I<sub>R</sub>*).

14.2.3 *Repeatability*—In comparing two test results for the same polyol, obtained by the same operator using the same

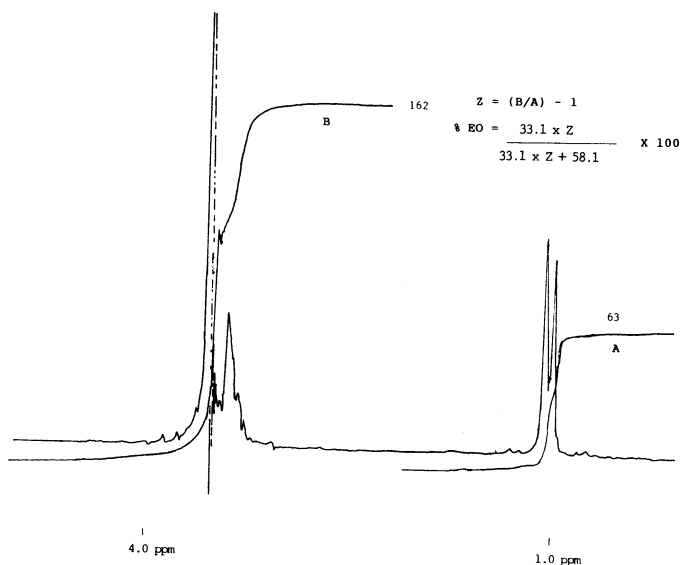


FIG. 1 <sup>1</sup>H NMR Spectrum of a Polyol Containing 45 % EO

<sup>5</sup> Highfield, FT spectrophotometers require less concentrated solutions. A 1 % solution is more appropriate for such spectrophotometers.

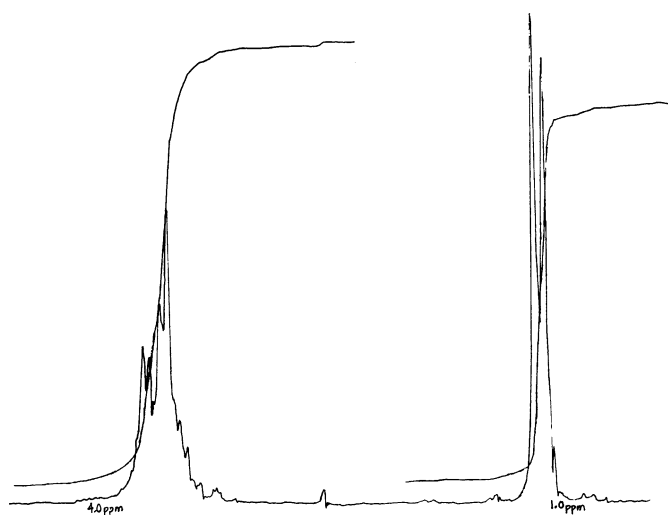


FIG. 2 <sup>1</sup>H NMR Spectrum of a Polyol Containing 8 % EO Uncorrected for Glycerin Initiator

TABLE 1 <sup>1</sup>H Method, % EO Content, for Eight Laboratories, Six Polyols

Sample	Mean	<i>S<sub>r</sub></i>	<i>S<sub>R</sub></i>	<i>I<sub>r</sub></i>	<i>I<sub>R</sub></i>
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

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

equipment on the same day, those test results should be judged not equivalent if they differ by more than the *I<sub>r</sub>* 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 should be judged not equivalent if they differ by more than the *I<sub>R</sub>* 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 may give somewhat different results.

14.3 For further information on the methodology used in this section see Practice E 691.

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 participat-

ing 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 should have a minimum signal-to-noise ratio of 70:1.

15.2 *NMR Sample Tubes*, with diameters of 8 mm or more.

### 16. Reagents

16.1 All reagents should be spectroscopic grade deuterated solvents.

16.2 *Deuterated Acetone*, NMR-grade, containing tetramethylsilane 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) may 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 The settings presented here apply to a Varian CFT-20 spectrometer. Instrument settings for other spectrometers may be different. Consult the manufacturer's operating manual.

19.2 Typical CFT-20 spectrometer parameters are as follows:

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	broadband, on at all times
Mode	autoshim

### 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. Add together 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 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 2.) Calculate the PO to EO ratio from the following equation:

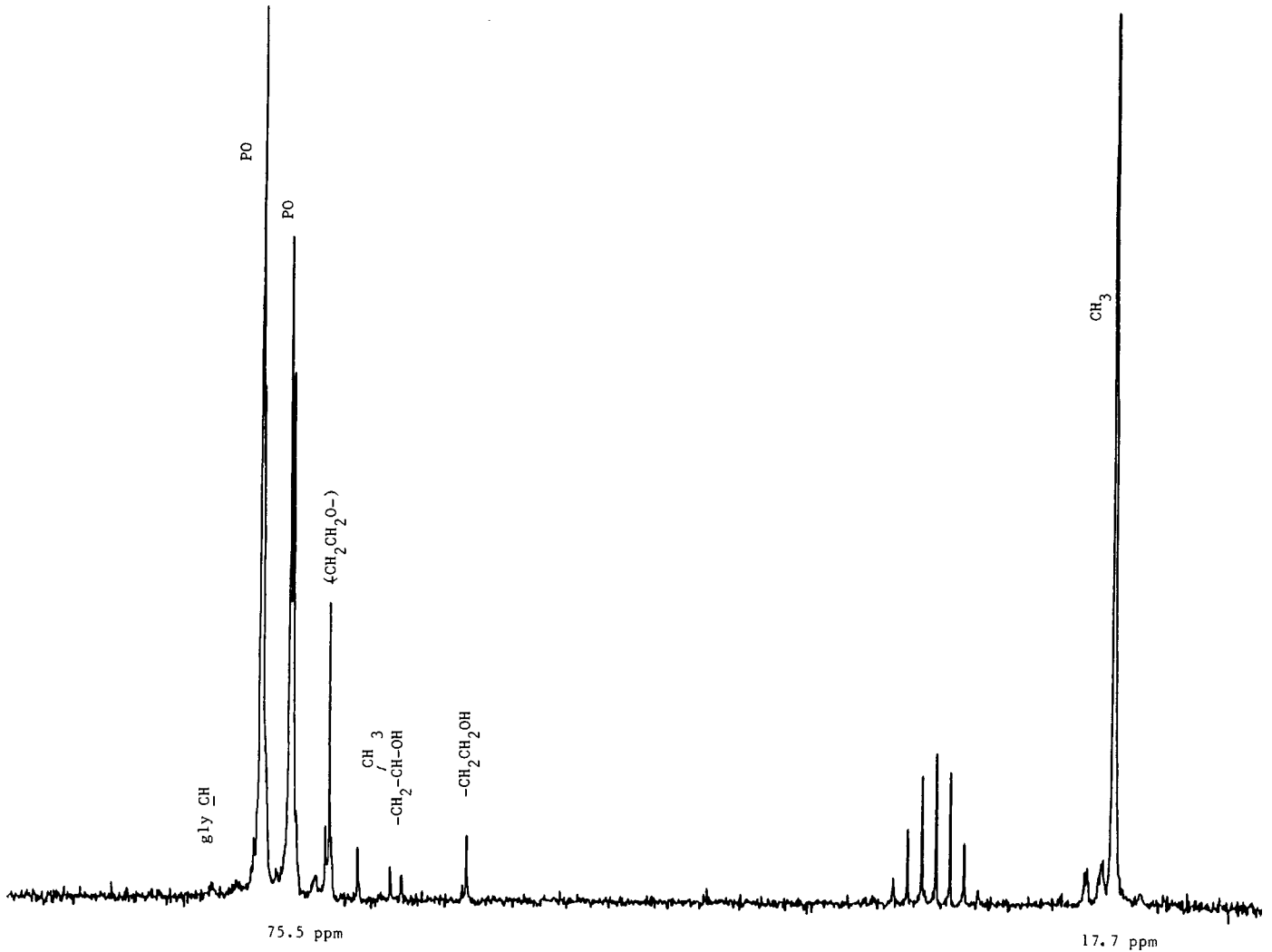


FIG. 3 <sup>13</sup>C NMR Spectrum of a Polyol With a 7 % EO Cap

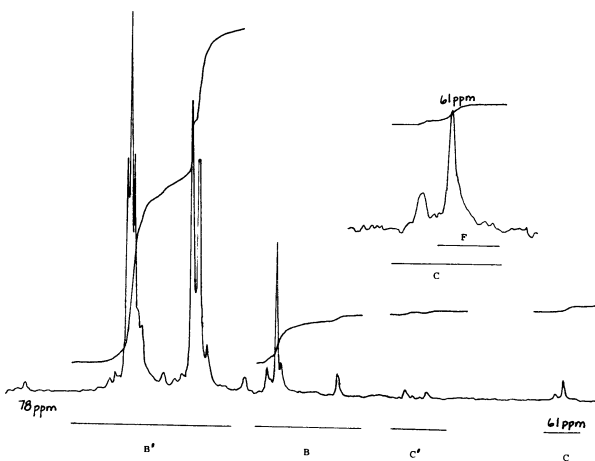


FIG. 4 <sup>13</sup>C NMR Spectrum: Polyether Methylene and Methine Region, % EO = 10

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

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:

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

## 22. Report

22.1 Report data to nearest tenth percent EO.

## 23. Precision and Bias <sup>6</sup>

23.1 Table 3 is based on a round robin conducted in 1981 in accordance with Practice E 691, involving six polyol samples

<sup>6</sup> Supporting data are available from ASTM Headquarters. Request RR: D20-1148.

**TABLE 3 <sup>13</sup>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

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  $I_r$ ).

**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

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

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 should 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 should 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.

23.2.6 Other polyols may give somewhat different results.

23.3 For further information on the methodology used in the section see Practice E 691.

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; ethylene oxide; NMR; polyethers; polyols; polyurethane raw materials

## SUMMARY OF CHANGES

Committee D-20 has identified the location of selected changes to these test methods since the last issue that may impact the use of these test methods:

D 4875–99:

(1) In 7.1, removed phrase concerning reasonably free from paramagnetic materials as this is unnecessary if solvents are NMR-grade. Added “NMR-grade” to clearly define purity in 7.3.

(2) In 9.1, added new footnote 5. Also, replaced “two drops” with “a drop” to reflect current practice.

(3) In 10.1, replaced “details of operation” with “suitable parameters” to emphasize that with current instrumentation, the settings will vary from those reported in this section.

(4) In 15.1, removed “Pulse” as it is too restrictive for current practice. Removed “and a carbon-13 resonance frequency of 15 MHz or higher,” and “based on the largest aromatic peak...mathematical transformations” to better reflect current practice.

(5) In 15.2, replaced 8 mm with 5 mm to better reflect current practice.

(6) In 16.1, removed phrase about reasonably free of paramagnetic materials, as it is unnecessary in current practice and if NMR-grade solvents are used.

(7) In 16.2, added “NMR-grade, containing tetramethylsilane as an internal standard” to clearly define purity and composition.

(8) In 18.1, replaced “Add 3 mL of polyol and 2 to 3 mL of deuterated acetone to an NMR tube. Cap and mix thoroughly.” with “Mix 3 mL of polyol with 1 to 2 mL of deuterated acetone. Transfer an appropriate amount to an NMR tube.” to better reflect current practice.

(9) Added Keywords, Section 24.

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