Designation: ~~D4875 – 11~~ D4875 – 18

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~~ content of ethylene ~~oxide-propylene oxide polyethers~~ oxide (EO) propylene oxide (PO) polyether polyols used in flexible ~~urethane~~polyurethane foams and ~~nonfoams.~~non-foams. It is suitable for diols ~~made from the commonly used initiators and~~initiated from glycols of EO or PO containing EO percentages ~~above five.~~ >5. For triols initiated with ~~glycerin and trimethylol propane,~~ glycerol (glycerin) and trimethylolpropane, 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~~ EO-PO polyether polyols used in flexible ~~urethane~~polyurethane foams and ~~nonfoams.~~non-foams. It is suitable for diols and triols made from the commonly used initiators and containing EO percentages ~~above five.~~>5.

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~~ safety, health, and ~~health~~environmental practices and determine the applicability of regulatory limitations prior to use.*

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

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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 (Withdrawn 2015)[3]~~

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

E2977 Practice for Measuring and Reporting Performance of Fourier-Transform Nuclear Magnetic Resonance (FT-NMR) Spectrometers for Liquid Samples

3. Terminology

3.1 *Definitions*—~~Definitions~~For ~~—Terminology in these test methods follows the standard terminology defined in~~ definitions of terms that appear in this method refer to Terminology D883 and Practice ~~E386~~E2977.

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.

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[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**

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~~ peaks. The first group corresponds to the methyl protons of propylene oxide ~~(PO) and~~ (PO). The second group corresponds to the methylene and methine protons of ~~EO and PO.~~ PO and the methylene protons of EO. 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. This calculation is outside the scope of this method.

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

5. Significance and Use

5.1 Measurements of EO content correlate ~~with~~to 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~~A—PROTON NMR

6. ~~Equipment~~Apparatus

6.1 ~~*NMR Continuous Wave (CW) or*~~ *Fourier Transform* ~~*(FT)*~~ *NMR (FT-NMR) Spectrometer,* with a ^{1}~~H~~proton resonance frequency of ~~60~~200 MHz or higher. The spectrometer is to have a minimum proton signal-to-noise ratio of 100:1 based on a 0.1 % ethylbenzene in deuterated chloroform ($CDCl_3$) sample that has been pulsed once using a 90° pulse angle under the conditions described in Practice E2977.

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

6.3 *NMR spinners.*

7. Reagents and Materials

7.1 All reagents are to be ~~ACS-certified or~~ spectroscopic grade ~~unless otherwise specified.~~and free of magnetic materials.

7.2 *Trifluoroacetic* ~~*Acid.*~~*acid.*

7.3 ~~*Chloroform-d*~~*Deuterated*~~*,*~~ *chloroform,* ~~NMR-grade,~~ containing tetramethylsilane (TMS) as an internal standard.

8. Hazards

8.1 *Magnetic Fields*—Follow the manufacturer's recommendation for the safe operation of the instrument.

8.1.1 Persons with implanted or attached medical devices such as pacemakers and prosthetic parts must remain outside the 5-gauss perimeter.

8.1.2 Objects made of ferromagnetic material will be attracted to the magnet and are to be kept a safe distance away.

9. Preparation of Apparatus

9.1 Prepare a proton NMR experiment selecting appropriate parameters to obtain quantitative integration of the spectrum.

9.1.1 *Pulse Angle and Sequence Delay Time*—Select a 90 degree pulse angle with a delay of $10 \times T_1$ of the peak with the longest relaxation time in the spectrum. It is acceptable to use a different pulse angle/sequence delay combination provided that quantitative data acquisition is not compromised.

9.1.2 *Number of Scans*—Select the appropriate number to yield a signal to noise of >100:1 between 2 and 0.5 ppm (usually 16 to 64).

9.1.3 *Sweep Width*—~14 ppm.

9.1.4 *Transmitter Frequency*—~6 ppm.

9.1.5 *Acquisition Time*—2 to 4 s.

10. ~~Standard~~ Calibration and Standardization

10.1 This test method does not require standards. To evaluate the test method, standards can be prepared ~~from~~ by blending commercially available poly(propylene oxide) and poly(ethylene ~~oxide).~~oxide) diols. The molecular weights of the diols should ideally be 300 or more since lower molecular weight polyols can contain structural configurations that are not typical of polyether polyols used in flexible polyurethane foams and non-foams.

~~9. Preparation of Sample~~

~~9.1 Mix a few drops of polyol with deuterated chloroform to prepare 1 mL of an approximately 10 %[4] 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~~ Procedure

11.1 Prepare a solution of the polyol in deuterated chloroform. A 0.5-5 % solution is recommended. Add one to two drops of trifluoroacetic acid and mix well. More acid will be required if a higher than recommended concentration of polyol is used (see NOTE 3).

11.2 Transfer an appropriate amount of the sample solution to an NMR tube.

11.3 Place the NMR tube ~~containing the polyol solution~~ into a spinner, adjust it to the appropriate depth and insert it 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~~ probe.~~Figs. 1 and 2 for examples of polyol spectra with high and low EO concentrations, respectively.~~

11.4 Obtain a stable lock on the solvent.

11.5 Tune and match the probe.

11.6 Shim the sample to optimize field-homogeneity.

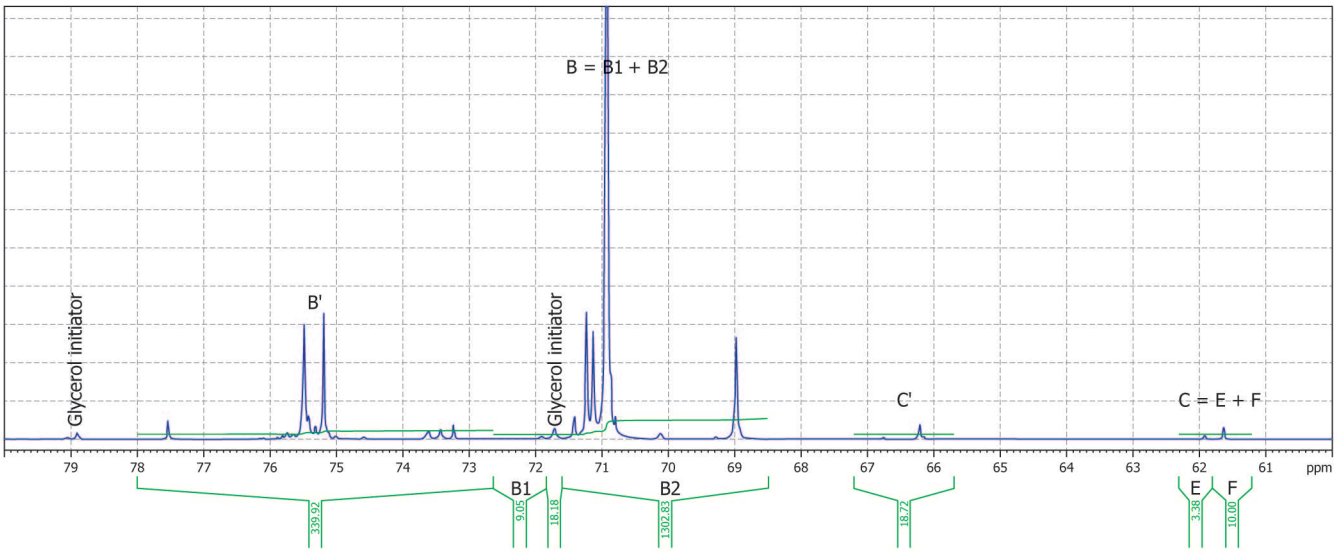

FIG. 2 $^{1+13}$HC NMR Spectrum of a ~~Polyol Containing 8 % EO Uncorrected for Glycerin Initiator~~Glycerol Initiated Polyol (BB23794)

11.7 Acquire the NMR data.

11.8 Zero fill the data. The recommended value is 1 or 2 x number of points.

11.9 Apply a spectral weighting function (apodization) and Fourier Transform the Free Induction Decay (FID). The recommended apodization is an exponential window multiplication and a typical line broadening value is 1/acquisition time.

11.10 Phase and baseline correct the spectrum.

11.11 Set the internal TMS reference to 0 ppm.

11.12 ~~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~~ Expand and integrate the peaks of interest. The methyl protons of PO typically resonate in the 0.5-1.7 ppm region (Area A). The methylene and methine protons of PO and the methylene protons of EO typically resonate in the 2.8-4.8 ppm region (Area B). An example is shown in ~~Figs. 1 and 2~~Fig. 1. (see Note 4).

NOTE 3—Trifluoroacetic acid is added to move hydroxyl (OH) protons to a higher chemical shift and away from the regions of interest. The sample should be run as soon as practical after preparation to minimize the formation of esters of trifluoroacetic acid.

NOTE 4—Allyl unsaturation, if present, will contribute to the integral value of Area B. This contribution is expected to be minor for typical EO-PO polyether polyols and can be corrected by subtracting the integral value of two ally protons that have chemical shifts outside the regions of interest. This correction is not included in the scope of this method.

~~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~~

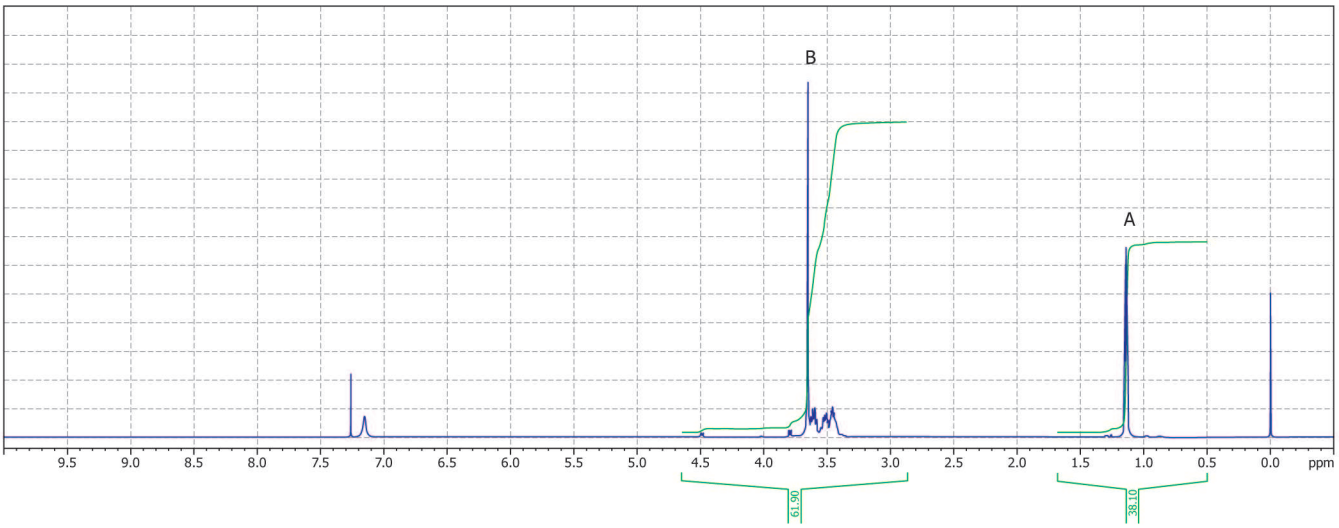

FIG. 1 ^{1}H NMR Spectrum of a ~~Polyol Containing 45 % EO~~DPG Initiated EO/PO Polyol (BB23798)

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~~ content using the following equation:

$$EO = \frac{33 \times Z}{33 \times Z + 58} \times 100 \quad (1)$$

$$EO, wt\% = \frac{C*44.05*100}{(C * 44.05)+(D * 58.08)} \times 100 \quad (1)$$

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.~~

A = area of methyl PO protons,
B = area of methylene and methine PO protons and area of methylene EO protons,
C = (B–A)/4 integral per EO proton,
D = A/3 integral per PO proton,
44.05 = g EO/mole, and
58.08 = g PO/mole.

13. Report

13.1 Report ~~results to the nearest tenth percent EO.~~the % EO content to two decimal places. For polyether polyols with initiators other than glycols of EO and PO, report that the value is uncorrected for the initiator.

14. Precision and Bias

14.1 Table 1 is based on a round robin conducted in ~~1981~~2016 in accordance with Practice E691, involving ~~six polyol samples with EO content ranging from 6 to 45 weight % (see~~ five materials ~~Table 2)~~ tested by ~~eight~~six laboratories. For each ~~polyol,~~material, all ~~of~~ the ~~samples~~samples were prepared at one source, but the individual specimens were prepared at the laboratories ~~that~~which tested them. Each test result was ~~obtained from one individual NMR run. Each lab~~a single determination. Each laboratory obtained two test results for each ~~material on two separate days.~~material.

14.2 *Caution*—The explanation of "r" and "R" is only intended to present a meaningful way of considering the approximate precision of this test method. Do not apply the data in Table 1 to accept or reject materials, as these data apply only to the materials tested in the round robin and are unlikely to be rigorously representative of other lots, formulations, conditions, materials, or laboratories. Users of this test method need to apply the principles outlined in Practice E691 to generate data specific to their materials and laboratory (or between specific laboratories). The principles would then be valid for such data.

14.3 *Repeatability*—Precision under repeatability conditions.

14.4 *Reproducibility*—Precision under reproducibility conditions.

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~~

TABLE 1 Polymerized Ethylene Oxide Content of Polyether Polyols by Proton NMR

Sample	Material	OH Value (mg KOH/g)	Mean	S_r[B]	S_R[C]	r[D]	R[E]
BB23794	Glycerol/EO-PO (EO+PO > 6.5) mixed feed	43	74.79	0.14	0.31	0.38	0.85
BB23796	EO/PO	30	16.62	0.11	0.53	0.31	1.49
BB23797	Blend of PPG 2000 and PEG 400[A]	69	4.95	0.17	0.63	0.49	1.75
BB23798	DPG/EO-PO (EO+PO > 4.5)	30	26.51	0.10	0.48	0.27	1.34
BB23799	DPG/EO-PO (EO+PO > 4.5)	31	20.30	0.07	0.50	0.19	1.40

[A] Phase separation was observed in sample BB23797. The data for this sample are expected to include this variability.
[B] S_r = within laboratory standard deviation for the indicated material. It is obtained by pooling the within-laboratory standard deviations of the test results from all of the participating laboratories:
$S_r = [\,[\,(S_1)^2 + (S_2)^2 + \ldots \ldots (S_n)^2\,]/n]^{1/2}$ where n = number of participating laboratories.
[C] S_R = between-laboratories reproducibility, expressed as standard deviation:
$S_R = [S_r^2 + S_L^2]^{1/2}$ where S_L = standard deviation of laboratory means.
[D] r = within-laboratory critical interval between two test results = 2.8 × S_r.
[E] R = between-laboratories critical interval between two test results = 2.8 × S_R.

14.5 ~~In~~Any ~~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:~~judgment in accordance with the repeatability and reproducibility statements shown would have an approximate 95 % (0.95) probability of being correct.

~~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.~~

14.6 There are no recognized standards ~~on~~by which to ~~base an~~ estimate ~~of~~ bias ~~for~~of 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~~Apparatus

15.1 *High Resolution Fourier-Transform NMR ~~(FT-NMR)~~ Spectrometer,* with carbon-13 ~~capability.~~ capability, and a carbon-13 resonance frequency of 50 MHz (proton resonance frequency of 200 MHz) or higher. The spectrometer is to have a minimum carbon-13 signal-to-noise ratio of ~~70:1.~~70:1 based on the benzene carbon signal in 60 % benzene-d6, 40 % p-dioxane (v/v) sample (ASTM NMR standard) that has been pulsed once using a 90° pulse angle under the conditions described in Practice E2977.

15.2 *NMR ~~Sample Tubes,~~sample tubes,* ~~with~~having outside diameters of 5 mm or more.

15.3 *NMR spinners.*

16. Reagents and Materials

~~16.1 All reagents are to be spectroscopic grade deuterated solvents.~~