

Structure of Toluene Sulfonamide Formol Resins: Molecular Models from Mechanistic Schemes and Analytical Results

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SYNOPSIS

Toluene Sulfonamide Formaldehyde Resins (TSFR), having elemental analyses close to $(C_8H_9NSO_2)_n$, are shown by GPC to exist as a mixture of a few (5 to 6) oligomers, having masses between 400 and 1900 g. A complete scheme of all the possible intermediates involved in their preparation is derived from the results of synthesis and from mechanistic steps; this allows one to propose the structure of oligomers having end groups OH and NH. IR, ¹H NMR, and ¹³C NMR data on oligomers, compared to those of authentic samples specially designed and prepared, agree with the structures proposed. These results are helpful in designing modified or new resins to be used in nail lacquers. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Cosmetics and toiletry products are finding worldwide increased interest. Over the past few years there has been a slow move towards new, "natural" cosmetics.¹ This move is a result of the interest of the consumer in products containing more biological or other natural ingredients and also is a result of new regulations (in Europe and the USA) that demand the use of safe and non-toxic materials according to specific analytical tests.

Nail polishes are subject to these trends and will have to fulfill soon the new strict regulations. A typical example concerns arylsulfonamides, used as "filling" resins in nail lacquer compositions: these resins should not expel formaldehyde, a chemical substance that has to be avoided for skin or its adjuncts. To determine the chemical conditions under which formaldehyde is expelled from the resin, we performed a detailed analysis of these compounds with complementary chemical, chromatographic, and spectroscopic methods (using recent techniques when available). We tried to obtain the best chemical models of the resins and we hoped that these models will help us in making improved resins or in

designing new ones. In this article we describe these models from analytical tests and mechanistic schemes.

EXPERIMENTAL

Product Analyses

GPC analyses were carried out on a Waters system with a wisp 712 injector; detection was made with a 480 (259 nm) spectrophotometer and a R 410 refractometer, columns (microstyrigel) 500 to 10⁴ Å, THF (0.05% hydroquinone) used as solvent; flow rate: 1 mL/min, GPC calibration standard: polypropyleneglycol (ppg).

The experimental molecular masses, shown in Table V, are calculated from the peak masses expressed in ppg equivalent (the ppg is used as a reference), modified by a correction factor; this factor is estimated with the following authentic samples (supposed to have a molecular shape close to that of the oligomers in Table V). $CH_3-C_6H_4-SO_2-NH-CH_3$ (a) commercial product; $(CH_3-C_6H_4-SO_2-N-CH_3)_2-CH_2$ (b), and $[CH_2-N-(SO_2-C_6H_4-CH_3)]_3$ (c) authentic samples (synthesis detailed in subsection Synthetic Procedures).

With correction factors ranging from 1.99 to 2.25, a value of 2.10 was selected (Table I). This means

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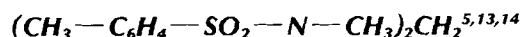
Table I Correction Factor

Products	<i>a</i>	<i>b</i>	<i>c</i>
Peak Masses (ppg eq.)	84	170	275
Real Masses (g)	185	382	549
Correction Factor	2.20	2.25	1.99

a 5% uncertainty on the mass values of the oligomers.

Elementary analyses were determined with a Technicon. ^1H NMR spectra were recorded on a Bruker AW 60 at 60 MHz, on a Bruker AC 100 at 100 MHz, and on a Bruker AM 400X at 400 MHz. ^{13}C NMR spectra were recorded on a Bruker AM 400X. Routine IR spectra were recorded on a MXS Nicolet FTIR. Mass spectrometry was recorded on a MS 50 Kratos. Quantitative OH was determined with a titrator 682 (Metrohm) and a combined pH glass electrode (Metrohm). Melting points were determined with a Heinzbank, Kofler system, type WME.

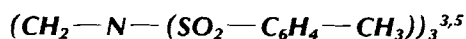
Synthetic Procedures



A three-necked flask, fitted with a reflux condenser and a dropping funnel, is charged with 50 mL of toluene, 3.7 g (0.02 mol) of *N*-methyl paratoluenesulfonamide, and 0.67 g (0.002 mol) of tetra-*n*-butylammonium hydrogen sulfate, and 50 mL of a solution of sodium hydroxide (50/50 in weight) is added dropwise (for controlling exothermicity). The mixture is refluxed and 1.74 g (0.0107 mol) of CH_2Cl_2 , diluted in 10 mL of toluene, is added, with magnetic stirring, over 1 h 30 min. Reflux is continued, with stirring, over 2 h 30 min. The reaction mixture is cooled to ambient and diluted with water.

After decantation, the organic phase is dried on MgSO_4 and toluene is evaporated. The product was crystallized from ethanol, yielding white crystals (75% yield): mp 120°C, ^1H NMR (400 MHz, CDCl_3) δ 2.40 (3H, s, ArCH_3), 2.80 (3H, s, NCH_3), 4.50 (2H, s, CH_2), 7.42 (4H, AB, ArH); ^{13}C NMR (400 MHz, CDCl_3) δ 21.5 (CH_3Ar), 33.0 (CH_3N), 64.6 (CH_2), 127.0 (CH aryl), 129.9 (CH aryl), 135.5 (CR aryl), 143.8 (CR aryl). Anal. calcd. for $\text{C}_{17}\text{H}_{22}\text{N}_2\text{S}_2\text{O}_4$: C, 53.38; H, 5.79; N, 7.32; S, 16.76. Found: C, 53.57; H, 6.06; N, 6.48; S, 16.05.

Using the same reagents and reaction conditions as above (except 4.00 g (0.0216 mol) of *N*-methyl, paratoluenesulfonamide; 1.87 g of CH_2Br_2 (0.0107 mol); 0.73 g ($2.16 \cdot 10^{-3}$ mol) of tetra-*n*-butylammonium hydrogen sulfate and mechanical stirring during the addition of CH_2Br_2), the yield of pure isolated compound is 84%.



A three necked flask, fitted with a reflux condenser, a thermometer, and a dropping funnel, is charged with 7 mL of sulfuric acid and 10.5 mL of glacial acetic acid. The mixture is cooled to 0°C and 3.10 g (0.0018 mol) of paratoluenesulfonamide are added, with magnetic stirring, during 10 min.

1.36 mL (0.018 mol) of formaldehyde (40% aq.) is added dropwise. After a night at room temperature, the mixture is neutralized by a sodium hydroxide solution.

The mixture is filtered. The crude solid is crystallized from ethanol giving white needles (31% yield): mp 172°C; ^1H NMR (400 MHz, CDCl_3) δ 2.43 (3H, s, ArCH_3), 4.55 (2H, s, CH_2), 7.28 (4H, AB, ArH); ^{13}C NMR (400 MHz, CDCl_3) δ 144.65 (CarylR), 134.9 (CarylR), 130.11 (CarylH), 127.86 (CarylH), 60.22 (CH_2), 21.74 (CH_3Ar); mass spectrum (70 ev), *m/e* (rel intensity), 549 (molecular

Table II Elemental Analyses

Resins	%C	%H	%N	%S	%O
VO 10137 or Santolite MHP ^a	51.15	5.08	7.85	16.60	19.32
VO 10138 or Ketjenflex MH ^b	50.74	5.15	7.50	16.40	20.21
VO 10139 or Ultralac ^c	50.96	5.20	7.97	16.50	19.47
Mean Value	50.95	5.14	7.77	16.50	19.64
Calculated Value ^d	52.45	4.91	7.65	17.48	17.51

^a Commercialized by Monsanto.

^b Commercialized by Akzo.

^c Commercialized by Telechemische.

^d For $(\text{C}_8\text{H}_9\text{NSO}_2)_n$.

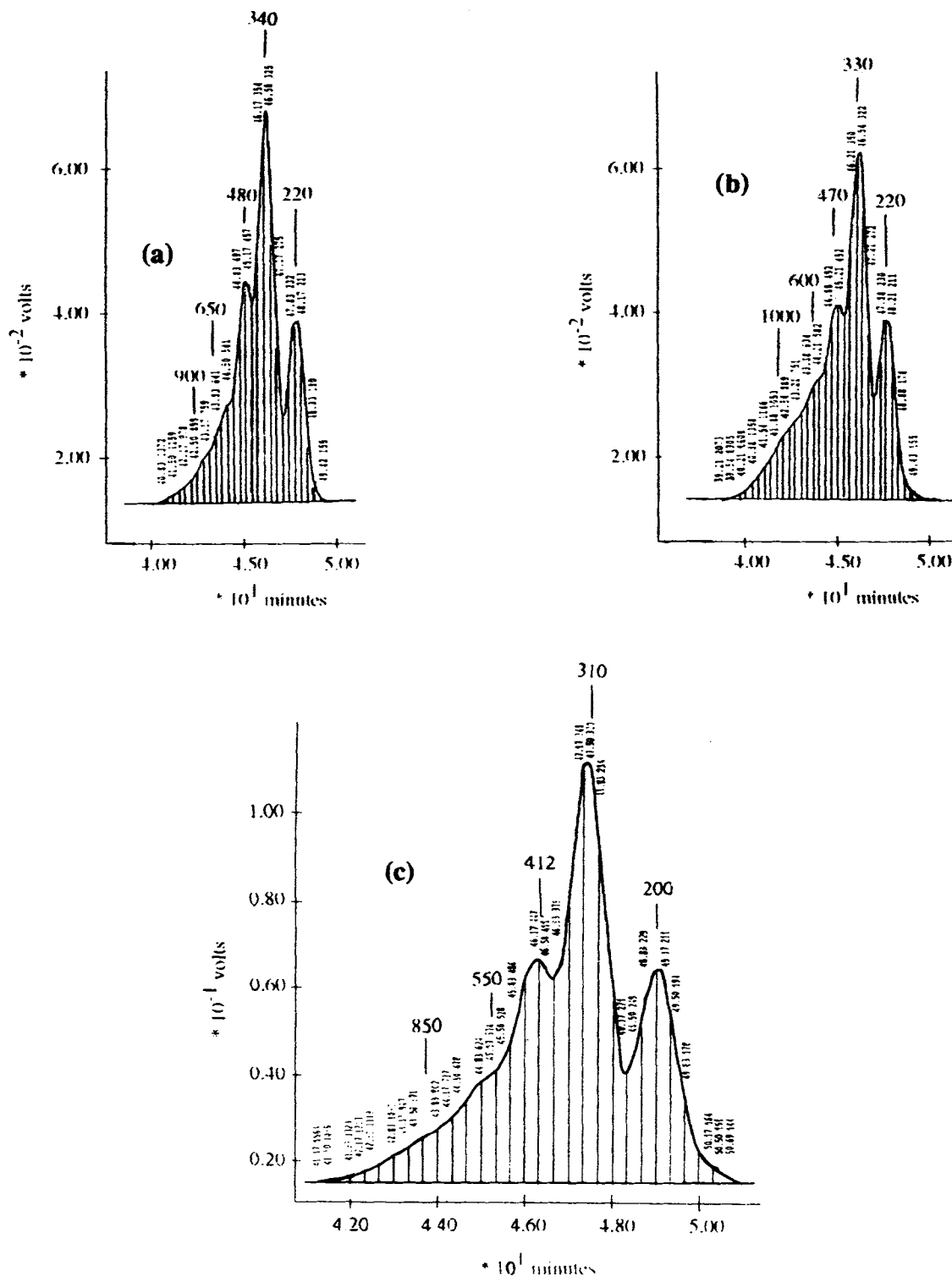


Figure 1 GPC curves of resins (peak masses are in ppg eq.): (a) Santolite MHP, (b) Ketjenflex MH, and (c) Ultralac.

Table III GPC Analyses

Resins	Peak Masses (ppg eq.)
Santolite MHP	900, 650, 480, (340), 220
Ketjenflex MH	1000, 600, 470, (330), 220
Ultralac	850, 550, 412, (310), 200

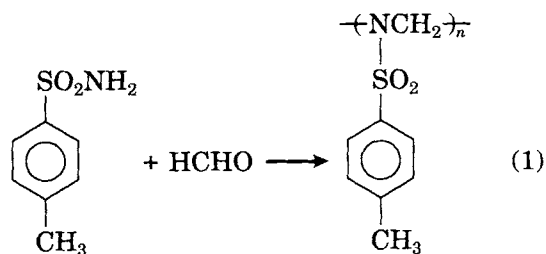
○ Circled items indicate major peak.

ion, 4.0), 394 (10.5), 238 (2.5), 211 (13.5), 184 (10.0), 155 (57.5), 139 (8.5), 91 (100), 65 (30). Anal. calcd. for $C_{24}H_{27}N_3S_3O_6$: C, 52.46; H, 4.92; N, 7.65; S, 17.48. Found: C, 52.54; H, 5.03; N, 7.73; S, 17.40.

RESULTS AND DISCUSSION

Toluene Sulfonamide Formaldehyde Resin (TSFR) is a low molecular weight material, used as a filling resin in fingernail lacquers for improving the quality of the film (adhesion, gloss, and flexibility).

TSFR is made by reacting paratoluenesulfonamide and formaldehyde, giving a compound with a formula depicted usually² as in eq. (1).



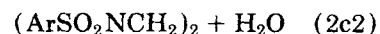
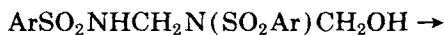
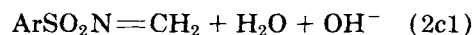
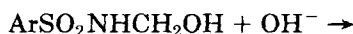
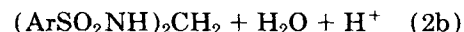
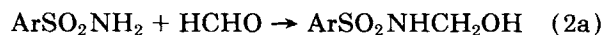
Analyses

Elemental analyses reported in Table II, show that the experimental values of the elemental composition (%) of commercial resins are very close to their mean value (indicating structural analogy), which is similar to that calculated for a polymer $(C_8H_9NSO_2)_n$.

However, this formula is clearly an oversimplification, because GPC and analyses, shown in Figure 1 and summarized in Table III, show the presence of a small number of oligomers (5 to 6), having masses ranging from 200 to 1000 ppg eq.

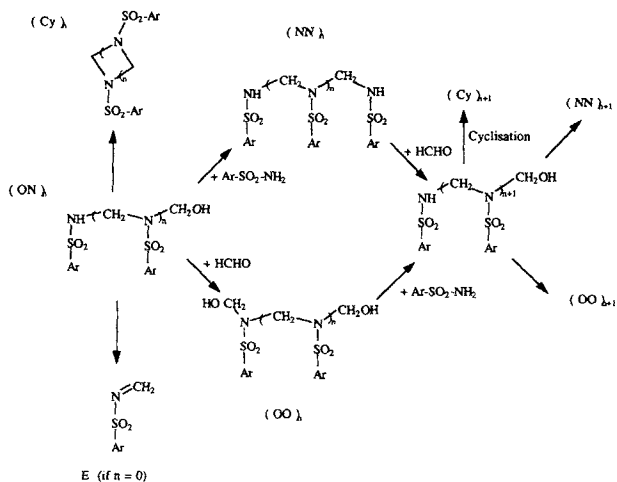
Possible formulae of these oligomers, and general rules for their formation, can be derived from pre-

vious studies in the literature,³⁻⁷ and from experiments in our laboratory. It appears that the formation of TSFR proceeds by the reactions depicted in eq. (2) (where are given typical examples of addition, substitution, elimination, and cyclization, but not the details of a step by step reaction involving all successive intermediates): (a) nucleophilic addition to a carbonyl group of the nitrogen atom of a sulfonamide, (b) nucleophilic substitution, by the nitrogen atom of a sulfonamide, of a protonated hydroxylic group, (c) side reactions involving (1) eliminations (under basic conditions) or (2) cyclizations.



General Scheme

The first step [eq. (2a)] is always the nucleophilic addition of PTSA to formaldehyde, but the course



Scheme 1 A general scheme of the reaction intermediates involved in TSFR formation. In all formulae n corresponds to the number of $\text{CH}_2\text{N}(\text{SO}_2\text{Ar})$ units with: E = elimination product (only if $n = 0$), $(\text{Cy})_n$ = cyclic derivatives, $(\text{ON})_n$ = CH_2OH and NH end groups, $(\text{NN})_n$ = NH and NH end groups, and $(\text{OO})_n$ = CH_2OH and CH_2OH end groups.

Table IV Masses of Oligomers in TSFR Formation

n	E	$(Cy)_n$	$(ON)_n$	$(OO)_n$	$(NN)_n$
0	183	no	201	231	354
1	No ^a	366	384	414	537
2	No	549	567	597	720
3	No	732	750	780	903
4	No	/	933	963	1086
5	No	/	1116	1146	1269
6	No	/	1299	1329	1452
7	No	/	1482	1512	1635
8	No	/	1665	1695	1818
9	No	/	1848	1878	2001

The formulae E , $(Cy)_n$, $(OO)_n$, and $(NN)_n$ correspond, respectively, to elimination and cyclization products and to intermediates with OH and NH, OH and OH, NH and NH end groups, respectively, as depicted in Scheme 1.

^a An elimination reaction occurs on $(ON)_n$ only when $n = 0$ (with a secondary nitrogen atom).

of the following steps will depend strongly on the nature of the catalysis (acidic or basic) and on the concentration and ratio of the reagents. According to patent literature,^{8a-f} industrial processes for preparing TSFR involve a reaction under acidic conditions, usually followed by a posttreatment. The detailed composition of the mixture of oligomers obtained under these conditions is not known, however, a general mechanistic scheme for the formation of the oligomers (involving all the previous observations) can be depicted in Scheme 1.

GPC Analyses

The corresponding masses of the oligomers, ranging between 400 and 1900 g (as observed by GPC), are recorded in Table IV.

In Table V is detailed the case of "Santolite," where the experimental masses (and %) of each

isomer detected by GPC are compared to calculated values of molecular models,¹⁵ derived from Scheme 1.

Spectroscopic Data

Spectroscopic data agree with these attributions and give further structural information. The IR bands are qualitatively consistent with the formulae in Scheme 1; they show, in addition, molecular vibrations characteristic of para- and orthodisubstituted benzene.

¹H NMR spectra, reported in Table VI, are consistent with 2 methyls bonded to an aromatic (2.40 and 2.60 ppm), with a methylene flanked by 2 heteroatoms (4.50–5.10 ppm), with 4 aromatic protons (7.10–8.00 ppm) and with a proton bonded to an heteroatom (N or O), which appears as a wide singlet (3.10 ppm in CD₃COCD₃, 5.80 ppm in CDCl₃).

Table V GPC of Santolite

Molar Percent	20%	43%	24%	9%	4%
Experimental					
Molecular Mass of the Oligomer ^a	462	714	1008	1365	1890
Calculated Mass of the Closest Model ^b	414	720	963	1329	1878
Formulae of the Closest Model ^c	$(OO)_1$	$(NN)_2$	$(OO)_4$	$(OO)_6$	$(OO)_9$

Note: All the masses given in this table are in g.

^a The masses are obtained from the values of peak masses (according to Table III) multiplied by 2.1 (correction factor).

^b According to Table IV.

^c According to Scheme 1.

Table VI ^1H NMR Spectra of Santolite at 100 and 400 MHz

Signal	At 100 MHz	At 400 MHz ^a	Integration	Nature
	Solvent $\text{CD}_3\text{COCD}_3^b$	Solvent CDCl_3^b		
	Shift ppm	Shift ppm		
Singlet	2.40	2.40	420	$\text{CH}_3\text{—Ar}$
Singlet	2.60	2.60	317	$\text{CH}_3\text{—Ar}$
Wide singlet	3.10	5.80	65	$\text{NH} + \text{OH}$
Broad Multiplet	4.50–5.10	4.50–5.10	469	CH_2
Multiplet	7.10–8.00	7.10–8.00	980	H—Ar

^a Spectra recorded at 400 MHz for a better separation of signals and evaluation of integration.

^b Use of TMS as an internal reference.

The position of the two methyls on the aromatic is attributed (by reference to authentic samples)⁹ to a para position ($\delta = 2.40$ ppm; 57% of the total ortho + para) and to an ortho position ($\delta = 2.60$ ppm; 43% of the total ortho + para).

^{13}C NMR signals, reported in Table VII, are attributed, by analogy with authentic molecules, by the use of a DEPT sequence, and by incrementation according to an adapted equation¹⁰ to: primary carbons (CH_3 at 20.2 and 21.3 ppm), secondary carbons (CH_2 bonded to two N between 52 and 60 ppm; CH_2 bonded to N and O between 68 and 76 ppm),¹¹ tertiary carbons (C at unsubstituted positions on benzene, between 128 and 133 ppm), quaternary carbons (C at substituted positions on benzene between 137 and 144 ppm). The presence of methyl groups in the ortho position, besides the expected para position (to which formulae of TSFR are usually limited), comes probably from the fact that the synthesis uses an industrial mixture of ortho- and paratoluenesulfonamide, from a process based on the chlorosulfonation of toluene (giving an ortho-para regioselectivity),¹² followed by reaction with ammonia.

The wide singlet in ^1H NMR (at 3.10 ppm in CD_3COCD_3 and at 5.80 ppm in CDCl_3) disappears

by exchange with D_2O , which is indicative of a proton bonded to an heteroatom (OH or NH). Due to the lack of reliability of the integration of this signal in ^1H NMR, a quantitative estimation of OH was determined: the hydroxylated compound is acetylated with acetic anhydride in pyridine. The excess of the reagent is hydrolyzed and the acetic acid is titrated by a standard solution of caustic soda. A blank is used to titrate the exact quantity of acetylated reagent employed for the nitration. From this test, the proportion of OH was estimated to be 1.20 eq/Kg.

CONCLUSION

In summary, the analysis of TSFR shows clearly that its commonly accepted representation of a polymeric structure is, at best, an oversimplification of what is a mixture of oligomers having functional end groups. A better knowledge of the actual structure of TSFR oligomers (described in this article), in connection with the determination of their chemical stability, will help us in designing and preparing improved or new resins. We are studying this point further.

Table VII ^{13}C NMR Spectrum of Santolite at 400 MHz

Chemical Shift ppm	Nature of Carbon
20.2	CH_3
21.3	CH_3
52.0–60.0	CH_2 (Between N and N)
68.0–76.0	CH_2 (Between N and O)
126.8, 127.3, 128.0, 129.0, 130.3, 133.3, 133.7	Aryl CH
137.5, 144.0, 144.6	Aryl CR

REFERENCES AND NOTES

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11. These signals are at the limit of detection at 100 MHz; they can hardly be differentiated from the background noise at this frequency.
12. Note that the ratio 43% ortho/57% para in the resin (which corresponds to a statistical occurrence of the isomers) may be slightly different from the composition of the mixture of toluenesulfonamide isomers, used in the synthesis of TSFR, due to the difference in reactivity of the isomers.
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15. The assignment of the formulae, presented in Table IV (for the oligomers of "Santolite"), is made from GPC data with a correction factor of 2.1; the error ($\pm 5\%$) on this factor means that if the number of units (n) of the oligomers is almost certain, the functionalities of the end groups may be slightly different [e.g., a difference in mass of 30 may imply a change of assignment from $(\text{NN})_n$ to $(\text{ON})_n$].

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