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Chemical Kinetics of the Aging of Estane 5703 in PBX 9501. I. First Preliminary Predictions

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Abstract

First preliminary predictions of the degradation of Estane® 5703 in PBX 9501 in the stockpile are reported. They are obtained by chemical kinetics modeling using a reasonable mechanism and parameters. They are **very** preliminary and intended be used to guide statistical studies and modeling of mechanical properties but **not** to make any decisions about any actual service lifetimes.

I. Introduction

The Estane® 5703 (herein called Estane) in the binder of the Plastic Bonded Explosive PBX 9501 is slowly aging. Since PBX 9501 is used in weapons applications, understanding this degradation is essential to any reliable prediction of its useful lifetime.

The nominal composition of PBX 9501 is 94.9% HMX, 2.5% Estane, 2.5% nitroplasticizer (NP), and 0.1% stabilizer (diphenylamine [DPA] or Irganox 1010). Estane® 5703, made by B. F. Goodrich, is a polyesterurethane elastomer ; it is used as a binder in high explosives (HE) to decrease their mechanical sensitivity. It is a copolymer, and its chain consists of alternating "soft segments" and "hard segments."[1] The soft segments are short polymers (oligomers) of the ester of adipic acid with 1,4 butanediol (BDO); they have a number average molecular weight (M_n) that is most probably in the range of 800 to 1050 Daltons (g/mol).[2] The hard segments consist of very short polyurethanes (with only 1 to 3 repeat units[3]) made from 4,4'-diphenylmethane diisocyanate (MDI) molecules bonded together by urethane links to the BDO's that serve as chain extenders. From the elemental composition of the Estane one finds that there are an average of 4 ester links per urethane link,[4] and this is confirmed by analysis of the Matrix Assisted Laser Desorption and Ionization (MALDI) spectra of Estane.[5] The ester links have the chemical structure RCOOR' where R and R' are polymeric alkyl radicals. The urethane links have the structure ϕNHCOOR' where ϕ is a polymeric aryl radical.

The chemistry of Estane degradation is very complicated.[6] The mechanisms thus far identified as most likely to be important are (in no particular order): (1) scission of urethane links by slow thermal degradation; (2) hydrolysis of the ester links by water; (3) crosslinking and also scission of the urethane links by free radicals such as NO_2 and ROO (peroxyl) that are oxidizers; and (4) crosslinking and also scission of bonds by free radicals R produced by ionizing radiation. In accelerated aging experiments, any of these four can be made to dominate. However, in weapon storage conditions, (1) the near ambient temperatures are expected to cause the thermal degradation to be slow. (2) The internal atmosphere in weapons is kept dry which should slow hydrolysis. (3) There is little or no oxygen present to produce ROO radicals. Some NO_2 could be present, but evidence for it is still tenuous. In addition, the stabilizer should rapidly remove such radicals. (4) A few free radicals R are produced by ionizing radiation, but the stabilizer should also remove them, and attempts to see their effects in this environment have thus far proved negative.[7] As a consequence of these conditions, the Estane in the stockpile is aging quite slowly, and it is difficult to determine just what is causing the observed slow decrease in its molecular weight. However, it *is* aging, and that needs to be understood.

In the present work the first mechanism just discussed is used with reasonable scenarios to model the degradation. Ongoing research will allow refinement of these predictions, and it is planned that future predictions will include the mechanisms not treated in this work.

II. Thermal Degradation

A. Reaction

Gajewski[6] and Fabris[8] have suggested that the reaction which dominates the thermal decomposition of urethanes at the lowest temperatures at which it is observed is

$$\phi NHCOOCH_2CH_2R' \Rightarrow \phi NH_2 + CH_2CHR' + CO_2, \qquad (1)$$

i.e., the urethane link scissions and produces a primary amine, an alkene, and carbon dioxide. The best low temperature thermal degradation study that we have found is that of Singh.[9] For a urethane similar (but not identical) to our Estane he found that, over the temperature range of 130 to 160 C, its decomposition had an activation energy (E_a) of 31.9 kcal/mol. We assume that Reaction (1) represents the reaction seen by Singh and that his activation energy applies. This is clearly an oversimplification as Singh found considerable reversibility to whatever reaction he was seeing, and, under his conditions, Reaction (1) would lose CO_2 gas rapidly and be irreversible. Furthermore, if one extrapolates Singh's rate constants down to the near ambient temperatures of weapon storage, one finds that Singh's rate constants are smaller than the observed rates, so we freely adjust the pre-exponential in the rate constant to match stockpile surveillance data. (The present study is intended to give a quick and dirty prediction; the reader should be seeing by now just how dirty it really is.) However, this approach does find support from the results of Taylor, et al.[10], and Foster[11]. In accelerated aging studies conducted over a range of temperatures, using PBX 9501 and the similar explosive LX-14, they[10, 11] observed a curved Arrhenius plot that had an activation energy at temperatures below 60 C that was consistent with hydrolysis (which we will treat in future reports) but had a much larger activation energy at higher temperatures that is consistent with some other reaction, such as Reaction (1) and the behavior found by Singh. Such a curved Arrhenius plot implies that two reactions were occurring in the accelerated aging studies. If we assume that the dry conditions in weapon storage effectively shut off the hydrolysis reaction, then the reaction still occurring is the one with the higher activation energy, and the present assumptions are consistent with that.

B. Kinetics

Reaction (1) has the advantage of having very simple first order kinetics. This means that, even if the reaction actually dominating the degradation is different from Reaction (1), all the present calculations will still be valid for any actual reaction that gives first order scission of polymer links. Now, if we let [U] be the concentration of urethane links in moles per kilogram of binder, then its time dependence is given by

$$d[U] / dt = -k_1[U], \qquad (2)$$

which has the simple analytic solution

$$[U](t) = [U](0) \exp(-k_1 t). \qquad (3)$$

Also, one sees from Reaction (1) that, for each mole of urethane links that scission, one mole of polymeric molecules is destroyed and two moles of (smaller) polymeric molecules are formed, so that there is a net gain of one mole of polymeric molecules. Hence, the change in the total concentration of polymer molecules [PT] with time is given by

$$[PT](t) – [PT](0) = [U](0) – [U](t). \qquad (4)$$

Then, we note that in the binder phase the number average molecular weight is related to the total concentration of polymer molecules by

$$M_n = 500 / [PT]. \tag{5}$$

(The 500 here is the number of grams of Estane per kg of binder.) Using (5) in (4) and then solving for $M_n(t)$ one obtains

$$M_n(t) = M_n(0) / \{1 + c[1-\exp(-k_1 t)]\}, \tag{6}$$

where

$$c = M_n(0)[U](0) / 500. \tag{7}$$

This simple analytic solution makes it easy for any reader who wishes to vary the parameters and see the effects.

C. Molecular Weight Distribution

In polymers such as Estane there is always a broad distribution of polymeric molecules with different molecular weights. If one labels all the possible polymeric molecules, so that P_i is the *i*-th polymer, and m_i is its molecular weight, then the total concentration of polymeric molecules is

$$[PT] = \Sigma_i [P_i], \tag{8}$$

and the number average molecular weight is[12]

$$M_n = \Sigma_i m_i [P_i] / [PT]. \tag{9}$$

This average molecular weight is the simple average one would expect. However, in many cases one needs the weight average molecular weight, which is given by

$$M_w = \Sigma_i m_i^2 [P_i] / \Sigma_i m_i [P_i], \tag{10}$$

and the ratio, MWD = M_w / M_n, is called the polydispersity index.

If one needs to know the entire distribution of molecular weights at all times, then one can start from the initial distribution, solve a set of coupled differential equations, and follow all the $[P_i]$ in time. Computer programs doing that for this present case have been written[13], and, if someone needs the detailed distributions, they will be generated on request. However, for the needs of most readers, we note that Reaction (1) is a random depolymerization reaction, and such reactions always make the MWD tend toward a value[14] of 2.0. From a careful fit to detailed initial distributions measured for new Estane both at B. F. Goodrich[1] and at Pantex[15], we find that the MWD of *new* Estane 5703 is significantly larger than 2.0. Furthermore, from our detailed studies[13] it turns out that there is a simple empirical relationship,

$$M_w = a\ M_n + b\ M_n^3, \qquad (11)$$

with a = 2.00 and b = 2.55e-09, which is accurate enough for most purposes to describe what happens to M_w and MWD during the degradation. That may be useful to readers.

D. Absolute Molecular Weights

The average molecular weights just discussed are the true or absolute average molecular weights. However, these are not easily measured. What is usually measured is the Gel Permeation Chromatography (GPC) mass distribution, which is a relative distribution that depends both on the solvent used and on the polymer used as the molecular weight standard. This happens because GPC really measures the hydrodynamic volumes of the molecules, and they depend both on the way the polymer molecules interact with the gel on the column and the way they interact with and are swelled by the solvent. Most GPC measurements on Estane have used polystyrene standards, and we label molecular weights thus obtained by "PS". Until recently, most GPC measurements on Estane used tetrahydrofuran (THF) as the solvent, and we thus label them. [Some recent measurements have used dimethylformamide (DMF) as the solvent]. Thus, THF PS M_w means the "weight average molecular weight relative to polystyrene standards in a tetrahydrofuran solvent."

To determine the absolute value of M_w requires light scattering measurements; it involves measuring the light scattering efficiency factor Q, and this is a matter of considerable interest. Early estimates of the Q factor for Estanes (Q_E) were quite crude.[16] However, a value of Q_E =25 that agrees fully with current values was measured at Allied Signal[17] in 1976, and this enabled Kohn[18] to make some estimates that were actually better than they were thought to be. More recently, it was measured in 1997 at Pantex by Lindemann.[19] A value of Q_E = 25.3 for new pellet Estane was obtained; with the value of Q_{PS} = 41.4 for polystyrene, this gives $r = Q_E / Q_{PS} = 0.61$ as the ratio of the true M_w of new Estane to its THF PS M_w. Of course, to be very useful in aging studies where the average molecular weights are decreasing, this ratio r needs to be essentially independent of molecular weight; fortunately, this has been shown to be the case by Spontarelli and King[20] of LANL. They made a series of light scattering measurements, carefully checking the concentrations, change of refractive index with concentration (dn/dc), etc., for 16 PBX library samples and 16 neat Estane library samples whose ages varied from new to 20 years old and whose THF PS M_w's varied from 119500 to 8140. No trend in the ratio r was found with either age or molecular weight of the samples. The average value of r found for the PBX samples was 0.59 with a standard deviation of 0.05, and the average for the Estane samples was 0.66 with a std. dev. of 0.07. Furthermore, this handy simplification has been verified by the analysis of very degraded samples. They were fractionated by GPC, and then their Fourier Transform Infrared (FTIR) spectra were analyzed by Lightfoot,[21] and their MALDI spectra were analyzed by Russell[5] and by Kober.[22] These analyses provide the unique identification of some of the very small fragments resulting from the aging of Estane and allow direct determination of their r values by comparison of their known absolute molecular weights with their THF PS values. A few of these results are shown in the following table. In it, B is BDO or its residue, A is adipic acid or its residue, and M is an MDI residue.

Table A

Molecule	*Absolute MW*	*THF PS MW*	*r*
B	90.12	186	0.485
A	146.14	312	0.468
AB	218.25	400	0.546
BAB	290.35	499	0.582
ABA	346.37	615	0.563
BMB	430.50	771	0.558
BABMB	630.73	1013	0.623
BMBMB	770.87	1386	0.556

One sees from this table that the ratio r is a little smaller for the monomers than for Estane polymer but that it rises rapidly for the oligomers to become within the uncertainty of the polymeric value.

In the present work we use the value of 0.61 ± 0.08 for r. This value can be refined in the future as needed.

E. Calculations and Results.

The results of calculations using the simple kinetics model discussed in the preceding paragraphs are shown as the line in Figure 1. In these calculations the rate constant was taken to have the Arrhenius form,

$$k_1 = A_1 \exp(-E_{a1} / R_g T), \tag{12}$$

where E_{a1} = 31.9 kcal/mol, A_1 = 1.4 e+18 /month, R_g is the universal gas constant, and T=307 K is the typical average absolute temperature.[23] The initial [U] concentration is taken to be 0.878 moles/kg binder, and [PT](0) is taken to be 0.0205. That gives the initial values of M_n, M_w, and the THF PS M_w as 24400, 85800, and 140700, respectively, in agreement with the measured initial distribution.[15]

The points in Figure 1 are the GPC THF PS M_w results for the Estane extracted from W76 and W78 surveillance samples. Different symbols are used for measurements made with different instruments. As we have discussed elsewhere,[24] we do not weight all these experimental points equally. As first noted by Lightfoot and Russell,[25] the large values at the shorter lifetimes are an artifact due to instrumentation. From the solid boxes on the plot, all one can say is that the Micromeretics instrument gave data with a large scatter. However, from the solid triangles, one can say that the Waters 200 instrument gave results significantly higher than newer instruments. From the solid triangles at the left edge of the plot, one finds that the Waters 200 value for the THF PS M_w of new Estane was 173,000 ± 23000. From the star symbols at the left edge, the current Waters 150 instrument gives a THF PS M_w for new Estane of 140,100 ± 4100. The results from any one instrument always give a M_w which simply slowly decreases with time. Hence, the current model considers only the data from the newer Waters 150 instruments, and its parameters for Figure 1 are intentionally chosen to make the calculated curve pass only through the lowest of the open triangles. We call this the “pessimistic” prediction as it is quite extreme and gives the fastest degradation likely with the present model.

Figure 2 shows the results of the same calculation with all the parameters held fixed except that now A_1 = 5.0 e+17. This value was chosen to make the calculated line pass about through the middle of the stars. The reason for this is that those points are the surveillance measurements made with the current Waters 150 instrument at Pantex, and they include measurements on both new and aged Estane. One sees that this leads to a much more “optimistic” prediction of the M_w at long times.

III. Half Life Predictions

The “pessimistic” and “optimistic” predictions of the THF PS M_w to long times are shown in Figures 1 and 2, and detailed values of the predicted absolute M_n and M_w and THF PS M_w are given in Tables 1 and 2, respectively. (Due to their lengths, only the first parts of these tables are given in the hard copy of this report; the full tables are included in the version posted on the www.)

To give a simpler quantity to list than all these details, we look at them to see at what age the M_w (either absolute or THF PS) has fallen to half its initial value. From Figure 1 or from Table II, one finds that, with the pessimistic values of the parameters, M_w falls to half its initial value in about 441 months (36.75 years). For the more optimistic calculation of Figure 2, from Table III, one finds that this occurs in about 1233 months (102.75 years). Hence, within the accuracy of the present calculations, we predict that the half life of the M_w of the Estane 5703 in the PBX 9501 stored in the stockpile will be between 35 and 105 years.

The relationships between the molecular weight of the Estane and the mechanical properties of the PBX are not simple and will be discussed elsewhere both by myself and others working on this project.

IV. Caveats

These estimates are intended mostly as input to others to use in modeling behavior all the way from here (the molecular level) to the whole system performance. They are intended to be a first exercise of the process of making estimates, **not** for use in making actual decisions about useful lifetimes. They will be followed by a series of increasingly serious and narrower estimates.

Could the actual half life of the Estane M_w be much **longer** than the 105 year "optimistic" estimate obtained herein? Yes, indeed. If, as we suspect, much of the observed aging is due to hydrolysis[26] caused by water initially present in the PBX, then the slow drying of the PBX in the weapon environment can cause hydrolysis to slow down at long times to give a curve that becomes essentially flat and has a half life much longer than the most optimistic present estimate.

Could the actual half life of the Estane M_w be much **shorter** than the 35 year "pessimistic" estimate obtained herein? Yes, again, in three ways that we know about. (1) If the weapon is subjected to wide temperature swings in storage, the effect on the kinetics will be very nonlinear, and the actual lifetime will be shorter than the lifetime at the mean temperature. This is due both to the exponential dependence of [U] on the rate coefficient shown in Eq. (6) and also the exponential dependence of the rate coefficient on temperature as shown in Eq. (12). I believe that our statisticians will be studying this effect. It should be noted, however, that the basic type of molecular weight loss seen in the present work will be characteristic of any chemical reaction that is simply a first-order or pseudo-first-order chain scission reaction, and it thus could hold for many types of reactions. In what ways could the degradation go faster at long times than a first order decay? We know of two, and they are the other two cases that follow.

(2) Hydrolysis. Hydrolysis of the ester links is acid catalyzed and also produces acid as a product, so it is autocatalytic and can speed up as time goes on.[26] However, this will only give a M_w curve that degrades very much faster at long times than that in Figure 1 if the water initially in the PBX cannot leak out of it at an appreciable rate. We are actively studying this possibility, and better estimates of it will be included in future reports.

(3) Stabilizer disappearance. The function of the stabilizer is to react with and remove any free radical oxiding agents before they can react with the Estane. If the stabilizer were to all react away, then the degradation could speed up markedly at long times. Campbell[27] has studied the stabilizer concentration in PBX 9501 and has found that, for samples stored in air, it slowly decreases with time. However, for samples stored in the inert atmosphere in the stockpile, she found no net decrease in stabilizer with time. Any changes in the stabilizer concentration appear to be occurring in processing before it goes into the stockpile or right after the PBX goes into the stockpile. Thereafter, no further change appears to be occurring.[27] Hence, this possibility does not appear likely, but methods for measuring the amount of *partially* reacted stabilizer are being vigorously pursued[28] and will yield further insight.

Before concluding, we note that some degradation processes can produce changes in the properties of the Estane *without* causing a decrease in its molecular weight. For example, decarboxylation of the carboxylic acid end groups, with the loss of CO_2, makes little change in the molecular weight but changes the ability of the end to react or form hydrogen bonds. It does occur but, at the moment, appears to be of minor importance in the stockpile. Also, free radical attack can cause crosslinking that *increases* the molecular weight, and this can markedly change the elastomeric properties of the polymer. In this connection Wrobleski[29] has found two indications of the formation of high molecular weight material in the Estane in certain aged PBX 9501 and binder samples. One of these is a very high molecular weight signal in GPC measurements and the other is the formation of a gel in solutions. The very high molecular weight GPC signal has now been shown by Russell[30] to be due to agglomeration of lower molecular weight species in the very polar DMF solvent rather than to true polymers of high molecular weight. The gel is being actively studied and will yield more information on crosslinking processes. These indications of high molecular weight species seem to be associated with oxidizing[31] free radicals and seem to mostly form after the stabilizer disappears. Research along this line will impact future reports.

V. Conclusion

We conclude that the present predictions of the half life of the M_w of the Estane 5703 in the PBX 9501 in the stockpile have large uncertainties, and the true uncertainties could be even larger. Work is ongoing which will narrow these uncertainties.

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Figure Captions

1. Plot of the THF PS M_w of Estane 5703 in PBX 9501 in W76 and W78 stockpile samples versus their age in months. The points are experimental data; the line is the result of calculations with the simple model and "pessimistic" parameters. The calculation is extended to long times to make a prediction.
2. Same as Figure 1 except that "optimistic" parameters are used.

Tables

1. A table of the predicted M_n, M_w, and THF PS M_w as functions of the age in months using the "pessimistic" parameters. Due to its length, only the first part of this table will be included in the hard copy of this report, but all of it will be included in the version posted on the www. Some of its data are plotted in Figure 1.
2. Same as Table 1 except that the "optimistic" parameters were used. Some of its data are plotted in Figure 2.

Table 1. Predicted average molecular weights vs. age in months. "Pessimistic" parameters.

t(mo)	M_n	M_w	THF PS M_w
0.	24390.	85819.	140687.
3.	24305.	85260.	139770.
6.	24220.	84707.	138864.
9.	24136.	84161.	137969.
12.	24052.	83622.	137084.
15.	23969.	83088.	136210.
18.	23886.	82561.	135346.
21.	23804.	82040.	134492.
24.	23723.	81525.	133648.
27.	23642.	81017.	132814.
30.	23562.	80513.	131989.
33.	23482.	80016.	131174.
36.	23403.	79524.	130368.
39.	23324.	79038.	129571.
42.	23246.	78558.	128783.
45.	23168.	78082.	128004.
48.	23091.	77613.	127234.
51.	23015.	77148.	126472.
54.	22939.	76688.	125719.
57.	22863.	76234.	124974.
60.	22788.	75784.	124237.
63.	22714.	75340.	123508.
66.	22639.	74900.	122787.
69.	22566.	74465.	122074.
72.	22493.	74035.	121369.
75.	22420.	73610.	120671.
78.	22348.	73189.	119981.
81.	22276.	72772.	119299.
84.	22205.	72360.	118623.
87.	22135.	71952.	117955.
90.	22064.	71549.	117293.
93.	21994.	71150.	116639.
96.	21925.	70755.	115991.
99.	21856.	70364.	115351.
102.	21788.	69977.	114717.
105.	21720.	69594.	114089.
108.	21652.	69215.	113468.
111.	21585.	68840.	112853.
114.	21518.	68469.	112245.
117.	21452.	68102.	111642.

120.	21386.	67738.	111046.
123.	21320.	67378.	110456.
126.	21255.	67022.	109872.
129.	21190.	66669.	109294.
132.	21126.	66320.	108721.
135.	21062.	65974.	108154.
138.	20998.	65632.	107593.
141.	20935.	65293.	107037.
144.	20872.	64957.	106487.
147.	20810.	64625.	105942.
150.	20748.	64295.	105402.
153.	20686.	63969.	104868.
156.	20625.	63647.	104339.
159.	20564.	63327.	103815.
162.	20504.	63010.	103296.
165.	20443.	62697.	102781.
168.	20383.	62386.	102272.
171.	20324.	62078.	101768.
174.	20265.	61774.	101268.
177.	20206.	61472.	100773.
180.	20148.	61173.	100283.
183.	20090.	60876.	99797.
186.	20032.	60583.	99316.
189.	19974.	60292.	98840.
192.	19917.	60004.	98367.
195.	19861.	59719.	97899.
198.	19804.	59436.	97436.
201.	19748.	59155.	96976.
204.	19692.	58878.	96521.
207.	19637.	58603.	96070.
210.	19582.	58330.	95623.
213.	19527.	58060.	95180.
216.	19472.	57792.	94741.
219.	19418.	57526.	94305.
222.	19364.	57263.	93874.
225.	19310.	57003.	93447.
228.	19257.	56744.	93023.
231.	19204.	56488.	92603.
234.	19151.	56234.	92187.
237.	19099.	55982.	91774.
240.	19047.	55733.	91365.
243.	18995.	55486.	90960.
246.	18943.	55240.	90558.
249.	18892.	54997.	90159.
252.	18841.	54756.	89764.
255.	18791.	54517.	89373.

258.	18740.	54280.	88984.
261.	18690.	54046.	88599.
264.	18640.	53813.	88217.
267.	18590.	53582.	87839.
270.	18541.	53353.	87463.
273.	18492.	53126.	87091.
276.	18443.	52900.	86722.
279.	18395.	52677.	86356.
282.	18346.	52456.	85993.
285.	18298.	52236.	85633.
288.	18250.	52018.	85276.
291.	18203.	51802.	84922.
294.	18156.	51588.	84570.
297.	18109.	51375.	84222.
300.	18062.	51165.	83876.
303.	18015.	50955.	83534.
306.	17969.	50748.	83194.
309.	17923.	50542.	82856.
312.	17877.	50338.	82522.
315.	17831.	50136.	82190.
318.	17786.	49935.	81860.
321.	17741.	49736.	81534.
324.	17696.	49538.	81210.
327.	17651.	49342.	80888.
330.	17607.	49147.	80569.
333.	17563.	48954.	80253.
336.	17519.	48763.	79939.
339.	17475.	48572.	79627.
342.	17431.	48384.	79318.
345.	17388.	48197.	79011.
348.	17345.	48011.	78706.
351.	17302.	47827.	78404.
354.	17260.	47644.	78104.
357.	17217.	47462.	77807.
360.	17175.	47282.	77512.
363.	17133.	47103.	77219.
366.	17091.	46926.	76928.
369.	17049.	46750.	76639.
372.	17008.	46575.	76353.
375.	16967.	46402.	76068.
378.	16926.	46229.	75786.
381.	16885.	46059.	75506.
384.	16844.	45889.	75228.
387.	16804.	45721.	74952.
390.	16764.	45553.	74678.
393.	16724.	45388.	74406.

396.	16684.	45223.	74136.
399.	16644.	45059.	73868.
402.	16605.	44897.	73602.
405.	16566.	44736.	73337.
408.	16527.	44576.	73075.
411.	16488.	44417.	72815.
414.	16449.	44259.	72556.
417.	16411.	44103.	72300.
420.	16372.	43947.	72045.
423.	16334.	43793.	71792.
426.	16296.	43640.	71540.
429.	16258.	43487.	71291.
432.	16221.	43336.	71043.
435.	16183.	43186.	70797.
438.	16146.	43037.	70553.
441.	16109.	42889.	70310.
444.	16072.	42742.	70069.
447.	16035.	42596.	69830.
450.	15999.	42451.	69593.
453.	15962.	42307.	69357.
456.	15926.	42165.	69122.
459.	15890.	42023.	68889.
462.	15854.	41882.	68658.
465.	15819.	41742.	68429.
468.	15783.	41602.	68201.
471.	15748.	41464.	67974.
474.	15712.	41327.	67749.
477.	15677.	41191.	67526.
480.	15642.	41055.	67304.
483.	15608.	40921.	67083.
486.	15573.	40787.	66864.
489.	15539.	40655.	66647.
492.	15504.	40523.	66431.
495.	15470.	40392.	66216.
498.	15436.	40262.	66003.
501.	15402.	40132.	65791.
504.	15369.	40004.	65580.
507.	15335.	39876.	65371.
510.	15302.	39750.	65163.
513.	15269.	39624.	64957.
516.	15235.	39499.	64752.
519.	15203.	39374.	64548.
522.	15170.	39251.	64346.
525.	15137.	39128.	64144.
528.	15105.	39006.	63944.
531.	15072.	38885.	63746.

534.	15040.	38765.	63548.
537.	15008.	38645.	63352.
540.	14976.	38526.	63157.
543.	14944.	38408.	62964.
546.	14912.	38291.	62771.
549.	14881.	38174.	62580.
552.	14850.	38058.	62390.
555.	14818.	37943.	62201.
558.	14787.	37828.	62013.
561.	14756.	37714.	61827.
564.	14725.	37601.	61642.
567.	14695.	37489.	61457.
570.	14664.	37377.	61274.
573.	14633.	37266.	61092.
576.	14603.	37156.	60911.
579.	14573.	37046.	60731.
582.	14543.	36937.	60553.
585.	14513.	36829.	60375.
588.	14483.	36721.	60199.
591.	14453.	36614.	60023.
594.	14424.	36508.	59849.
597.	14394.	36402.	59675.
600.	14365.	36297.	59503.
603.	14336.	36192.	59331.
606.	14307.	36088.	59161.
609.	14278.	35985.	58992.
612.	14249.	35882.	58824.
615.	14220.	35780.	58656.
618.	14191.	35679.	58490.
621.	14163.	35578.	58324.
624.	14135.	35478.	58160.
627.	14106.	35378.	57997.
630.	14078.	35279.	57834.
633.	14050.	35180.	57672.
636.	14022.	35082.	57512.
639.	13994.	34985.	57352.
642.	13967.	34888.	57193.
645.	13939.	34792.	57035.
648.	13912.	34696.	56878.
651.	13884.	34601.	56722.
654.	13857.	34506.	56567.
657.	13830.	34412.	56413.
660.	13803.	34318.	56259.
663.	13776.	34225.	56107.
666.	13749.	34132.	55955.
669.	13722.	34040.	55804.

672.	13696.	33949.	55654.
675.	13669.	33858.	55505.
678.	13643.	33767.	55356.
681.	13616.	33677.	55209.
684.	13590.	33588.	55062.
687.	13564.	33499.	54916.
690.	13538.	33410.	54771.
693.	13512.	33322.	54626.
696.	13486.	33235.	54483.
699.	13461.	33147.	54340.
702.	13435.	33061.	54198.
705.	13410.	32975.	54057.
708.	13384.	32889.	53916.
711.	13359.	32804.	53777.
714.	13334.	32719.	53638.
717.	13309.	32635.	53499.
720.	13284.	32551.	53362.
723.	13259.	32467.	53225.
726.	13234.	32384.	53089.
729.	13209.	32302.	52954.
732.	13185.	32220.	52819.
735.	13160.	32138.	52685.
738.	13136.	32057.	52552.
741.	13111.	31976.	52420.
744.	13087.	31896.	52288.
747.	13063.	31816.	52157.
750.	13039.	31736.	52027.
753.	13015.	31657.	51897.
756.	12991.	31578.	51768.
759.	12967.	31500.	51640.
762.	12943.	31422.	51512.
765.	12920.	31345.	51385.
768.	12896.	31268.	51258.
771.	12873.	31191.	51133.
774.	12849.	31115.	51008.
777.	12826.	31039.	50883.
780.	12803.	30963.	50759.
783.	12780.	30888.	50636.
786.	12757.	30813.	50513.
789.	12734.	30739.	50392.
792.	12711.	30665.	50270.
795.	12688.	30591.	50149.
798.	12666.	30518.	50029.
801.	12643.	30445.	49910.
804.	12621.	30372.	49791.
807.	12598.	30300.	49673.

810.	12576.	30228.	49555.
813.	12553.	30157.	49438.
816.	12531.	30086.	49321.
819.	12509.	30015.	49205.
822.	12487.	29945.	49090.
825.	12465.	29875.	48975.
828.	12443.	29805.	48860.
831.	12422.	29735.	48747.
834.	12400.	29666.	48633.
837.	12378.	29598.	48521.
840.	12357.	29529.	48409.
843.	12335.	29461.	48297.
846.	12314.	29394.	48186.
849.	12292.	29326.	48076.
852.	12271.	29259.	47966.
855.	12250.	29192.	47856.
858.	12229.	29126.	47747.
861.	12208.	29060.	47639.
864.	12187.	28994.	47531.
867.	12166.	28928.	47424.
870.	12145.	28863.	47317.
873.	12124.	28798.	47211.
876.	12104.	28734.	47105.
879.	12083.	28670.	46999.
882.	12063.	28606.	46895.
885.	12042.	28542.	46790.
888.	12022.	28479.	46686.
891.	12001.	28416.	46583.
894.	11981.	28353.	46480.
897.	11961.	28290.	46378.
900.	11941.	28228.	46276.
903.	11921.	28166.	46174.
906.	11901.	28105.	46073.
909.	11881.	28043.	45973.
912.	11861.	27982.	45873.
915.	11841.	27921.	45773.
918.	11822.	27861.	45674.
921.	11802.	27801.	45575.
924.	11783.	27741.	45477.
927.	11763.	27681.	45379.
930.	11744.	27622.	45282.
933.	11724.	27563.	45185.
936.	11705.	27504.	45088.
939.	11686.	27445.	44992.
942.	11667.	27387.	44896.
945.	11648.	27329.	44801.

948.	11628.	27271.	44706.
951.	11609.	27213.	44612.
954.	11591.	27156.	44518.
957.	11572.	27099.	44424.
960.	11553.	27042.	44331.
963.	11534.	26986.	44239.
966.	11516.	26929.	44146.
969.	11497.	26873.	44054.
972.	11478.	26817.	43963.
975.	11460.	26762.	43872.
978.	11442.	26707.	43781.
981.	11423.	26651.	43691.
984.	11405.	26597.	43601.
987.	11387.	26542.	43512.
990.	11368.	26488.	43422.
993.	11350.	26434.	43334.
996.	11332.	26380.	43245.
999.	11314.	26326.	43157.

Table 2. Predicted average molecular weights as functions of the age in months. "Optimistic" parameters.

t(mo)	M_n	M_w	THF PS M_w
0.	24390.	85819.	140687.
3.	24360.	85618.	140358.
6.	24329.	85419.	140031.
9.	24299.	85220.	139705.
12.	24268.	85022.	139380.
15.	24238.	84825.	139057.
18.	24208.	84629.	138736.
21.	24178.	84433.	138415.
24.	24148.	84239.	138096.
27.	24118.	84045.	137779.
30.	24088.	83852.	137462.
33.	24058.	83660.	137147.
36.	24028.	83469.	136834.
39.	23998.	83278.	136521.
42.	23969.	83088.	136210.
45.	23939.	82899.	135901.
48.	23910.	82711.	135592.
51.	23880.	82524.	135285.
54.	23851.	82337.	134979.
57.	23822.	82151.	134675.
60.	23793.	81966.	134371.
63.	23763.	81782.	134069.
66.	23734.	81599.	133768.
69.	23705.	81416.	133469.
72.	23676.	81234.	133170.
75.	23648.	81053.	132873.
78.	23619.	80872.	132577.
81.	23590.	80692.	132283.
84.	23562.	80513.	131989.
87.	23533.	80335.	131697.
90.	23505.	80158.	131406.
93.	23476.	79981.	131116.
96.	23448.	79805.	130827.
99.	23420.	79629.	130540.
102.	23391.	79455.	130254.
105.	23363.	79281.	129968.
108.	23335.	79107.	129684.
111.	23307.	78935.	129401.
114.	23279.	78763.	129120.
117.	23251.	78592.	128839.

120.	23224.	78421.	128560.
123.	23196.	78252.	128281.
126.	23168.	78082.	128004.
129.	23141.	77914.	127728.
132.	23113.	77746.	127453.
135.	23086.	77579.	127179.
138.	23058.	77413.	126906.
141.	23031.	77247.	126634.
144.	23004.	77082.	126364.
147.	22977.	76917.	126094.
150.	22949.	76754.	125826.
153.	22922.	76591.	125558.
156.	22895.	76428.	125292.
159.	22868.	76266.	125027.
162.	22842.	76105.	124762.
165.	22815.	75944.	124499.
168.	22788.	75784.	124237.
171.	22761.	75625.	123976.
174.	22735.	75466.	123715.
177.	22708.	75308.	123456.
180.	22682.	75151.	123198.
183.	22655.	74994.	122941.
186.	22629.	74838.	122685.
189.	22603.	74682.	122430.
192.	22576.	74527.	122176.
195.	22550.	74373.	121923.
198.	22524.	74219.	121670.
201.	22498.	74066.	121419.
204.	22472.	73913.	121169.
207.	22446.	73761.	120920.
210.	22420.	73610.	120671.
213.	22394.	73459.	120424.
216.	22369.	73308.	120178.
219.	22343.	73159.	119932.
222.	22317.	73010.	119688.
225.	22292.	72861.	119444.
228.	22266.	72713.	119202.
231.	22241.	72566.	118960.
234.	22215.	72419.	118719.
237.	22190.	72272.	118479.
240.	22165.	72127.	118240.
243.	22140.	71981.	118002.
246.	22114.	71837.	117765.
249.	22089.	71692.	117529.
252.	22064.	71549.	117293.
255.	22039.	71406.	117059.

258.	22014.	71263.	116825.
261.	21989.	71121.	116592.
264.	21965.	70980.	116361.
267.	21940.	70839.	116130.
270.	21915.	70699.	115899.
273.	21891.	70559.	115670.
276.	21866.	70419.	115442.
279.	21841.	70281.	115214.
282.	21817.	70142.	114987.
285.	21793.	70005.	114762.
288.	21768.	69867.	114537.
291.	21744.	69731.	114312.
294.	21720.	69594.	114089.
297.	21695.	69459.	113866.
300.	21671.	69323.	113645.
303.	21647.	69188.	113424.
306.	21623.	69054.	113204.
309.	21599.	68920.	112984.
312.	21575.	68787.	112766.
315.	21551.	68654.	112548.
318.	21527.	68522.	112331.
321.	21504.	68390.	112115.
324.	21480.	68259.	111900.
327.	21456.	68128.	111685.
330.	21433.	67998.	111471.
333.	21409.	67868.	111258.
336.	21386.	67738.	111046.
339.	21362.	67609.	110835.
342.	21339.	67481.	110624.
345.	21315.	67353.	110414.
348.	21292.	67225.	110205.
351.	21269.	67098.	109997.
354.	21246.	66971.	109789.
357.	21222.	66845.	109582.
360.	21199.	66719.	109376.
363.	21176.	66594.	109170.
366.	21153.	66469.	108966.
369.	21130.	66345.	108762.
372.	21108.	66221.	108558.
375.	21085.	66097.	108356.
378.	21062.	65974.	108154.
381.	21039.	65851.	107953.
384.	21016.	65729.	107753.
387.	20994.	65607.	107553.
390.	20971.	65486.	107354.
393.	20949.	65365.	107156.

396.	20926.	65244.	106958.
399.	20904.	65124.	106761.
402.	20881.	65005.	106565.
405.	20859.	64885.	106370.
408.	20837.	64767.	106175.
411.	20814.	64648.	105981.
414.	20792.	64530.	105787.
417.	20770.	64413.	105594.
420.	20748.	64295.	105402.
423.	20726.	64179.	105211.
426.	20704.	64062.	105020.
429.	20682.	63946.	104830.
432.	20660.	63831.	104641.
435.	20638.	63716.	104452.
438.	20616.	63601.	104264.
441.	20594.	63486.	104076.
444.	20573.	63372.	103889.
447.	20551.	63259.	103703.
450.	20529.	63146.	103517.
453.	20508.	63033.	103332.
456.	20486.	62920.	103148.
459.	20465.	62808.	102965.
462.	20443.	62697.	102781.
465.	20422.	62585.	102599.
468.	20401.	62475.	102417.
471.	20379.	62364.	102236.
474.	20358.	62254.	102056.
477.	20337.	62144.	101876.
480.	20316.	62035.	101696.
483.	20294.	61926.	101517.
486.	20273.	61817.	101339.
489.	20252.	61709.	101162.
492.	20231.	61601.	100985.
495.	20210.	61493.	100809.
498.	20189.	61386.	100633.
501.	20168.	61279.	100458.
504.	20148.	61173.	100283.
507.	20127.	61067.	100109.
510.	20106.	60961.	99936.
513.	20085.	60855.	99763.
516.	20065.	60750.	99591.
519.	20044.	60646.	99419.
522.	20024.	60541.	99248.
525.	20003.	60437.	99077.
528.	19983.	60333.	98907.
531.	19962.	60230.	98738.

534.	19942.	60127.	98569.
537.	19921.	60024.	98401.
540.	19901.	59922.	98233.
543.	19881.	59820.	98066.
546.	19861.	59719.	97899.
549.	19840.	59617.	97733.
552.	19820.	59516.	97568.
555.	19800.	59416.	97403.
558.	19780.	59315.	97238.
561.	19760.	59215.	97074.
564.	19740.	59116.	96911.
567.	19720.	59016.	96748.
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