

Computer simulation of polycondensation reactions.

In this report a short explanation of a MonteCarlo simulation program will be given. It is based on random collisions between particles that contain functional groups (OH, COOH).

Principle of the simulator

During many years now, people that work in the field of any kind of polyester development, are familiar with the Gel Constant (K). This constant is the result of a statistical interpretation of the number of functional groups and the number of particles, present at the start of the condensation reaction.

K is described as follows:

$$K = \frac{\sum m}{\sum f}$$

where $\sum m$ = the total amount of moles
and $\sum f$ = the total amount of equivalents of the functional groups, present in short measure.

If $K > 1$, no gellification will occur

If $K < 1$, gellification will take place below a certain acid value.

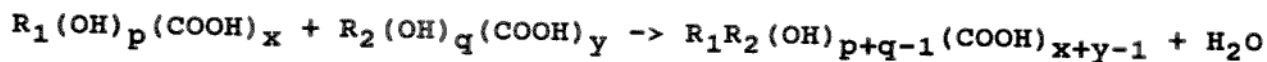
In general: the Gel Constant can be used in any system where a functional group A reacts with a functional group B.

Although we may say that the Gel Constant gives us a good picture of the behaviour of polycondensates, often slight deviations are noticed. The explanation lies in the assumptions made in deducing the equation; particularly the following:

- a) No intramolecular reactions occur; that is to say that each reaction between A and B is assumed to join 2 molecules together to give a higher molecular weight product.
- b) All groups are equally reactive.
- c) No side reactions (like etherification or double bond polymerisation) take place.

This statistical approach is the basis of the simulator.

A polycondensation reaction obeys the following general reaction equation:



It can be considered as the chance that a particle with a functional group A collides with a particle that contains a functional group B to result in the chemical bond AB.

Because of the analogy with a roulette gambling game, computer simulators acting according to this principle are often called MonteCarlo simulators.

This program gives a molecular weight distribution output. It can be used by the applicant to determine whether the product will be a gel; if there is very high or very low molecular material present or not; do some observations with respect to the size of the distribution; check the amount of unreacted material after a reaction. If the simulator is used before an actual lab. experiment, in some cases it may point out that the experiment will fail. A lot of time can be saved.

Translating chemistry into software

The "reaction vessel" is the computer's memory, in which random collisions between ± 60000 particles are simulated. The information about a particle is present in a 9 - byte memory block. This means that a memory space of $9 * 60000 = 540$ kByte is used to contain all particles at the start of the reaction. Because there are so many particles involved, the statistical reliability is very accurate.

Together with the memory to store both the program and DOS, a computer with at least 640 kByte memory is needed. The simulator runs without problems on the IBM PS 2 models. The average processing time on a Model 50 is only 5 minutes!

Performing a reaction

Because the program uses ± 570 kByte memory, the best thing to do is remove all resident programs. When the picture appears on the screen, press ENTER and you will go to the main menu. There are 4 options:

- a) With the cursor (up,down) you can adjust the reaction speed.
- b) F1 - Perform a reaction
- c) F2 - Loading a file of a previous reaction
- d) ESC- Leave the program

Input of components

Usually in any calculation program for polyester synthesis the raw materials are given as a chemical substance. In this case, however, the computer only needs data for molecular weight, amount and functionality of a raw material. The reason why the program was set up in this way is that not only raw materials can be used as inputs, but also all kinds of reaction products like for instance alcoholysis mixtures, oligomers, Diels-Alder adducts. The only parameters that count are molecular weight, OH and COOH functionality of the components. **Anhydride and epoxy compounds however, should be recalculated to their di-acid or di-hydroxy equivalents.**

After choosing an endpoint by setting an acid value, the relative molar amounts of the components are transformed into numbers of particles. Then, as a result of these calculations, all 60000 particles are put into the computer's memory.

When the status register appears on the screen, the actual process starts. During the reaction samples are taken. The reaction can be stopped by pressing "ESC". When the reaction is complete, a reliability check is done and a message appears on the screen, informing you about the outcome, together with a beep. The computer waits until a key is pressed and then the table + graph of the end sample are displayed. The graphs and tables respond to the "ESC" key. After having displayed graph + table, you will arrive at the end menu.

Output

- a) A number molecular weight distribution (Mn)
- b) A mass molecular weight distribution (Mw)
- c) Endgroup analysis

The molecular weight distributions have log MW -scales between 1 and 6.

The functions of the end menu are:

- F1 Shows the progress of the reaction in table form
- F2 Shows the progress of the reaction in graphics
- F3 Saves the data of the results on disk
- F4 Shows the functional groups in the end sample, per molecule, per log MW unit.

"ESC" stops the program (back to DOS).

This report was written in 1992 by me (Hans Hendriks).

The simulating software is now (2021) made available for use in smartphones as a program running under the phone app "Dosbox". Therefore the F-keys are replaced by easy to use keys provided by Dosbox. Information about the use of all functions is available in the program. Of course the simulator can also be applied using Dosbox on a regular laptop / PC. The simulator was recently extended with a tool to create .csv files from samples, for use in spreadsheets.

Additional remark:

The value "K" as gel constant is now expressed as "Conv-gel", indicating the conversion at the gel point.

EXAMPLES

1: Polyester

| <u>Moles</u> | <u>Raw Material</u> | <u>Grams</u> |
|--------------|---------------------|--------------|
| 1.000 | Fumaric acid | 116 |
| 1.016 | Ethylene glycol | 63 |
| 0.506 | Phthalic acid | 84 |
| 0.513 | Propylene glycol | 39 |

2: Alkyd with high molweight

| <u>Moles</u> | <u>Raw Material</u> | <u>Grams</u> |
|--------------|---------------------|--------------|
| 0.500 | Fatty acid | 140 |
| 1.000 | Pentaerythritol | 136 |
| 0.994 | Phthalic acid | 165 |

3: Alkyd with low molweight

| <u>Moles</u> | <u>Raw Material</u> | <u>Grams</u> | |
|--------------|---------------------|--------------|--------------------|
| 1.000 | Glycerol | 92 | } Vegetable oil |
| 3.000 | Fatty acid | 840 | |
| 1.000 | Phthalic acid | 166 | |
| 1.000 | TriMethylolPropane | 134 | |

4: Alkyd with 'normal' molweight

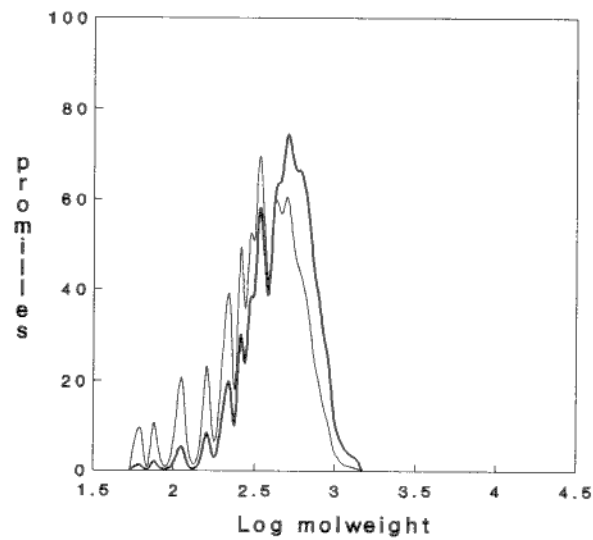
| <u>Moles</u> | <u>Raw Material</u> | <u>Grams</u> | |
|--------------|---------------------|--------------|--------------------|
| 0.500 | Glycerol | 46 | } Vegetable oil |
| 1.500 | Fatty acid | 420 | |
| 1.265 | Phthalic acid | 210 | |
| 1.000 | Pentaerythritol | 136 | |

5: Prop. glycol - Fumaric acid - Prop.glycol ester

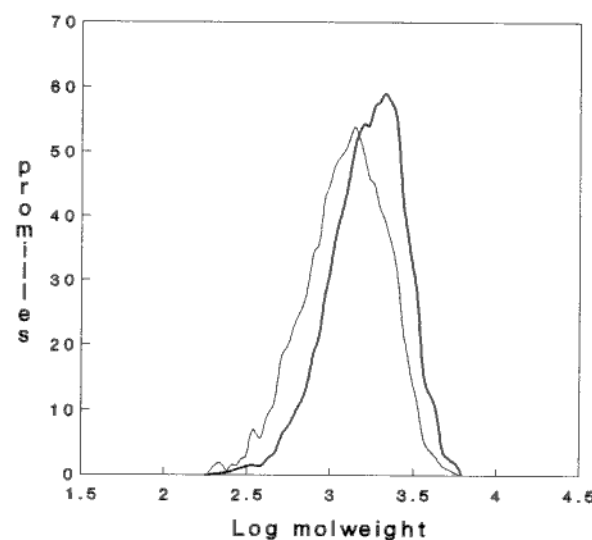
| <u>Moles</u> | <u>Raw Material</u> | <u>Grams</u> |
|--------------|---------------------|--------------|
| 1.000 | Fumaric acid | 116 |
| 2.000 | Propylene glycol | 152 |

Sample 1: Polyester

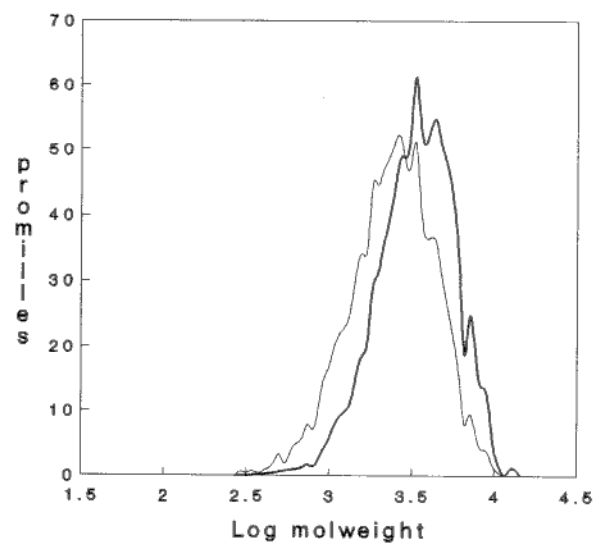
Acidvalue=127.6 MN=422
80.4 % Conversion



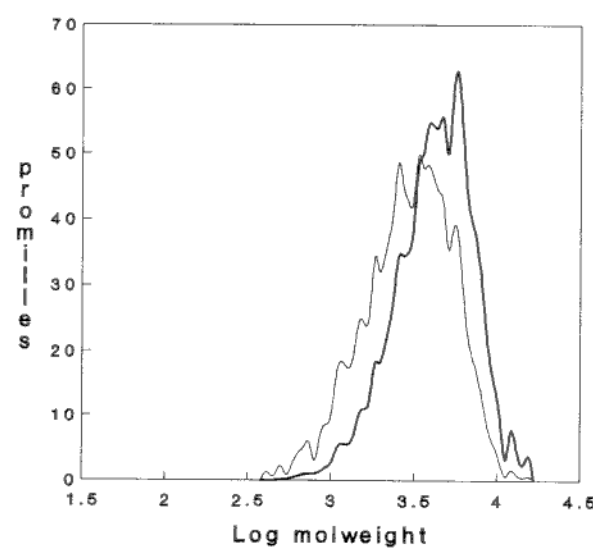
Acidvalue=32.3 MN=1492
95.2 % Conversion



Acidvalue=13.6 MN=2965
97.9 % Conversion

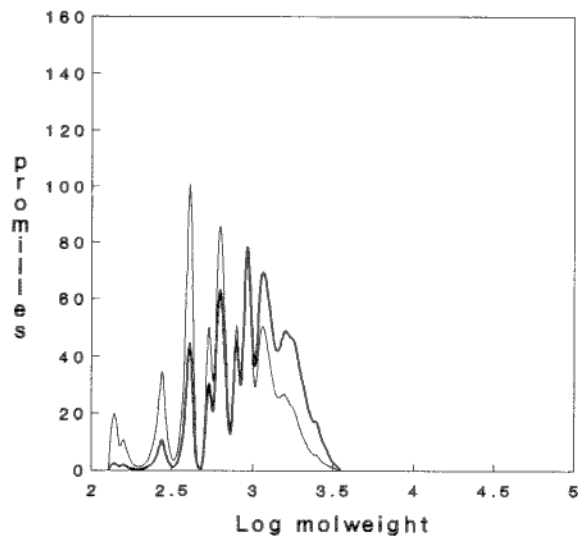


Acidvalue=9.9 MN=3675
98.5 % Conversion

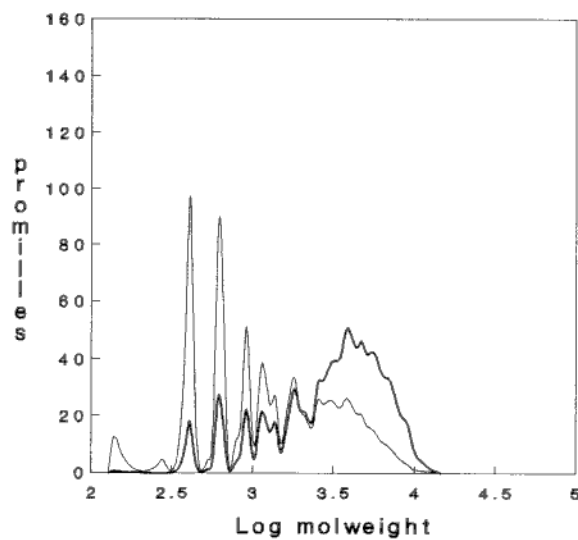


Sample 2: High MW Alkyd

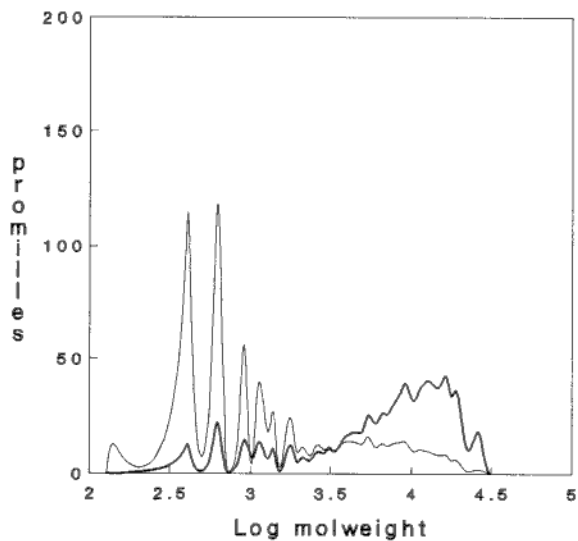
Acidvalue=61.7 MN=895
67.3 % Conversion



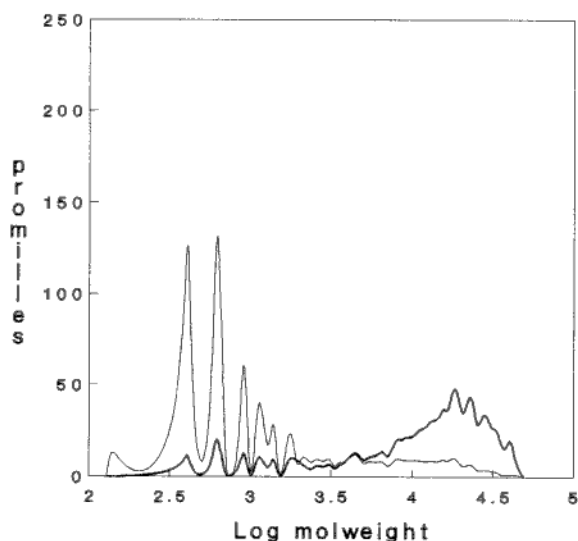
Acidvalue=25.4 MN=2126
76.0 % Conversion



Acidvalue=15.0 MN=3506
78.4 % Conversion

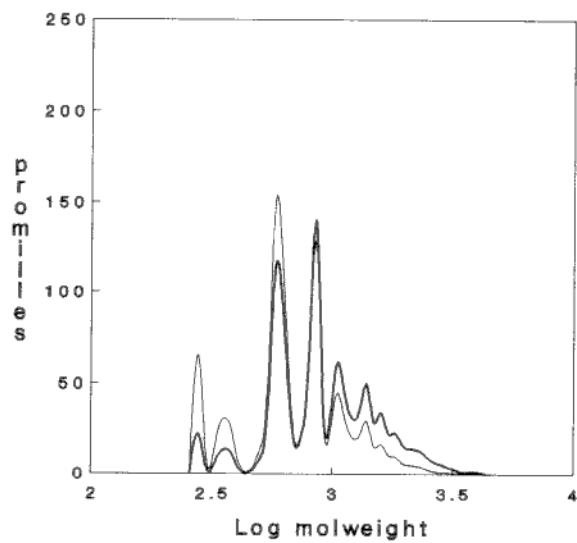


Acidvalue=11.9 MN=4318
79.1 % Conversion

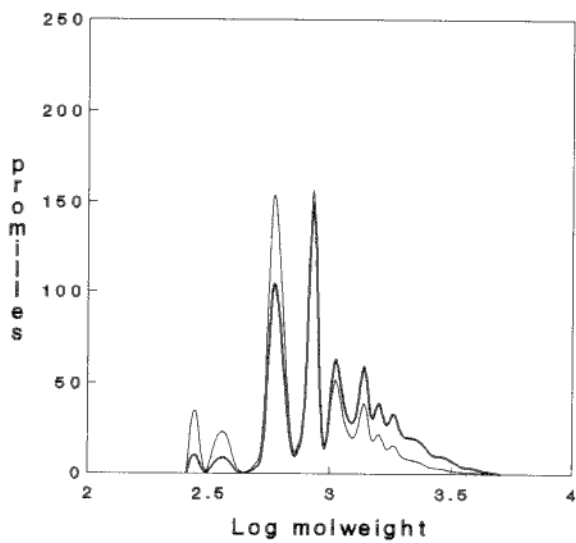


Sample 3: Low MW Alkyd

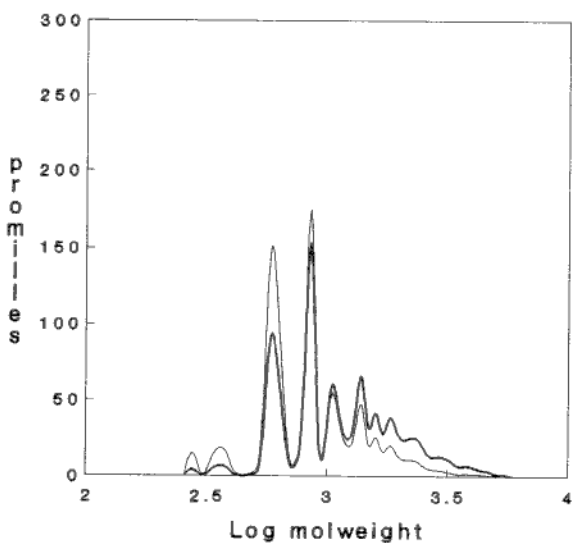
Acidvalue=19.6 MN=818
91.8 % Conversion



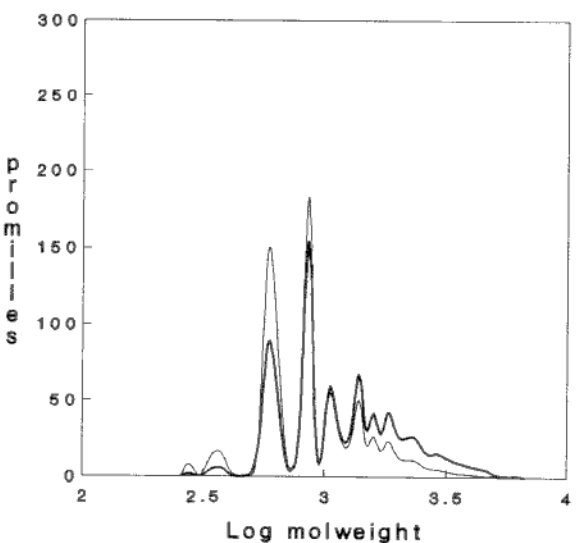
Acidvalue=11.3 MN=928
95.3 % Conversion



Acidvalue=6.1 MN=1016
97.4 % Conversion

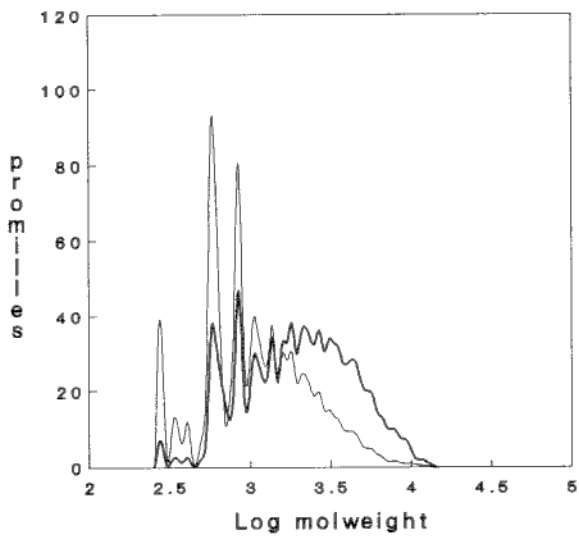


Acidvalue=3.9 MN=1056
98.3 % Conversion

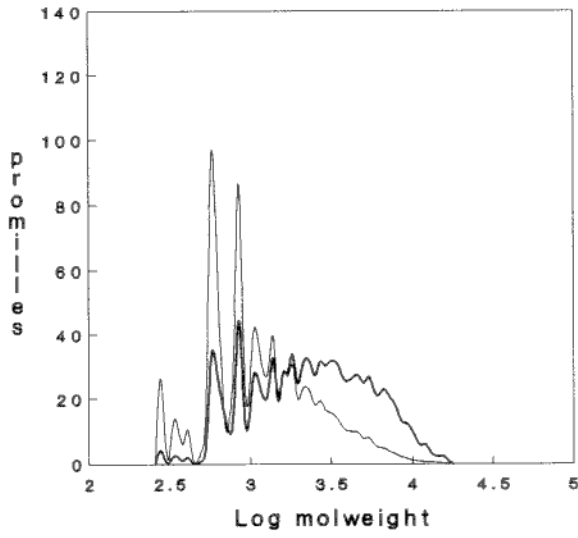


Sample 4: 'Regular' Alkyd

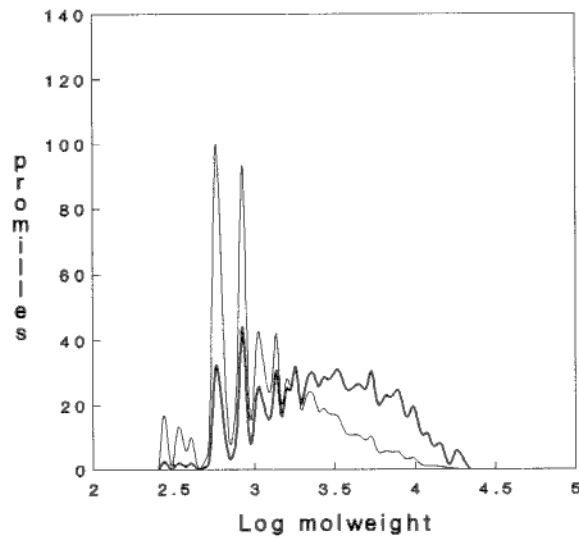
Acidvalue=19.0 MN=1521
84.3 % Conversion



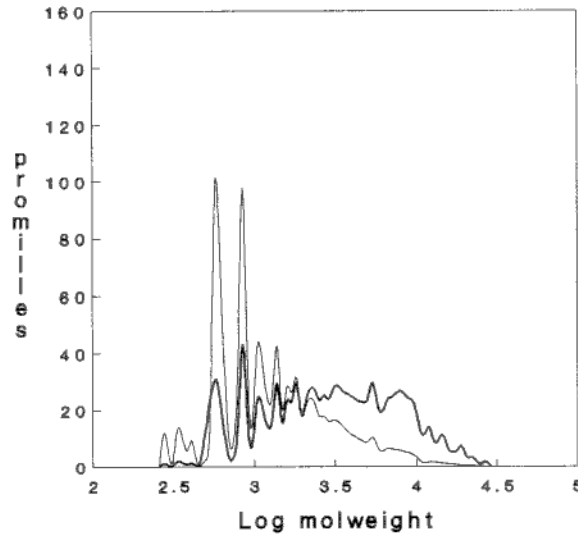
Acidvalue=14.8 MN=1713
85.5 % Conversion



Acidvalue=11.8 MN=1886
86.4 % Conversion

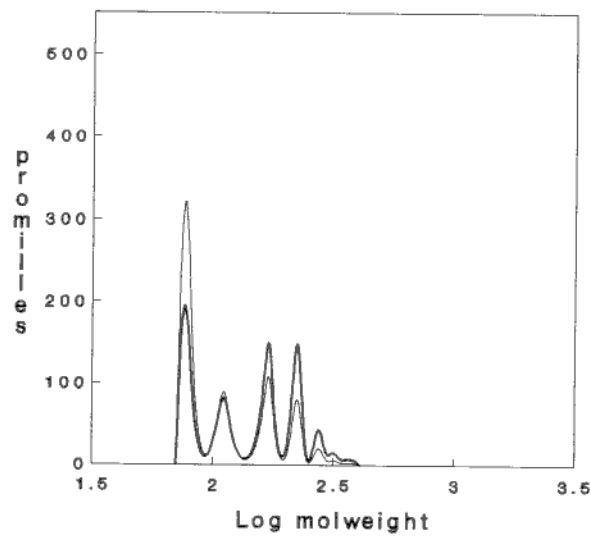


Acidvalue=9.9 MN=2015
87.0 % Conversion

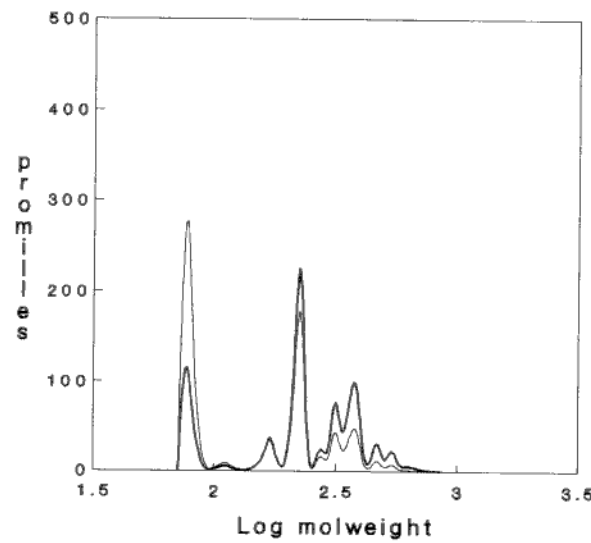


Sample 5: Prop.glycol-Fumaric Acid-Prop.glycol

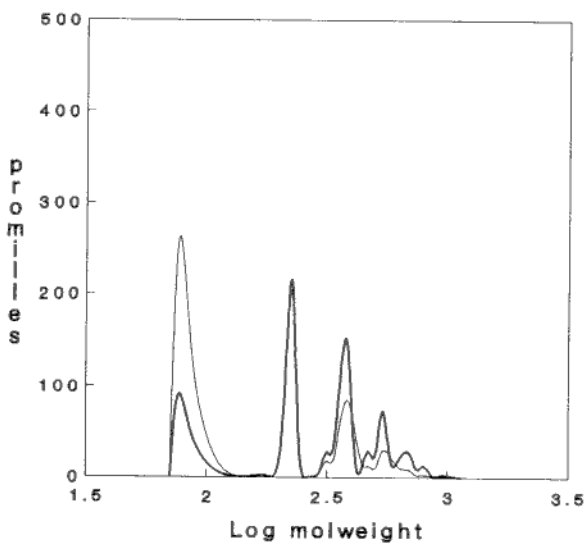
Acidvalue=223.6 MN=125
50.1 % Conversion



Acidvalue=70.5 MN=182
85 % Conversion



Acidvalue=17.7 MN=217
96.2 % Conversion



Acidvalue=0.1 MN=231
99.9 % Conversion

