

DryAdd Demonstration

DryAdd – as the name implies – lets you ‘add’ monomers to make polymers and networks, cutting down the amount of ‘wet’ lab work you need to do. This demo aims to show you the basic capabilities of **DryAdd** and let you interact with a few selected example, which we hope will illustrate the power of this software package in helping your materials design.

DryAdd fits into your research program by letting you try out new ideas – for example, what happens if you use a different material, or different amounts of a material. What happens if you accelerate the reactivity (perhaps by adding a catalyst) for a particular reaction? Do the overall properties change? By doing such ‘what if’ experiments on your computer, you can focus your laboratory work on your best ideas and gain new insights into your polymer system.

DryAdd comes in two forms, **DryAdd-Pro** and **DryAdd-Pro+**. This demonstration shows you the capabilities of **DryAdd-Pro**. **DryAdd-Pro+** has a larger range of reaction types including condensation reactions in which a reactive product molecule is formed, transfer, transesterification and first order reactions. It also has the ability to remove monomers during the simulation to model effects such as the evaporation of solvents or reaction products at user-specified increments of temperature or conversion.

DryAdd Installation

1. If you have downloaded from the web site, unzip the file da-demo.zip into a temporary directory.
2. Run the file setup.exe from the temporary. You can run this simply by double-clicking on the file’s icon.
3. The default directory into which **DryAdd Demo** is installed is *c:\Program Files\OxMat\DryAdd Demo*. You may alter this if you wish. A new item *DryAdd Demo* will be added to your Taskbar, and can be accessed using the *Programs* option from the Windows *Start* button.

What’s in the Demo

The **DryAdd** demo has been designed to show you what the software can do for some specific examples. **DryAdd** can cope with more chemistries than are illustrated here – in particular, it has been used previously for polyesters, siloxanes, phenolics and mixed chemistries as well as the polyurethanes and epoxies discussed here. If you are interested in a chemistry that has not been included in this demonstration, please contact us and we will be happy to run a data set for you.

The main applications included in the demo are:

Polyurethanes

1. Dataset *TPU.set* describes a thermoplastic polyurethane - only linear chains are formed. It mixes pure MDI (functionality 2) with a (polyether) diol of molecular weight 1000, and a chain extender, 1,4-butanediol. We have assumed that the chain extender OH groups are four times as reactive as those for the polyether - an arbitrary assumption in this case. Reactions are set up for reaction of the OH groups with the NCO groups. Note that we have also set up ‘phantom’ urethane groups on the MDI. When urethane groups are formed, we have assumed that there is a small probability that they can go on to react with more NCO groups to give allophanates. You could also add water to get urea linkages, and by setting up these as phantom groups, look at biuret formation..
2. Dataset *flexfoam.set* simulates the formation of a flexible water-blown polyurethane foam. The two polyols here (polyol_2 and polyol_3) are used in equimolar ratios to represent a polyol with molecular weight 2000 and average functionality 2.5. For the fully-functional **DryAdd-Pro** and **Pro+**, of course, you could form a pre-polymer first, and use that as your starting material. The MDI is set up as two materials, pure MDI, and a trifunctional variety with 3 NCO groups. Conversion has been set up with respect to OH groups. (See in the General parameters menu.) Reaction rates have been taken from the ICI Polyurethanes Book. Carbon dioxide is evolved; by monitoring its evolution compared to the rise in

secondary cycles (an indicator of gelation) you can see the effect of changing monomers and reaction rates.

3. Dataset *rigifoam.set* uses two polyols with functionality 3 and 5, and mixture of polymeric MDI with average functionality 2.7. Two materials are used to simulate the MDI. There is an excess of isocyanate, because the MDI can react with itself, once the temperature rises. For the polyol, there are primary and secondary OH groups with different reactivity. The reactions are set up to model this. Initially, the reaction of isocyanates to give trimer groups (note that the 't' group is an intermediate) is set to zero, since the reaction does not occur at low temperatures. Once the reaction has run for a while, you can pause the simulation and set non-zero rates for these. You can see what happens with and without this second set of reactions - with the isocyanurate reactions switched on, you will get more secondary cycles (i.e. harder material) and all the NCO will be used. When they are not switched on, you will have an excess of NCO at the end of the simulation.

Epoxies

1. Data set *epoxprim.set* is a 'textbook example' of a primary amine reacting with an epoxide group, based on published work by Cheng and Chiu (1994). The amine is DDS. The epoxy is a mixture of DGEBA and a hydroxyl-containing derivative of DGEBA, and is based on a commercial resin DER332. Note that phantom groups are set up - when the epoxide group opens, a hydroxyl group is formed. A secondary amine (40% as reactive as the primary amine) is also formed upon reaction. The reaction scheme allows for reaction of primary amine with epoxide group. There is then a further reaction of the secondary amine with another epoxide group. We have allowed for the OH group to ring-open epoxide groups. This may not occur at low temperatures; you have the option to set the rate to zero if you want to ignore it. By varying the relative amounts of epoxy and amine, you can see big changes in the gel point. Plots of largest group by number, vs conversion, show this clearly.

2. Data set *epoxtrin.set* illustrates cure by a tertiary amine. Here, we have used diethyl amino propylene (DEAP) with DGEBA. The reaction is catalytic; the tertiary amine opens the epoxide group to give an O- like species, which then goes on to open more rings.

There are two reactions:

- (i) The initiator site on DEAP attacks the ring, making an Oxygen ion site
- (ii) The Oxygen ion site attacks a ring, making another Oxygen ion site

This give a very tightly crosslinked system. You can see this by the high number of secondary cycles. The gel point, and ultimate amount of crosslinking, depend on how much tertiary amine is present at the outset. You can see this by changing relative amounts.

3. Data set *epox-rad.set* shows how you might tackle an epoxy system which uses a free radical initiator. It is assumed that all of the initiator is dissociated at the beginning, and it has converged part of the DGEBA to free radical form. Only one reaction is needed; the radical reacts with an epoxide group to form a new radical. The system becomes very highly crosslinked, depending on the amount of initiator which is used. See this by looking at the rise in secondary cycles. For DryAdd Pro and Pro+, you can of course examine the network during the cure process with the Network Analysis.

4. Data set *epox-mix.set* is possibly the most interesting of the epoxy examples in this demo version. A tertiary amine initiator is used (at 1% of the concentration of the DGEBA) and the primary amine DDS is also added, with 0.8 moles of DDS to each mole of DGEBA.

Reactions include:

anions opening rings to give more anions - VERY fast
primary amine reacting with epoxide to give secondary amine and OH
secondary amine reacting with epoxide group to give another OH
OH group opening an epoxidel group - assumed to be relatively slow

Rate information is taken, in part, from published work by Cheng and Chiu. With DryAdd Pro and Pro+, you can search for sequences of ether links (from the tertiary amine initiated reactions) and see in detail the effect of the amine groups.

Quick Tour

We hope that you will find the layout of the menus understandable and easy to use. We have used standard Windows conventions, will pull-down menus for **File** handling, **Control** of the simulation, **Edit** to transfer data to the Windows clipboard, looking at **Results**, handling **Windows**, and giving comprehensive on-line **Help**.

First of all, a quick word about the results, since that is probably what, ultimately, you are after. The reports are spreadsheet-enabled, which means that you can cut-and-paste to the Windows clipboard and, via that, into your favourite spreadsheet package. The plots are all set up for 'graph zooming', which lets you expand selected bits in the x-direction, to view them in more detail. Both the reports and the plots remain after the simulation has been aborted (see below) so that you can compare results from one run to another.

If you are in a hurry to get on with things, you might want to move straight on to the next section on **Applications**, and save yourself some reading, coming back to this Quick Tour if necessary to understand what's going on.

For the rest of us who believe more haste, less speed, here is an introduction to the menus...

1. File pull-down menu

The File options let you create **New** data sets, **Open** existing data sets, and **Save** files. All of these are disabled in this demo version. You can print results – even from the demo version – in case you want to produce a report to show to your management. The associated things you'd expect – like **Print Setup** and **Print Preview** – are also found under the File pulldown. These should all be familiar to regular Windows users.

2. Control pull-down menu

This gives you access to the screens you need to set up and control the simulation.

- 2.1 **Notes** lets you write any notes that you wish to keep with the simulation, for example to remind you what you have done in a particular data set, and why. The **Notes** are stored with the data sets so are available for future reference. In the demo version, if you change the notes, they will not be saved for future use, since the save feature has been disabled.
- 2.2 **General** parameters control the overall simulation. They are disabled for the demo, and shown with 'pre-loaded' values only. In the full version, you can set up the population, and the number of runs to average. (Remember that DryAdd is based on a Monte Carlo simulation, so you will get some statistical variation from one run to another.) You can also choose which group you wish to use to monitor conversion.
- 2.3 **Initiator Setup** is used for free radical simulations. It is not applicable for any examples in this demo.
- 2.4 **Materials** allows you to set up what materials you use, what their functional groups are, and how much of them is present. The **Materials** workscreen is based on a spreadsheet functionality, so if you change the weight of material added, the number of moles is recalculated. If you change the number of moles, then the weight is recalculated. We have disabled the **Add** and **Delete** buttons, and you will find that you cannot change the name of the materials in this demonstration version.

Groups

In order for the molecules to react, DryAdd will need to know what reactive groups are present. If you press the **Groups** button, you will see the ones that have been set up. For the example TPU.set, you will see 'phantom groups' on MDI-2. Phantom groups are groups that are created in the initial reaction, that can go on to take part in later reactions.

In this case, we have set up urethane groups that, once formed, can go on to react with isocyanate to give allophanates.

Feed

The **Feed** button allows you to control how your materials are fed in to the reaction pot. If you click on the **Feed** button, you will see a screen showing the **Feed** schedule for the particular material which was selected in the **Materials** workscreen. We have assumed that all materials are present at the start. Suppose you want to change this, and feed material in during the process. Double click on the field next to **0% Conversion** to highlight it, and type 0 (zero) or another value into the field, for the starting amount in the pot. Then press the **Program** button. You will be asked to specify how much you want to feed (by percentage) in how many steps.

The actual **Feed** within the program is added in smaller steps than those specified in the **Feed**, so you are not simulating big slugs of material going in, but rather a gradual feed process.

Database

DryAdd is shipped with a database of standard materials. You can view this by clicking on the **Database** button. The toggle buttons let you filter out the particular materials you want – click on a few to see what happens. There is also the ability for the user to supply their own database of materials – see the toggle buttons at the top right of the screen to see the option of selecting the **User** or **Supplied** databases.

The **==>** button transfers materials from the **Database** to the **Materials** workscreen, together with the reactive groups needed for the simulation. However, this button is not operational in the demo version; the database features have been disabled.

- 2.5 **Reactions** are set up in a separate workscreen. In this screen, you tell **DryAdd** which reactions can take place. Again, reactions are set up in the form of a spreadsheet, for convenience of input.

Add and **Delete** have been disabled in the **DryAdd** demo – of course, you have this ability in the full version.

In the fully functional version of **DryAdd**, to modify one of the existing reactions, double click on the relevant field. You will get a small window that lists all of the groups that have been set up. Select one of these (your selection will be highlighted) and then click on **OK**. The **Reactions** screen will be updated with your new value. The reactions have been fixed in this demo version of **DryAdd**.

Reaction rates are either relative or absolute rates, and are user-supplied. In the demo version, we have used relative rates exclusively. The reaction displayed in red is the reference reaction; if **Time and Kinetics** parameters(see later for details) are set up, this is the reaction to which they refer. If you want to change the reference reaction, make sure that the correct reaction is selected in the **Reactions** screen, then press the **Reference** button. You will see that your choice is now displayed in red, with other reactions in black.

Other buttons can also be seen on the **Reactions** screen. **Make** will set up most reactions automatically, provided you have specified the group codes on the materials. This saves you some effort in setting up the reaction scheme. **Substitutions** lets you look at the effect of steric hindrance, by modifying the relative reaction rates. It is set up mainly for trifunctional materials, as the phrases 'One Reacted' and 'Both Reacted' indicate – see the window that pops up when you press the Substitutions button to see what we mean.

You can change the reaction rates within the demo if you want. In particular, setting a rate to zero switches off that reaction. This can be useful for a two-step simulation, since

you can put all the materials in, but leave the rates for the reactions that refer to the second step set to 0.

General guidelines exist to help you to set up the right reaction rates. For example, second hydroxyls are less reactive than primary hydroxyls. This means that you can explore what would happen if you change materials, or add catalysts that speed specific reactions, quickly and reliably using **DryAdd**.

- 2.6 **Endpoints** produces the screen you use to let **DryAdd** know what to give up. You can tell the program to stop when a particular amount of material has been used up, or at a specific point of conversion.

Because **DryAdd** is a Monte Carlo simulation, it will continue to select monomers and try to react them even if this is not chemically feasible. Therefore, the **Endpoints** also include **Misses before quitting**, which is usually set to 10,000. If DryAdd tries this many times to carry out a reaction, and fails each time, then it probably is time to stop the simulation.

- 2.7 **Time and Kinetics** is a screen which you can use if you wish to set a time base, or if you wish to compare with thermal analysis results like DMA or DSC. This is also where you can impose a temperature profile on your reaction. A heating ramp consisting of up to 100 nodes is available if the **Time and Kinetics** function is switched on. However, this is not available in the demo version.

2.8 Preview Simulation and Run Simulation

The remaining items under the **Control** menu are **Preview Simulation** and **Run Simulation**. Both give you the same **Simulation Dialog** screen. **Preview Simulation** is mainly used to ensure that you have set things up correctly. Both the **Materials** and **Groups** buttons on this screen pop up a little window, and both can be up at the same time. They tell you how much material is in the pot, and how many reactive groups there are. If you want to remove these windows, select the **Hide** option.

If you preview the simulation and things look OK, you can go on to run the simulation by selecting the **Resume** button.

You have the option to **Abort** the simulation, but be warned – if you do this for a running simulation, all results will be lost. The alternative is to **Pause** the simulation, whereupon you can use the **Results** pull-downs to examine plots or reports, then **Resume** once you are ready to start up again.

If you **Resume**, you will be asked if you wish to reset conversion. Whether or not you select Yes depends on your particular project; do what makes sense in your context.

3. Results

The Results menu gives you a number of pull-down options, some of which are discussed here.

- 3.1 **Save to Pre-polymer File** lets you save the results of the simulation to use in a later run. This is an advanced feature of the program, since specifying the reaction pot needs careful thought – you can't use 'part of a pot' in later simulations. This feature is not available in the demo version.
- 3.2 **Edit Run Title** lets you change the title of the outputs from the **Results** section. The default is the path and filename of the dataset of the simulation. To return the title to the default, click on the **Restore Default** button.
- 3.3 **General Results** is a report of the simulation conditions and also of the results e.g. Mn, Mw, polydispersity etc. which are produced by the simulation. As mentioned previously, you can cut and paste this report, or selected bits of it, into your spreadsheet package via the Windows clipboard.

- 3.4 **Averaged Results** are only available if you have selected more than one run to average in the **General** parameters of the **Control** menu. The averaged results give you an idea of the 'shimmer' that you find in the Monte Carlo simulation. In the demo, the ability to do multiple runs has been disabled.
- 3.5 **Plots** gives you a screen that lets you choose which plots you want, including the largest groups, secondary cycles, and remaining unreacted monomers and sites.
- 3.6 **Data Tables** does what it says – instead of plotting the results, this lists them in a table so that you can export them to other packages.
- 3.7 **Weight Distribution** allows you to generate the weight distribution of molecules in the **DryAdd** simulation. This information is available in the form of a **Table** or plots of **Number at Weight** or **Weight at Weight**. The plots are available with linear or log scale x-axes, for easy comparison with GPC outputs.
- 3.8 The **Analysis Functions** in many ways are the real strength of **DryAdd**.

A **Sequence Analysis** lets you determine how often a particular sequence occurs. This can be useful, for example, in polyurethanes if you know that you need a certain sequence of a specific length in order to get hardblock segregation.

Network Analysis is based on sophisticated graph theory, and provides results that compare favourably with Miller-Macosko branching theory. **DryAdd** treats the largest molecule as the gel, and the Network Analysis works on this molecule. It factors the molecule into the Elastically Effective Component (which contributes to the mechanical properties) and the Pendant Fraction (which doesn't but which may, for example, have compatibilizers for a particular environment). Most of the parameters reported are directly related to rubber elasticity theory – for example, **DryAdd** calculates M_c , the number-average molecular weight between cross-links. This relates directly (via the density) to the elastic and shear moduli of the material.

Formula Analysis is mainly useful if you want to see how much of a material has a specific functionality. For example, if you have added a water-solubiliser to the formulation for a dispersion, you can extract information on how much of the material is likely to be found in the cores of the particles and how much in solution, using the **Formula Analysis**.

Chain Analysis looks at up to 1000 chains, starting by default with the lowest molecular weights, and gives a detailed report on their composition. For each molecule, the size, molecular weight, and conversion is displayed. There then follows a breakdown of each molecule in terms of monomer types.

System Analysis generates a report on the distribution of reacted sites on material units in the entire system. It will also tell you the proportions of each configuration of the reacted sites in cases where there is more than one option.

Block Sequence Analysis is used to analyse the length, weight and frequency of linear sequence blocks. The information is available as a table or as plots in terms of combinations of weight and number. The block sequence analysis will work only for unbranched chains.

4. **Windows**

This contains standard stuff e.g. **Tile**, which lets you look at two windows side by side. This can be really useful if you want to compare two plots from two different runs, or edit the **Materials** and **Reaction** screens simultaneously.

5. **Help**

The name says it all. This gives you access to the extensive on-line **Help** within **DryAdd**.

6. A Final Note on Menus

Most of the popular menu items have been included in the Toolbar, so that you can select the appropriate icon rather than needing to wade through the pull-down menus. It all depends on your personal preference!

Applications

The applications are all selected from the **Load Examples** item in the **File** menu. **Load Examples** is specific to the demo version – it is not available in the full version of the program.

For all the applications, you can change relative reaction rates and amounts of materials, to see what effect this has on the simulation **Results**. To run the simulations, select **Run Simulation** from the **Control** menu. **Results** will be available once the simulation has started – you can **Pause** the simulation to examine interim results if you wish.

1. TPU.set

This describes a thermoplastic polyurethane, formed by the reaction of a difunctional isocyanate, MDI, with two different difunctional polyols. If you look at the Groups for the polyols, you will see that they have been set up with primary hydroxyl groups.

The 'standard' reaction of a hydroxyl group with isocyanate gives a urethane bond. But side reactions can also occur. For example, the urethane might react with an isocyanate group, to give an allophanate. If you examine the **Groups** on MDI-2, you will see that there is a 'phantom' urethane group. There are none of these groups at the outset, but are created during the reaction. By looking at the **Reactions**, you can see that we have allowed the urethanes to react with isocyanate. We have set this to have a small relative reaction rate, compared to the reaction of the isocyanate with the hydroxyl groups.

If you run this simulation, you will see that you get a few 'secondary cycles' – this happens even if you set the relative rate for allophanate formation to 0. This happens because some of the chains form 'rings' – the tail of one chain reacts with its head, to give a cyclic structure. In the full version, you can prevent this happening by changing the secondary cyclization parameter, in the **General** simulation parameters.

2. Flexfoam.set

This data set describes a mixture of a difunctional polyol, a trifunctional polyol, a difunctional isocyanate (MDI-2) and a trifunctional isocyanate (MDI-3). In addition, there is some water present. As you can see from the **Materials** screen, even a relatively small weight of water equates to a large number of moles, simply because of water's low molecular weight. Water reacts with the isocyanate group to produce an amine functionality. Carbon oxide is generated during the reaction. By controlling the carbon dioxide evolution, it is possible to use the gas as a blowing agent for the foam.

For this data set, we are monitoring the reaction as a function of the conversion of the OH groups. You can see this by looking at the **General** simulation parameters under the **Control** menu – the bottom field, **Conversion based on**, shows that it is based on all OH groups, denoted by *.OH to show that it does not matter which material the OH group is on.

The water molecule has one OH group for the purposes of the **DryAdd** simulation. This is because only one of the OH will react with an isocyanate. An amine group is produced, and we have set this up as a phantom group. In addition, so that we can keep track of the number of carbon dioxide groups, we have set up a phantom group called CO2.

The isocyanates have also been set up with a number of phantom groups, including urethane (reaction of isocyanate with hydroxyl), urea (reaction of isocyanate with amine), allophanate (reaction of urethane with isocyanate) and biuret (reaction of urea with isocyanate). This allows us to monitor the number of allophanate and biuret groups that are generated.

Reaction rates have been taken from the ICI Polyurethanes Handbook. The reaction scheme takes advantages of the 'generic groups' capability of **DryAdd** whereby, for example, all

primary OH groups have the same reactivity. The reaction of water with isocyanate, generating an amine group, shows a value of -44 in the Loss/Gain column of the reaction scheme. Carbon dioxide, generated during this reaction, has a molecular weight of -44 , so its evolution must be accounted for by the loss of molecular weight of 44 for each group generated.

If you run the reaction, you will see that the number of secondary cycles rises rapidly. Plotting the largest group by weight, and the number of secondary cycles, against the % conversion shows that the steepest rise in the size of the largest group, and also the rapid rise in the number of secondary cycles (which corresponds to gelation) occurs at about 60% conversion.

3. Rigifoam.set

This is a rigid polyurethane foam system. Two polyols, one with functionality of 3 and one with functionality of 5, are mixed with di- and tri-functional isocyanate. The di- and tri-functional isocyanate have been set up with amounts to model an MDI with average functionality of 2.7. There is an excess of isocyanate, because the MDI can react with itself once the temperature rises. (The formation of the urethane linkage is an exothermic reaction.) The isocyanates have been set up with phantom groups, called 't'.

Initially, the reaction of isocyanates to give trimer groups (note that the 't' group is an intermediate) is set to zero, since the reaction does not occur at low temperatures. Once the reaction has run for a while, you can pause the simulation and set non-zero rates for these.

You can see what happens with and without this second set of reactions - with the isocyanurate reactions switched on, you will get more secondary cycles (i.e. harder material) and all the NCO will be used. When they are not switched on, you will have an excess of NCO at the end of the simulation.

4. Epoxprim.set

Epoxides can react in a number of ways with various materials. One possibility is the reaction of a primary amine with the epoxide group. The materials here are standard ones in epoxy chemistry. The system consists mainly of DDS mixed with DGEBA. Some hydroxylated DGEBA-derivative is also present in a small amount.

Again, the **Reactions** screen shows that we have used the 'generic groups' capability in order to simplify the reaction scheme. Relative reaction rates have been taken from the literature. The main reaction is that between the primary amine and the epoxide ring. This gives two new product sites (hence the bond type BF2P, bond formation with 2 product sites) – a secondary amine, and a hydroxyl. Both of these have been set up as phantom groups, with the amine group on the DDS and the hydroxyl group on the DGEBA materials.

In subsequent reactions, the epoxide group can react with the secondary amine, with the hydroxyl group on the DGEBA-derivative, or with the hydroxyl groups produced during the initial ring-opening reaction. This last reaction generally only takes place at elevated temperatures, and is one of the reasons that cure in epoxy systems can sometimes be classed as self-catalytic.

By varying the relative amounts of epoxy and amine, you can see big changes in the gel point. Plots of largest group by number, vs conversion, show this clearly.

5. Epoxtrin.set

Tertiary amines act as catalysts for the epoxide ring-opening. The tertiary amine attacks the ring, leaving an O⁻-like species. This goes on to attack more rings, giving a highly crosslinked system with many ether linkages.

A typical example is the reaction of diethyl amino propylene (DEAP) with the difunctional amine DGEBA. DEAP is set up with one group, called initiator. A reaction is set up, in which initiator attacks the epoxy group. There are two epoxy groups on DGEBA, and we also set up a phantom group **Oxygen ion**, which is formed in the reaction. In subsequent reactions, the **Oxygen ion** group can react with more epoxide groups, forming new Oxygen ions.

The reaction is initiated when the tertiary amine DEAP reacts with an epoxide ring, producing a site which is effectively an oxygen anion. The oxygen anion can then go on to react with subsequent epoxide rings. Each ring-opening produces a new oxygen anion.

If you run the simulation, you will see that you get a very tightly cross-linked system. This is shown not only by the high number of secondary cycles, but also from an examination of the results of a Network Analysis.

The degree of crosslinking and the gel point depend on how much tertiary amine is present at the outset. If there is a lot, gelation is delayed. You might want to vary the amount of the **Materials**, to confirm this.

6. Epox-rad.set

This follows a similar reaction scheme to that for the tertiary amine cure, discussed above. The assumption is made that a percentage of the epoxy (e.g. DGEBA) exists in a free radical form, following reaction with the free radical initiator.

It is assumed that all of the initiator is dissociated at the beginning, and it has converted part of the DGEBA to free radical form. As can be seen from the **Reactions** screen, only one reaction is needed; the radical reacts with an epoxide group to form a new radical.

The system becomes very highly cross-linked, depending on the amount of initiator which is used. See this by looking at the rise in secondary cycles. You can of course examine the network during the cure process with the **Network Analysis**, as well.

7. Epox-mix.set

Any or all of the above reaction schemes, in examples 4 to 6, can be set up simultaneously, to give what is possibly the most interesting of the epoxy examples. For *epox-mix.set*, we have set up a system containing DGEBA which is cured by a tertiary amine initiator DEAP (present at the level of 1%), and which contains the primary amine DDS as well. The reaction of the initiator produces an anion site (which is like an O^- ion) on DGEBA; this can go on to react with further DGEBA to give more anion sites, in a catalytic reaction. Ether links are produced. The primary amine can also react with the epoxide groups, leading to ring opening.

Reactions include:

- anions opening rings to give more anions - VERY fast
- primary amine reacting with epoxide to give secondary amine and OH
- secondary amine reacting with epoxide group to give another OH
- OH group opening an epoxide group - assumed to be relatively slow

Rate information is taken, in part, from published work by Cheng and Chiu.

Using the **Sequence Analysis**, you can search for sequences of ether links (from the tertiary amine initiated reactions) and see in detail the effect of the amine groups.

Summary

We hope that these examples are sufficient to give you an appreciation of **DryAdd's** capabilities. By testing out your ideas on your computer – trying 'what if' experiments using **DryAdd's** virtual reaction pot – you can cut down on your lab time, and make sure that your efforts are focused productively for you and profitably for your business. **DryAdd** also adds to your characterization capabilities, allowing you to find out more about what your experimental results are really telling you – see OxMat's *Polymer Physics Guide* for more details.

We are always pleased to hear about successes – and to find out what you think should be in future versions of **DryAdd** – so please give us any feedback that you wish, on your experiences with this demo. Thanks for your help!