

## DMA 2980 Dynamic Mechanical Analyzer Time-Temperature Superposition

### Basic Time-Temperature Superposition Theory

The linear viscoelastic properties of polymers are both time and temperature dependent. When considering a material for an application, many times we want to know how the viscoelastic properties will change over a long period of time (very low frequencies) such as months or even years. Other times, we want to know the viscoelastic properties under very high frequency (very short time) applications such as high speed impact strength. Often the response times of interest are inconveniently long or outside the measurable limits of analytical instruments.

However, there is an empirical relationship between the time and temperature dependent properties of viscoelastic materials known as the time-temperature superposition principle. Both time and temperature have a similar effect on the linear viscoelastic properties of polymers. At low temperatures, the relaxation processes of a polymer, as measured in both dynamic and transient (creep and stress relaxation) testing, take longer than at higher temperatures. The extent to which these relaxation processes are slowed or accelerated are *sometimes* in proportion to the magnitude of temperature decrease and increase respectively.

If the polymer of interest obeys the time-temperature superposition principle, then the viscoelastic properties measured at different temperatures, but over a fixed period of time (a fixed range of frequencies) have similar shape and can be exactly superimposed by shifting the curves horizontally along the time (frequency) axis. In effect, by changing temperature we are able to rescale time.

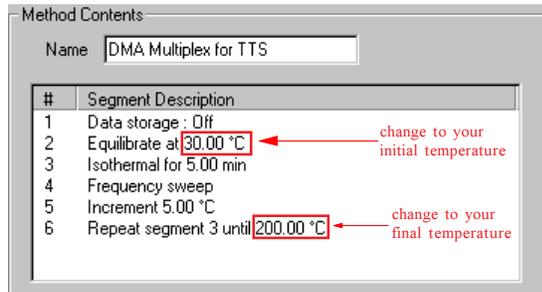
Time-temperature superposition (TTS) allows us to characterize the viscoelastic properties of a material at various temperatures over an experimentally convenient time or frequency range. The data taken at various temperatures can be superimposed to a reference temperature of interest to extend the time range of response. The curve created by superposition is called a “master curve” and represents the time response of the material at the reference temperature.

### **Programming a TTS Experiment on the DMA 2980**

Prior to programming the instrument parameters, we need to stop and think about what we want to accomplish using TTS. The first step is to decide on the reference temperature ( $T_r$ ), or our temperature of interest. In other words, what is the use temperature of the material? If you want to obtain information at higher frequencies or shorter times, you will need to conduct frequency (or stress relaxation or creep) scans at temperatures lower than  $T_r$ . If you want to obtain information at lower frequencies or longer times, you will need to conduct frequency (or stress relaxation or creep) scans at temperatures higher than  $T_r$ . It is a good idea, as a starting point to scan your material at single frequency to get an idea of modulus-temperature and transition behavior. This will let you know how wide of a temperature range you can cover on the DMA 2980 relative to your reference temperature.

## Creating The Method

Thermal Solutions™ for Windows NT® comes complete with preprogrammed method files. Among them is a file called ***DMATTS.mth***. The easiest way to begin programming a TTS method is to open this file and modify it to suit your needs.



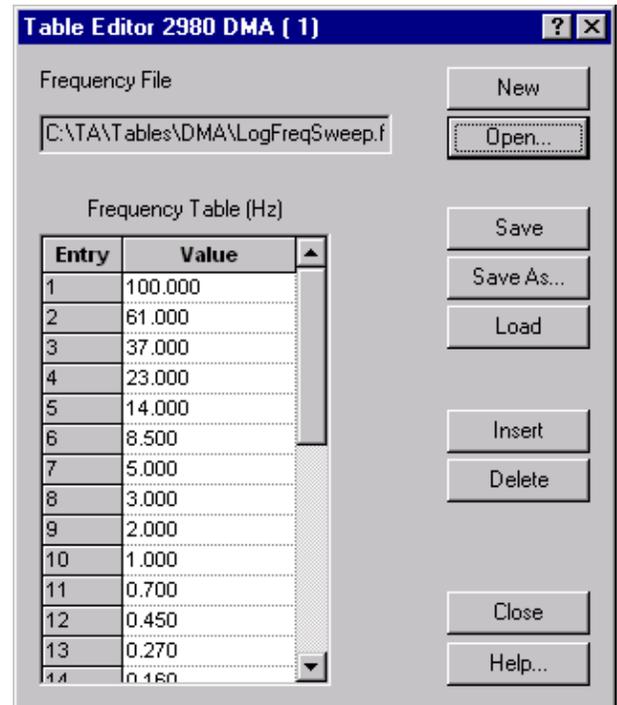
The figure to the left shows the required segments for conducting TTS. **Do NOT** change any of the steps in the method. Only change the initial and final temperatures in the method to the values you require for your analysis. The only other value you may need to change is the increment. This is because the total number of frequency scans allowed so that TTS data can be shifted is 32. You should satisfy the following equation to make sure you do not have any problems:

$$(T_f - T_i)/I_t \leq 32$$

where  $T_f$  = final temperature,  $T_i$  (°C) = initial temperature, (°C) and  $I_t$  = Increment size

## Creating The Frequency Table

Thermal Solutions for Windows NT comes complete with preprogrammed frequency files. TTS is best run with frequency scans that will result with data points evenly spaced on a logarithmic scale. This is because linear viscoelastic information is interpreted using log-log scales. It is therefore recommended that, as a starting point, you load directly a preprogrammed frequency file named ***LogFrqSweep.frq***. This file ranges from 0.1 Hz to 100 Hz. There is another file called ***log4decades.frq*** that covers a frequency range of 0.01 to 100 Hz. If you prefer to program a series of frequencies on your own, you may do so. The DMA 2980 will allow for a maximum of 28 incremental frequencies to be programmed. You should keep in mind that the lower frequencies will require longer times and they will dominate the time required to run a test. It is recommended that when programming a range of frequencies, start with the highest frequency and end with the lowest.



## Programming Instrument Parameters

The final step in programming a test is to set up the instrument parameters. The instrument parameters menu is shown below. For TTS experiments set the data sampling interval to 2 sec/pt.

When setting the amplitude, remember that TTS relies on linear viscoelastic information. The data generated therefore needs to be within the linear viscoelastic region. It is up to you to determine an amplitude that is in the linear region. A good rule of thumb is that polymer solids are linear up to 0.1% strain. You can refer to *Chapter 6 of the DMA 2980 Dynamic Mechanical Analyzer Operators Manual* to calculate the amplitude that translates to 0.1% strain. Remember 0.1% strain is 0.001 strain units when you do your calculations. Other instrument parameters, such as AutoStrain and static force, should be set using guidelines outlined for the clamp of choice.

The screenshot shows a dialog box titled "Instrument Parameters for 2980 DMA [ 1 ]". It contains the following settings:

- Data Sampling Interval: 1.0 sec/pt
- Amplitude: 10.0  $\mu\text{m}$
- Auto-strain: 125 %
- Static Force: 0.010 N
- Method Start Conditions:
  - Auto Zero Displacement:  No,  Yes
- Auto End on Modulus:
  - Below: 0.000 MPa
  - Above: 0.000 MPa
- Method End Conditions:
  - Return to Temp Range: 25.00 to 25.00  $^{\circ}\text{C}$
  - Furnace:  Open,  Closed
  - Clamp:  Up,  Float,  Lock
  - GCA Autofill

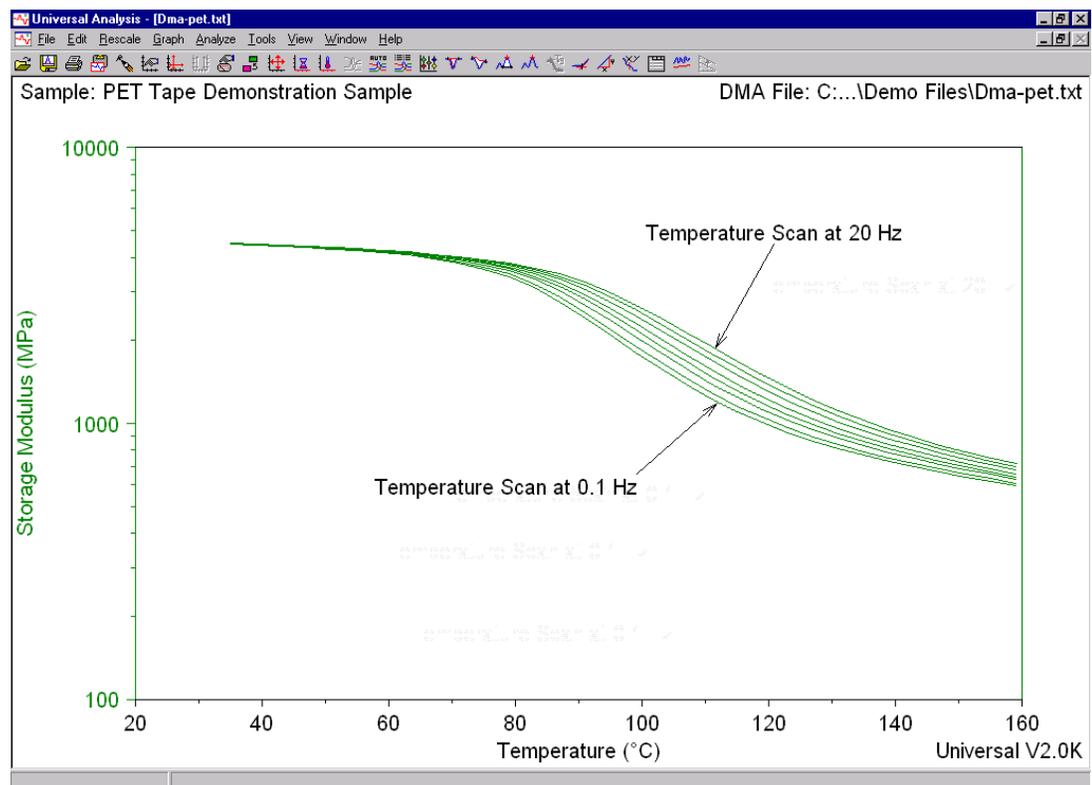
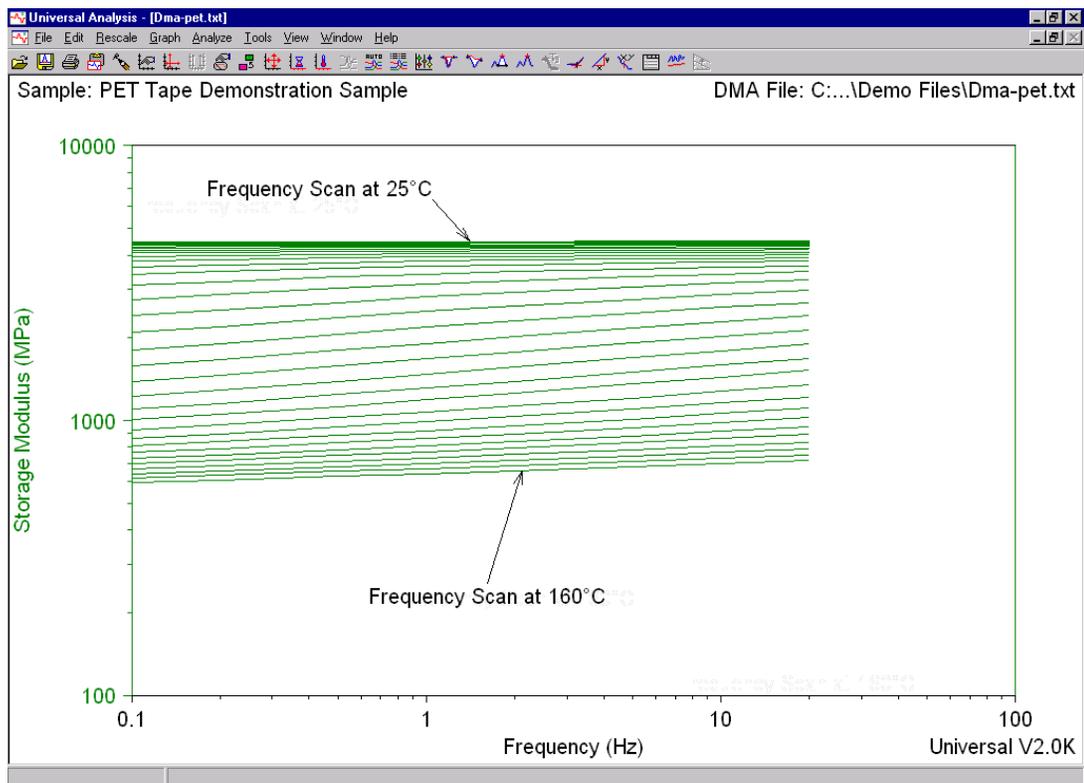
Buttons at the bottom: OK, Cancel, Help.

## Viewing and Shifting Data

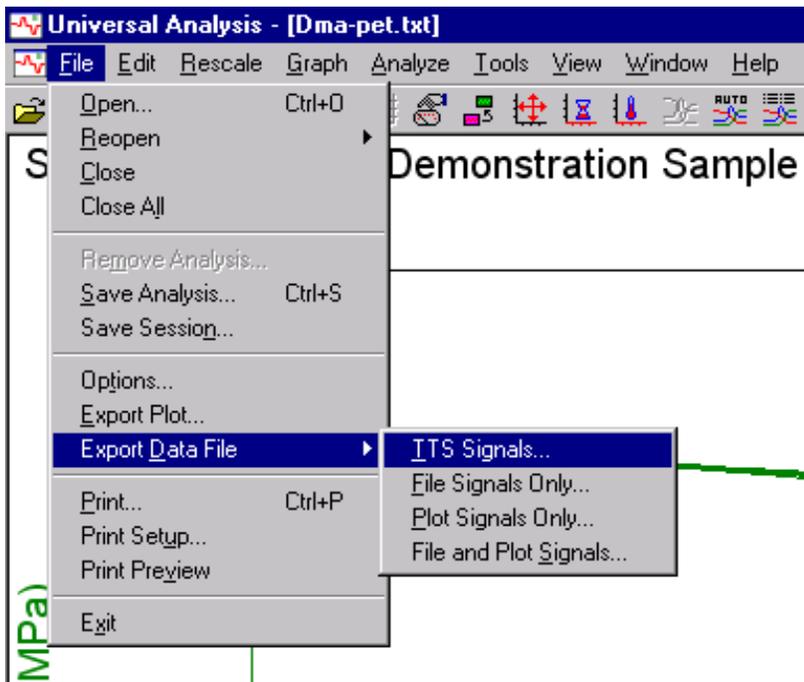
The following will cover viewing multiplexed data generated on the DMA 2980 in *Universal Analysis* for Windows NT and shifting the data using the *TTS Data Package*. The example that follows uses a demonstration file that comes with *Universal Analysis*. It is called *Dma-pet.001*. If you would like to practice shifting data along with this tutorial, open this file in *Universal Analysis*.

## Viewing data in Universal Analysis NT

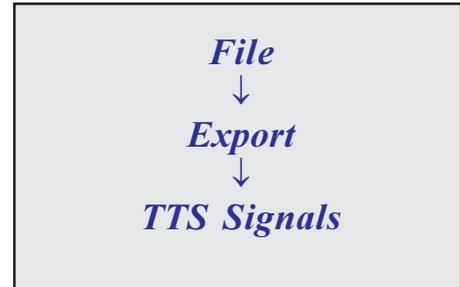
The raw DMA 2980 data are typically viewed as frequency scans at different temperatures or as temperature scans at different frequencies. Examples of both scenarios are shown below.



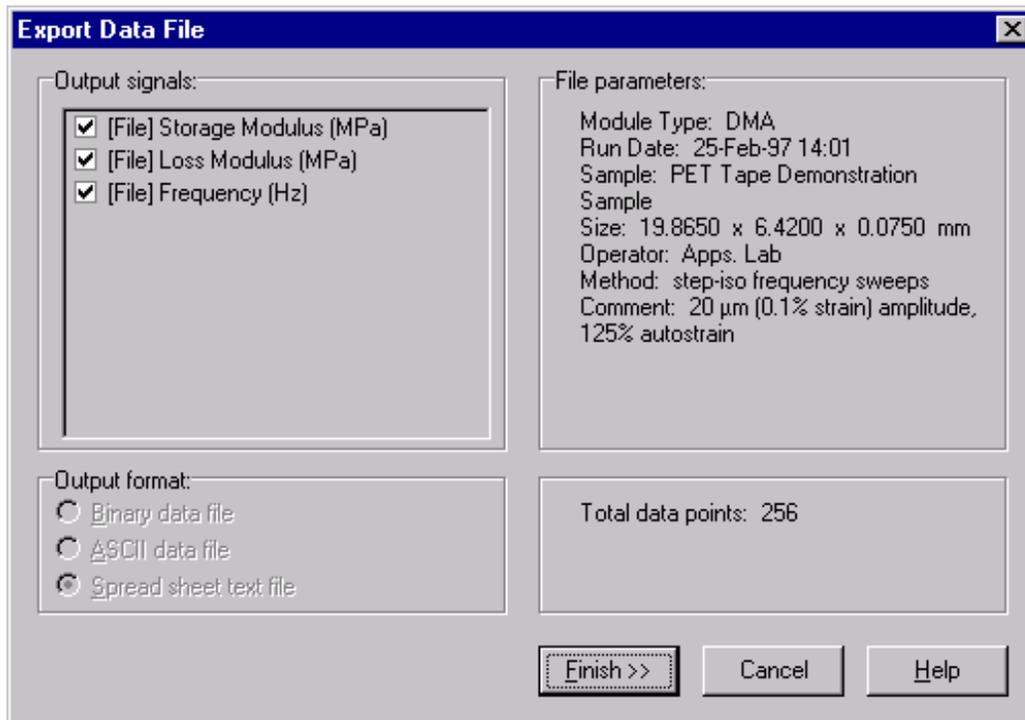
## Converting DMA 2980 Data File to TTS Data Format



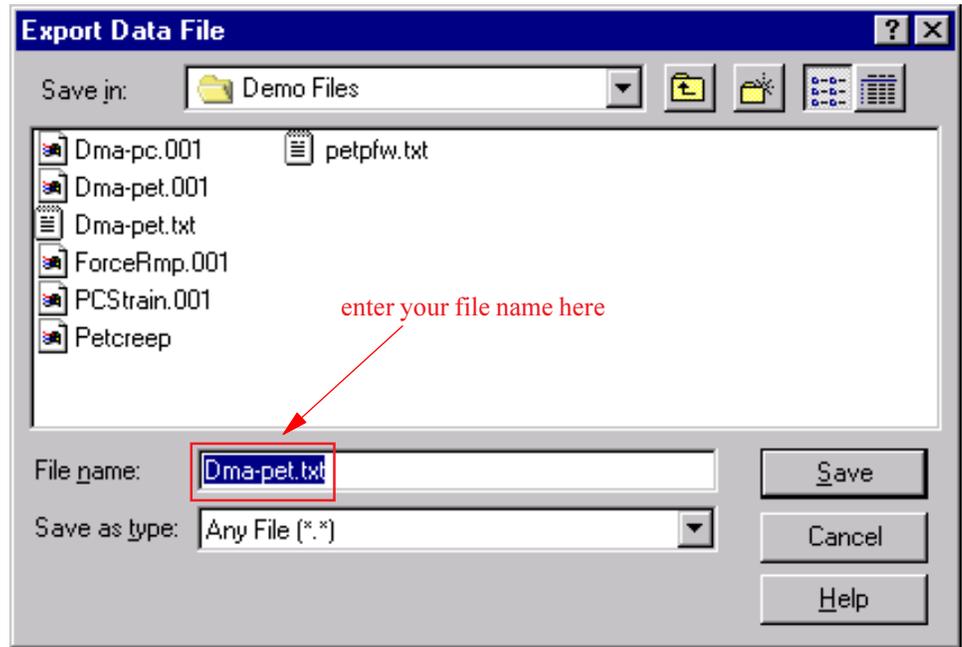
Once the data are plotted in *Universal Analysis*, the file needs to be converted into a new text format prior to shifting in the *TTS Data Analysis* software. To Convert a file to the text format required for shifting the DMA 2980 data, go to



This will bring up the “Export Data File” window shown below. It is recommended at this point that you review the information in this window and press the **Finish** button without changing anything.

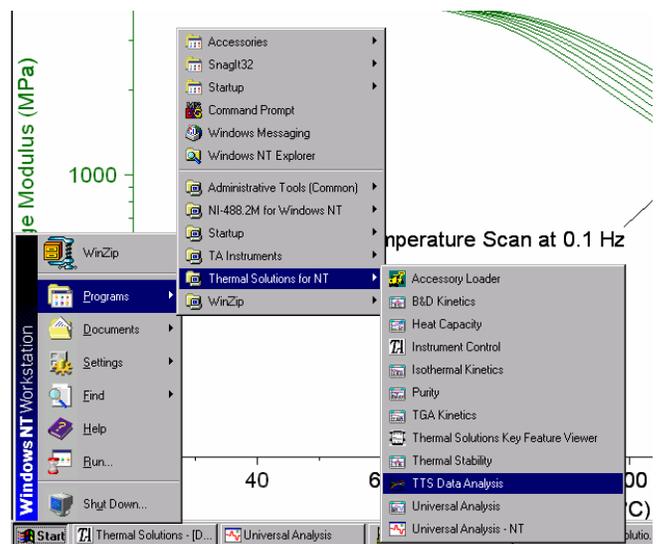


After pressing the *Finish* button, the program will automatically assign a “.txt” extension to your file. If you would like to change the file name, enter the new name in the appropriate field. If you want to keep the same file name with the new extension just press the *Save* button. You are now ready to shift the data in the *TTS Data Analysis* package.

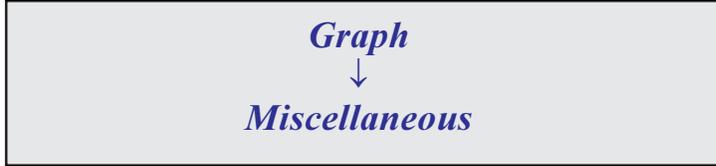


### Shifting The TTS Data

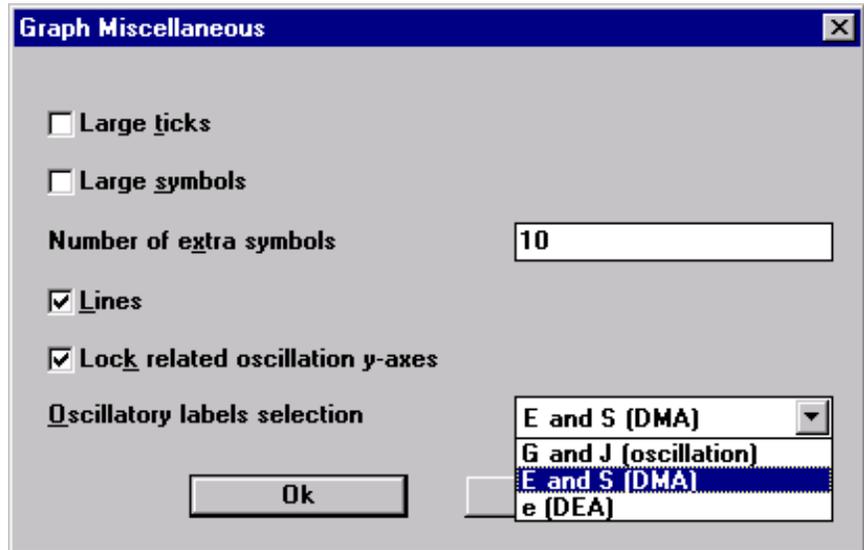
Once you have converted the file to a “.txt” format you will need to start the TTS Data Analysis package. To launch the TTS Data Package go to



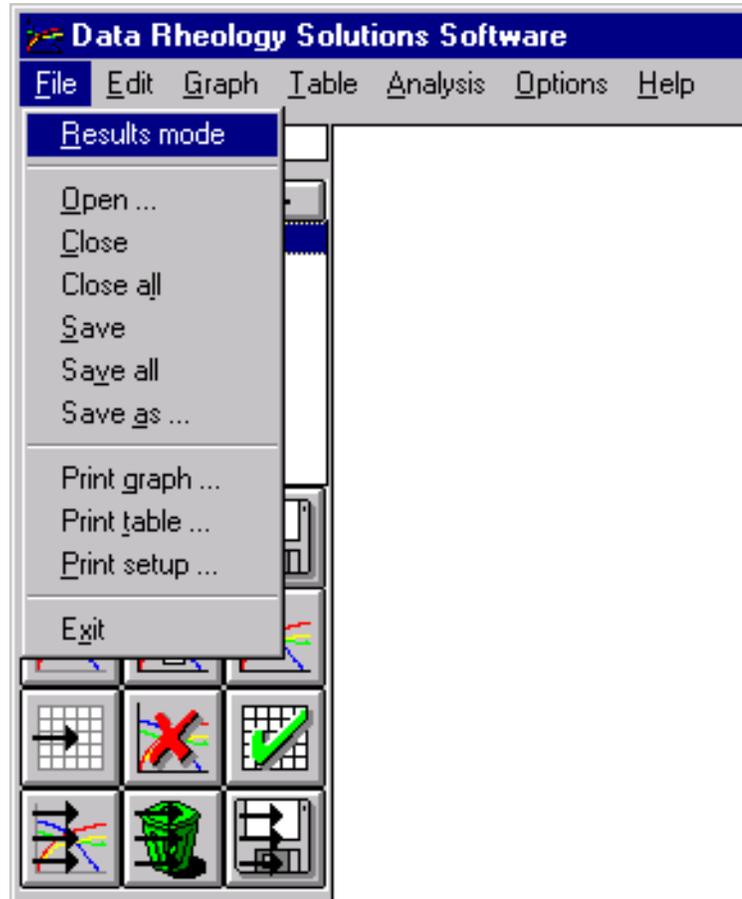
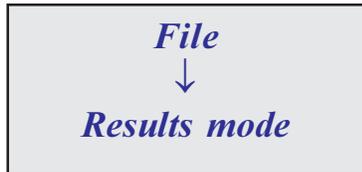
If data on the DMA 2980 are generated using tension, compression, or bending clamps, then the moduli will be denoted by the letter E. If the data are generated using the shear sandwich clamp, then the moduli are denoted by the letter G. The TTS Data Analysis software must be set up for the correct type of modulus you want to shift. The modulus type is set up by going to



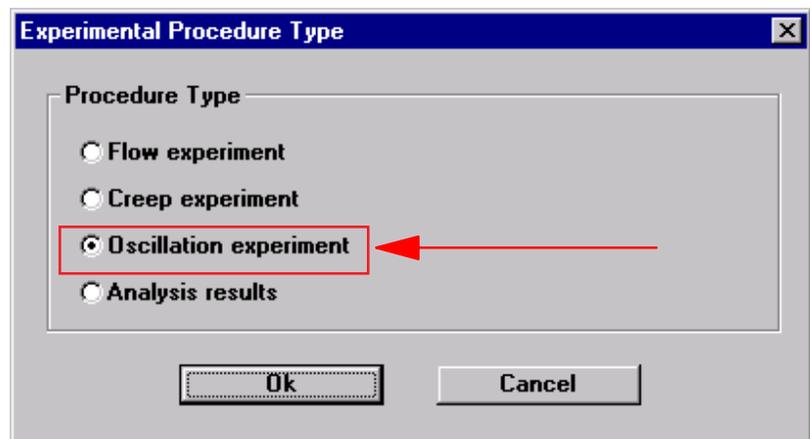
The following menu will be displayed upon this selection. Select the appropriate modulus from the *Oscillatory labels selection* and click on the **OK** button.



Once you have selected the correct labels, you will need to ensure the *TTS Analysis Software* is set to the correct results mode. *The TTS Analysis Software* is also used for analysis of data generated using TA Instruments AR 1000 and CSL<sup>2</sup> rheometers which use different analysis modes for curve fitting of rheological data. To set the results mode go to



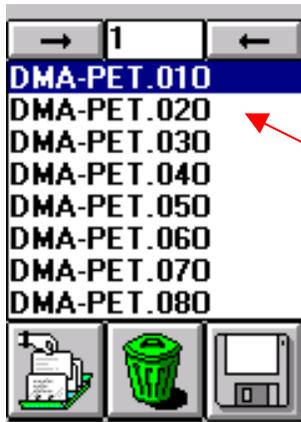
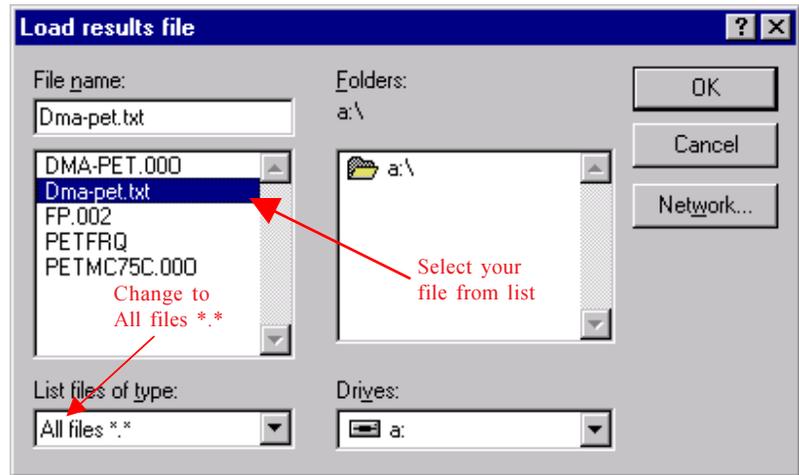
After selecting the results mode, you will be prompted to select the correct procedure type. Select *Oscillation experiment* from the list given.



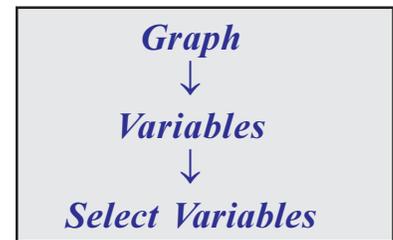
Once you have selected the correct labels, open the **“\*.txt”** file previously created in *Universal Analysis NT*. Go to



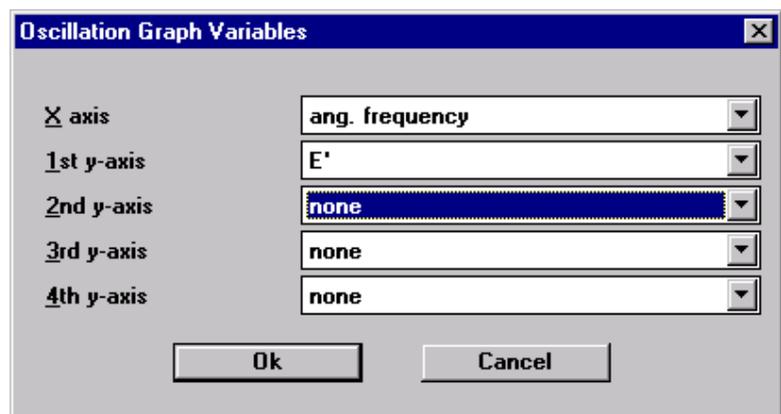
Change the file type to **“All files \*.\*”** and select your file from the list. Once selected click the **OK** button.

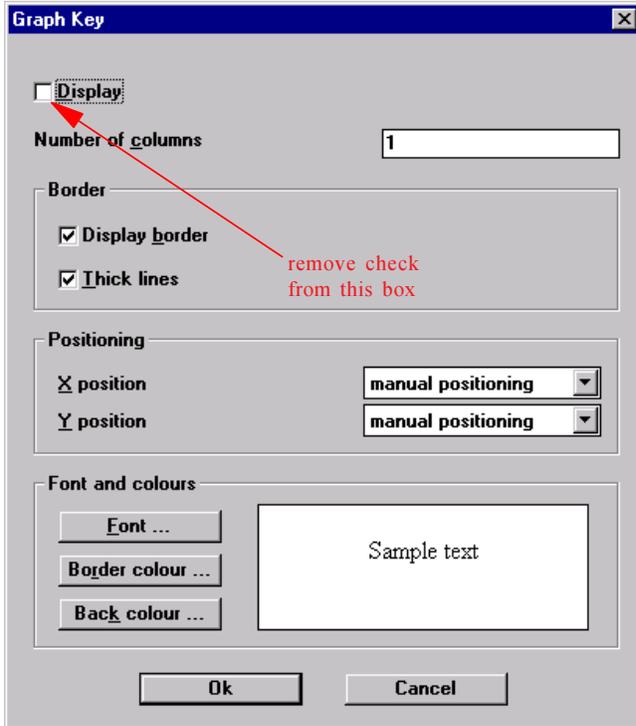


The TTS Analysis software will break the experiment up into individual frequency scans at the different temperatures scanned. You will see a list of files loaded in the upper left hand corner of the screen. Next we will set up the variables we want on the plot. Go to

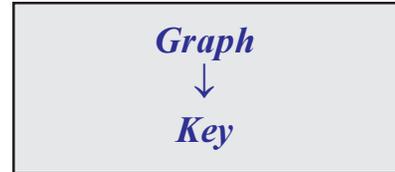


The software will now prompt you to select an x-axis variable and up to four y-axis variables. The x-axis variable **must** be set to angular frequency. A TTS plot can easily become a very busy plot. It is typically easier to plot only one variable until the shift is completed. Once the shift is completed the other variables can easily be loaded by following the same procedure just outlined.



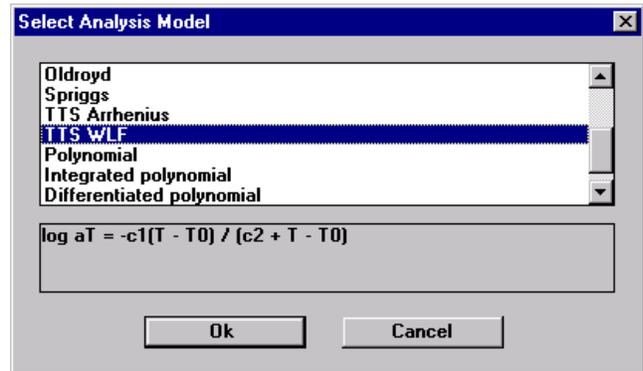
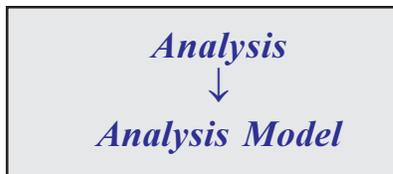


The next step is recommended but not a required step for conducting the analysis. It is highly recommended that you conduct the following step if you are not familiar with the TTS Analysis software. This step involves turning off the graph key. Go to

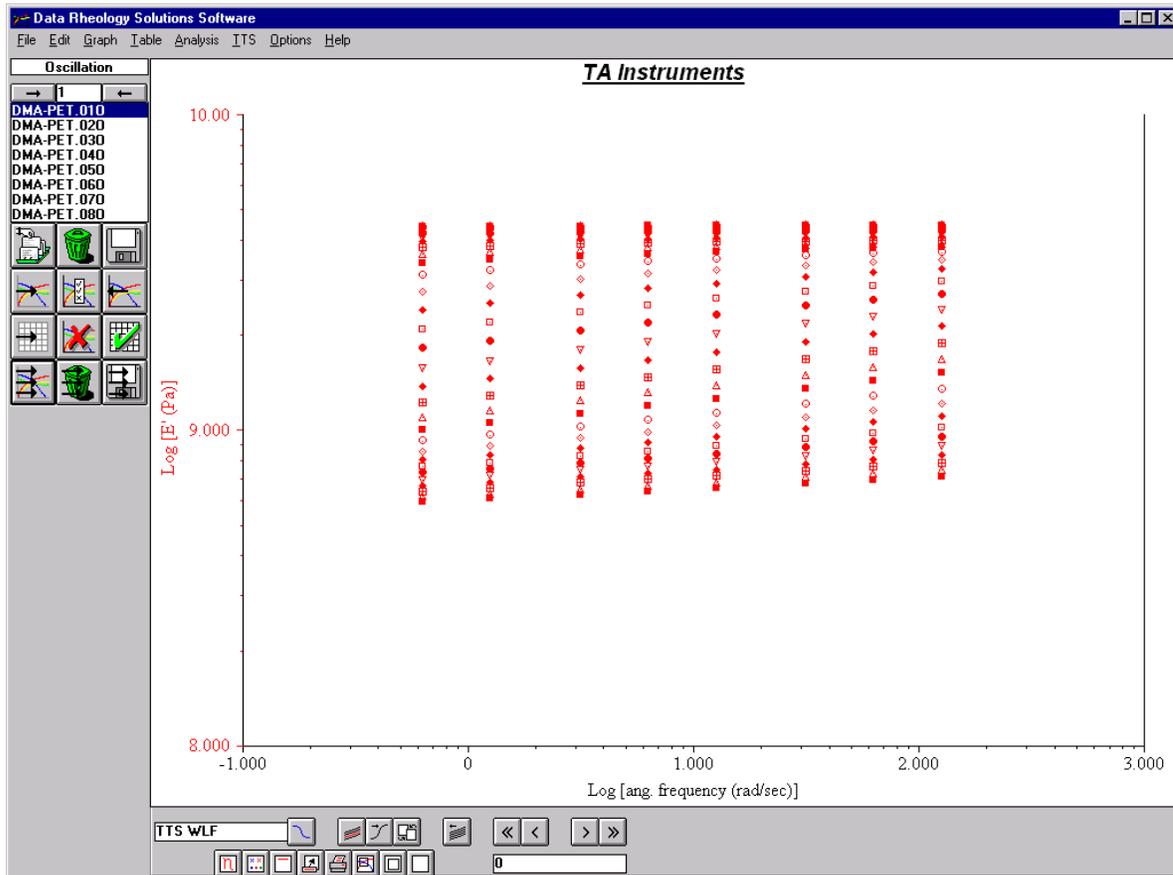


This step will remove the key from the plot. Typically the key in a TTS plot can overtake the plot and hide the data. The key can also be confusing for those not familiar with the TTS analysis package.

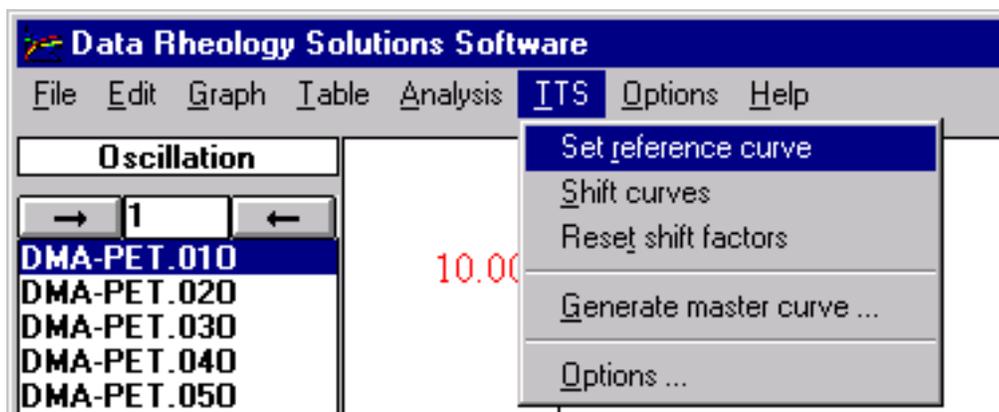
The next step is to select the analysis model. There are two TTS analysis models, they are TTS Arrhenius and TTS Williams-Landel-Ferry. If you are not sure which of the two analysis models to use, you should consult a book which covers the topic. To select the model go to



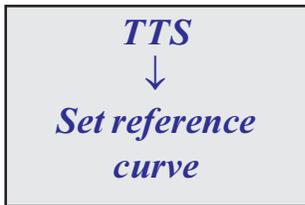
Once you have selected the model, click the **OK** button. We are now ready to plot the data. This is done simply by pressing the **Plot All Curves** icon located below the file list.



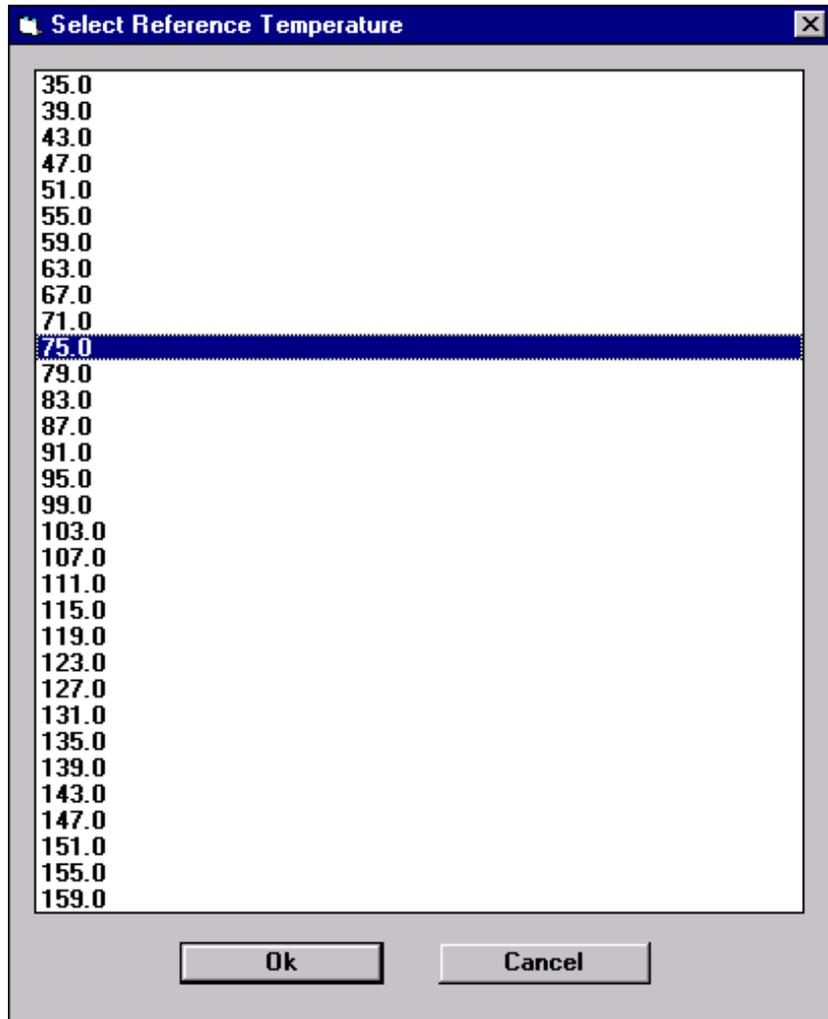
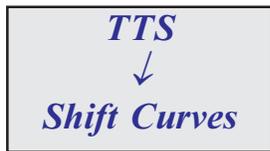
The next two steps will all involve the *TTS* menu shown below.



Before actually shifting the data we need to set the reference curve. By selecting a reference curve (frequency scan) at our temperature of interest. The curve we select will remain unchanged and all other curves will be shifted relative to the reference curve. Higher temperature frequency scans will shift to the left of the reference curve (lower frequencies or longer times) and lower temperature data will shift to the right of the reference curve (higher frequencies or shorter times). To select the reference curve simply go to

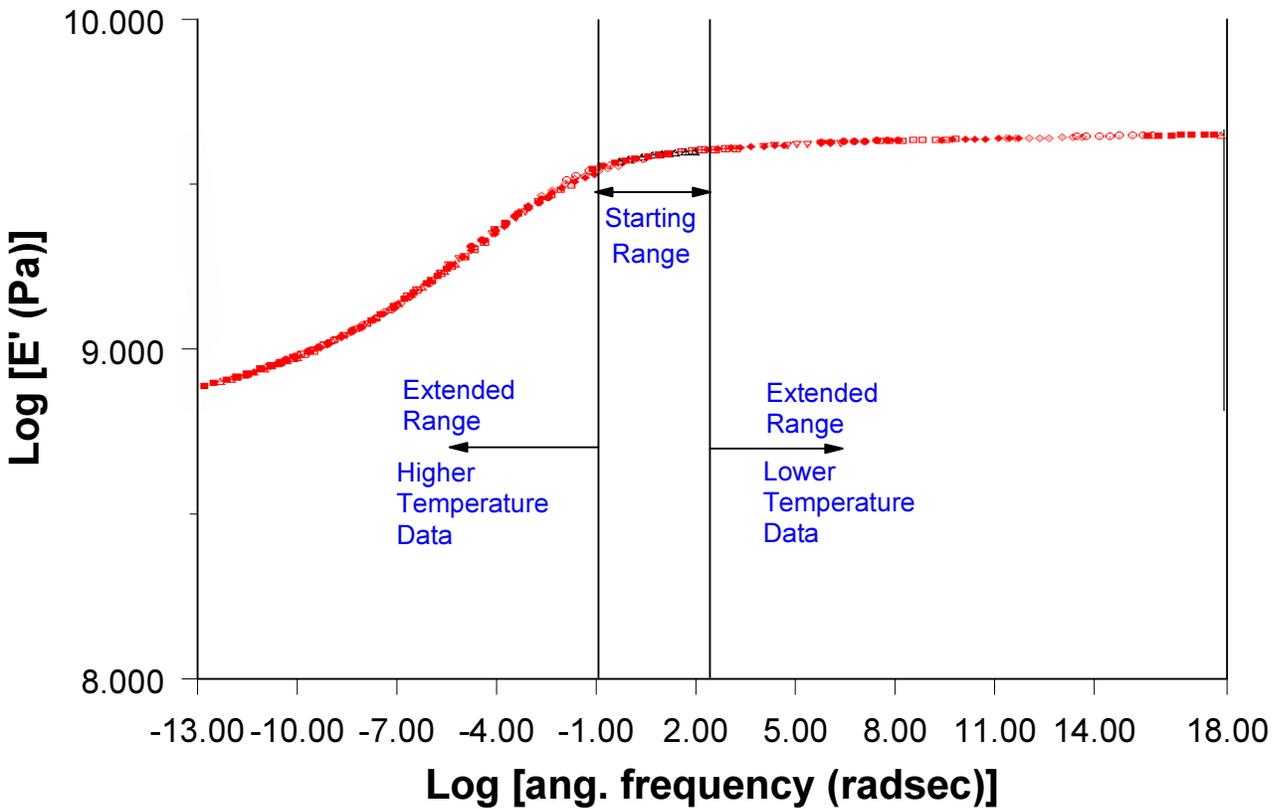


The menu to the right titled "Select Reference Temperature" will be displayed showing a list of temperatures. You simply need to pick the temperature of interest from the list and click the OK button. The example on the right shows 75°C selected as the reference temperature. This means the shift that follows will expand the frequency range (time scale) of the data at this temperature. Now that the reference curve is selected we can shift the curves. To shift the curves go to



The software will now physically move the curves relative to the reference curve. The following figure shows the results of shifting the PET data to a reference temperature of 75°C.

**TA Instruments: Polyethylene Terephthalate Shifted curves at Reference Temp of 75°C**

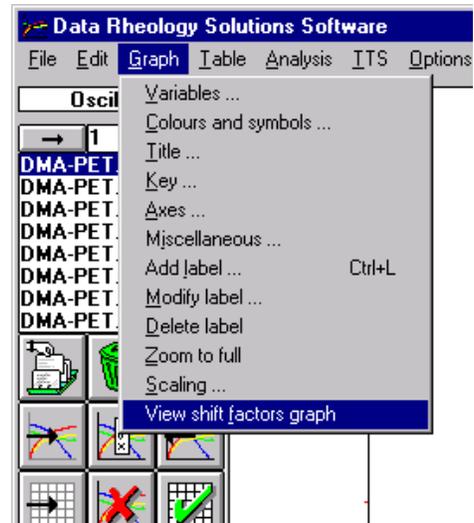
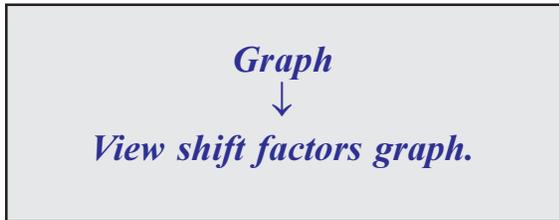


If you look back on the data we plotted before the shift you will see the data covered a frequency range of -1 to 3. The frequency range of the shifted data covers a log frequency range of -13 to 18. We have extended the log (Hz) frequency range from 4 decades to 21 decades. This clearly demonstrates the power of time-temperature superposition for extending the time (frequency) range of your experiment.

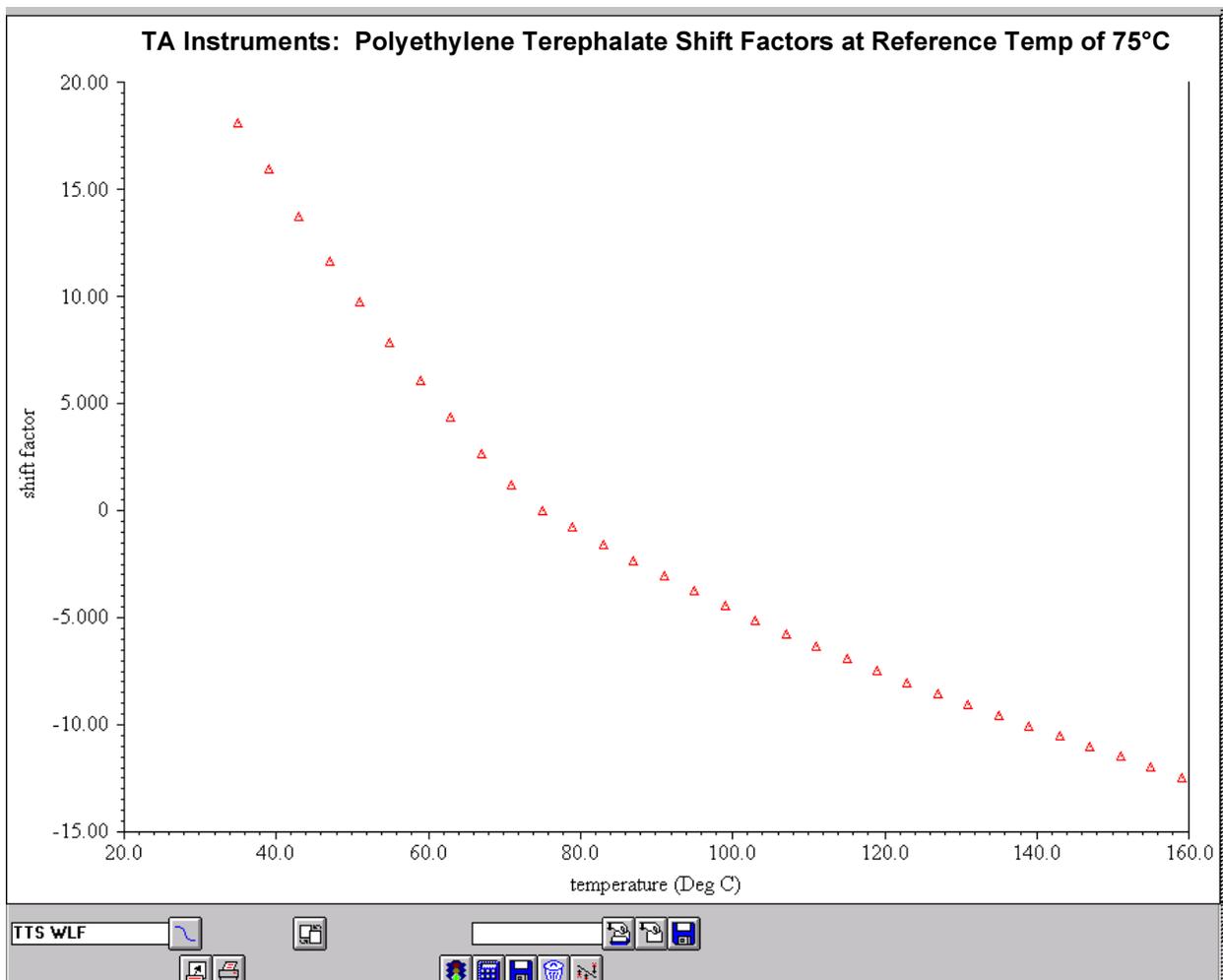
The next step is to generate the final master curve file. The plot shown above represents all the individual plots with the shift factors applied. What we haven't created yet is a file which contains the master curve information in a useable format. Prior to creating the final master curve file it is a good idea to assess how well the data shifted by viewing the shift factors and how well the data fit the model you are using.

The following steps will cover analyzing the TTS data using plots of shift factors. If you are not comfortable with the concept of shift factors it is recommended you consult a reference which covers the topic. The end of this tutorial lists several references which cover time-temperature superposition in detail.

Viewing the shift factors and fitting the data to the selected model are steps we take prior to generating the final master curve file. Remember TTS is an empirical relationship and we must ascertain for ourselves how well the data fit the model before we can make any predictions about material performance from the model. To view the shift factors go to



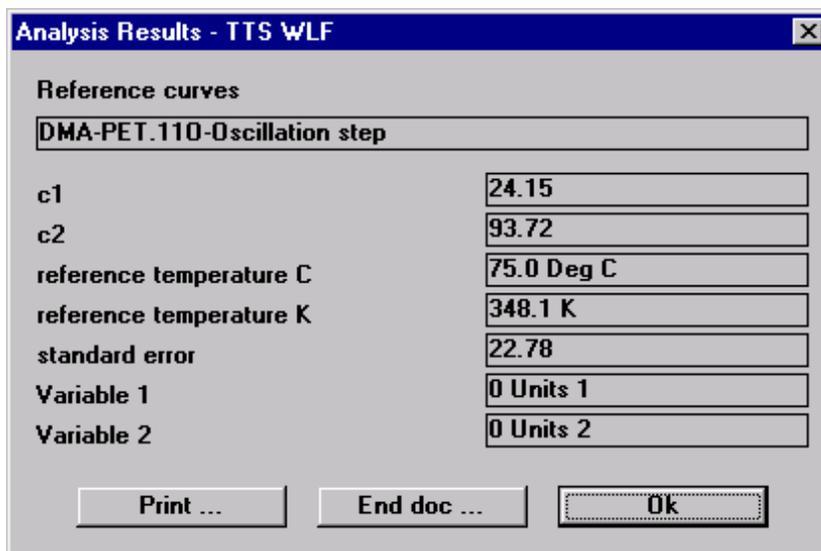
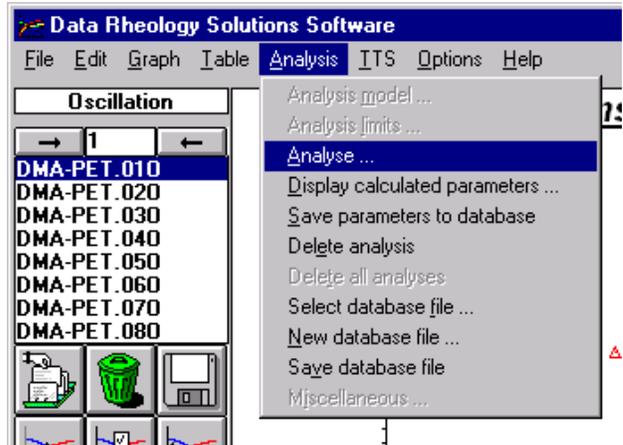
A plot of the shift factors versus temperature will replace the plot of the shifted data. The shift factors plot for the PET data at a reference temperature of 75°C is shown below.



The data can now be fitted to the model. The fit we are going to use for this example is the WLF fit. To fit the data to the selected model go to



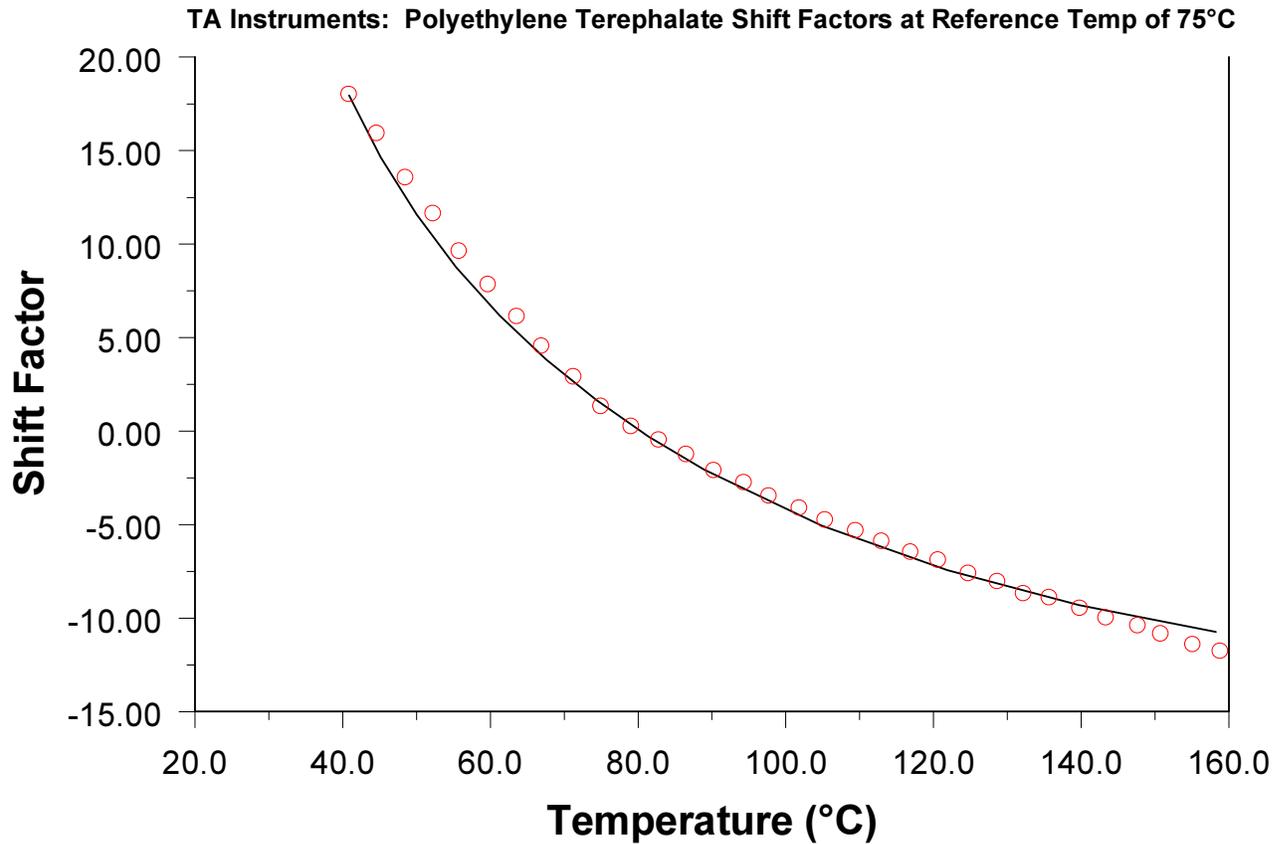
The software will fit the data and display the calculated parameters as shown below.



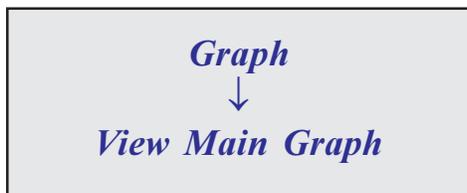
The fit reports back information specific to the WLF or Arrhenius curve fits. The WLF fit, which was chosen for this example, will report two constants C1 and C2. The Arrhenius fit will report an activation energy. Consult a reference for more details on these parameters. The parameter that we want to focus in on for the validity of the fit is the standard error. The standard error measures how well the data fit the model. It is up to the users discretion to determine whether or not the standard error is too large to be considered acceptable. A discussion of the standard error of a curve fit can be found in any basic text on statistics which covers regression. Since the WLF and Arrhenius are different

models, data that superimpose very nicely may have a large standard error for one model and a small standard error for the other. You can try both models to see which model best fits your data.

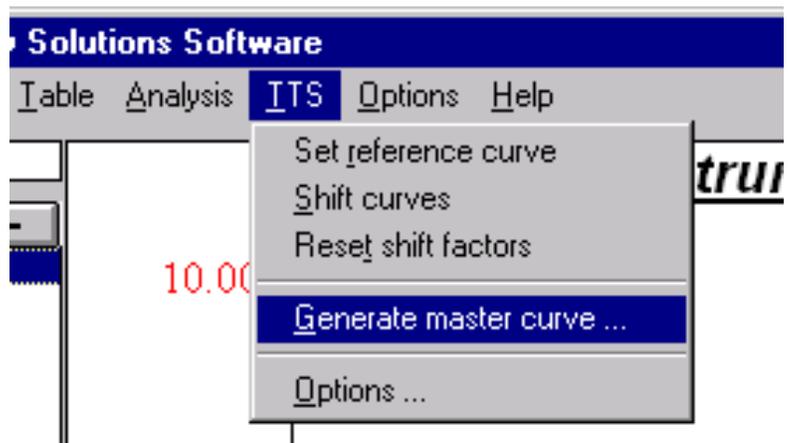
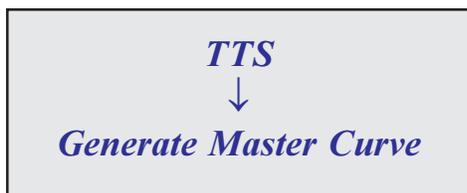
After viewing the parameters, hit the **OK** button. You will now see the shift factors versus temperature plot displayed with the fit on the plot. This plot will show you visually how well the data fit the model. The WLF fit for the PET example covered here is shown below.



If you are satisfied with the TTS analysis after fitting the data to the chosen model, then you can finish TTS by creating a master curve file. To create the master curve file go to



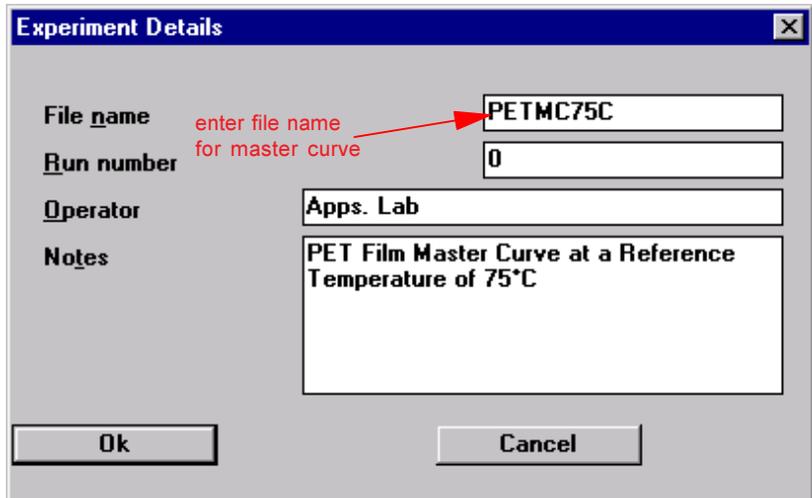
Then go to



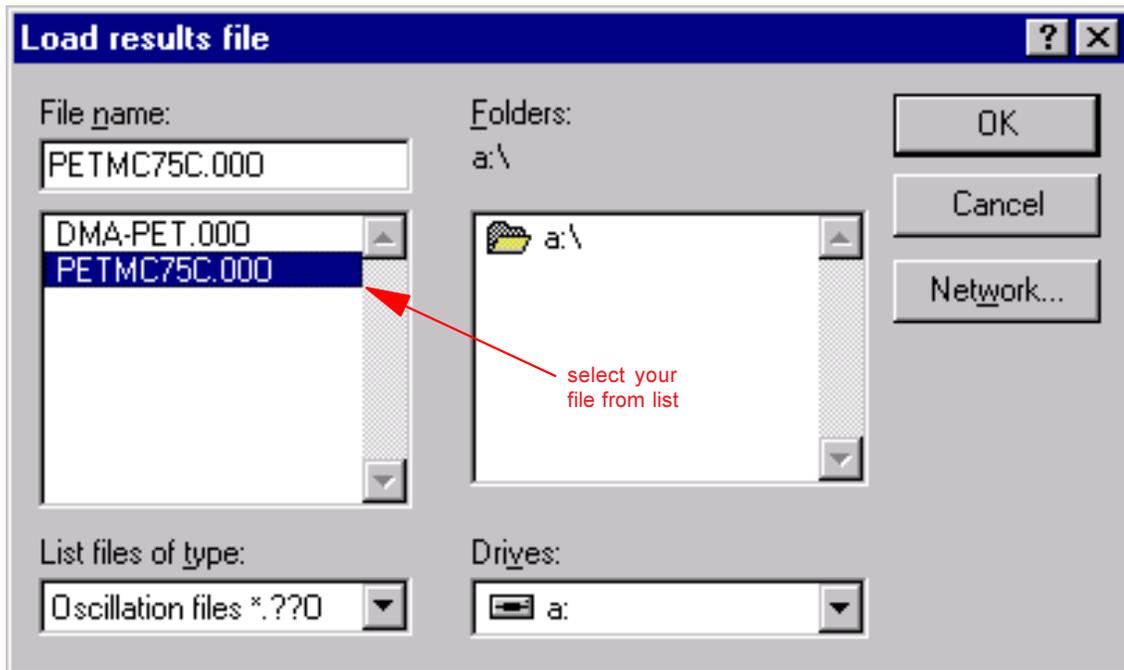
The purpose of generating a master curve file is to put the data into a useable format. This is the form you want to have

the data in to make predictions based on the shifted data. When you select generate master curve from the TTS menu you will be prompted to enter a file name for the master curve. Enter the file name and any desired notes and click on the OK button.

To view the newly created master curve, you need to open the file just created. To open the master curve go to

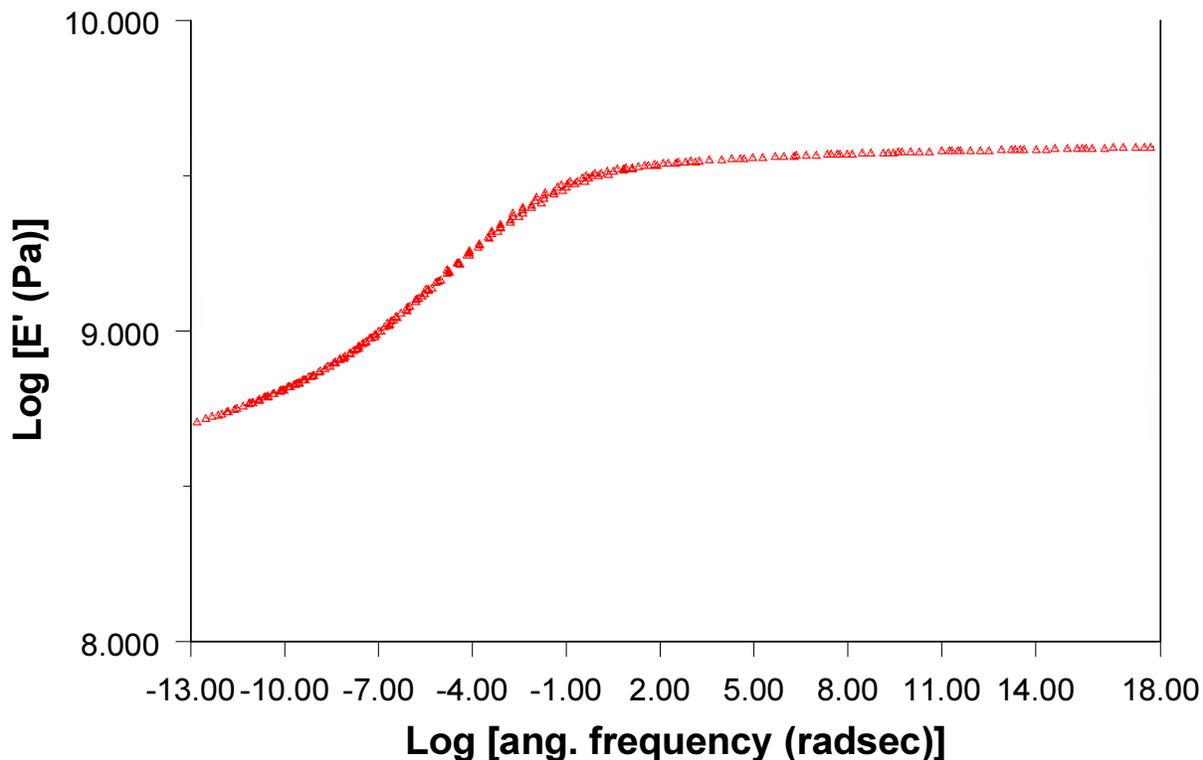


The file will be stored as an oscillation file. If your file does not show in the list, check to see if your list of file types is set to "*oscillation \*.??O*". Simply select your file from the list and click the **OK** button.



The resulting master curve of for the PET sample is shown below.

**TA Instruments: Polyethylene Terephthalate Shifted curves at Reference Temp of 75°C**



*Suggested References for TTS*

Ferry, J.D., Viscoelastic Properties of Polymers, John Wiley & Sons, Inc. New York, 1980.  
ISBN 0-471-04894-1

McCrum, N.G., Read, B.E., and Williams, G., Anelastic and Dielectric Effects in Polymeric Solids, Dover Publications, Inc., New York, 1991. ISBN 0-486-66752-9 (Copyright 1967 by John Wiley & Sons Ltd. and reprinted in 1991 by Dover)

Ward, I.M. and Hadley, D.W., An Introduction to the Mechanical Properties of Solid Polymers, John Wiley & Sons Ltd., West Sussex, England, 1993. ISBN 0-47193887-4

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