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Thermal analysis of polymers using virtual instruments A tool for teaching and training

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Abstract

It's expensive in terms of time and equipment to give students the necessary exposure to a wide variety of polymer behaviors in thermal analysis. One type of 'Virtual Instrument' (VI) has been developed that demonstrates the effects of changing input variables in classic polymer equations. Another type of VI more closely resembles real instruments such as DSC/DTA, DMTA and other thermal methods. These VIs consist of software developed using Labview® from National Instruments and currently running on a PowerMac; the VIs are readily adapted to run on other platforms. These VIs are not intended to replace hands-on experiments with real instruments, rather they are designed to provide the student with exposure to a range of typical thermal responses experienced with changes in various parameters. In the DSC/DTA unit such parameters include copolymer composition, randomness, heating and cooling rate. The DMTA unit incorporates the effects of variables such as percentage crystallinity, cross-linking, molecular weight and compatibility. These VIs and others are described and their development and assumptions are discussed. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

It is generally agreed that one of the best ways to learn is to do it yourself. However, that approach can also be very inefficient given the time scale of some experiments or the availability and cost of modern instruments. There is also potential danger when you put instruments into untrained hands. The standard academic response is 'the lecture' but that generally removes listeners from active discovery. One alternative is to provide 'virtual' instruments (VIs). The term VI is used here to describe software that is written to accept input from on-screen controls (knobs, sliders, etc.), whose values are changed using the computer mouse. These inputs are then used in a set of equations that define instrument or equipment response. Results are output to a screen in an appropriate form (graph, table, indicator, warning signal, etc.). Like any software, its utility is only as good as the equations used to describe the situation (GIGO).

Many different VIs corresponding to different instruments can be contained in a single computer, with a huge saving in cost and a corresponding increase in availability. VIs are not intended to replace hands-on experiments in the lab but rather to expand and complement a typical lecture or lab. However, the ability of VIs to decrease time required to complete a project in a real lab, to minimize required assistance in the real lab, and to increase the level of satisfaction that students have with the real lab have been documented [1]. The VIs presented here also act to summarize a great deal of fundamental polymer

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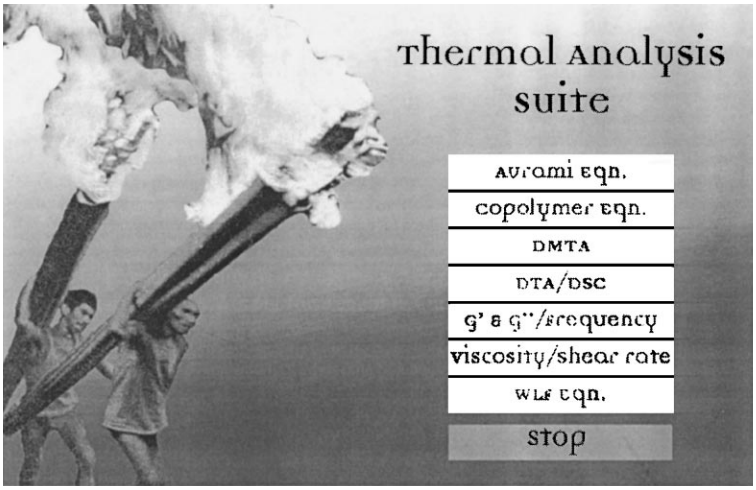


Fig. 1. Front panel for the Thermal Analysis Suite of Virtual Instruments.

information. The front selection panel for a suite of thermal based VIs is shown above (Fig. 1), these VIs enable users to discover for themselves basic thermally oriented structure–property–process relationships in polymers.

2. VI development

The various VIs contained in the thermal analysis suite (TAS) were largely developed to fill the needs of a course in solid state properties of polymers taught by the author for a number of years. A significant portion of the course is dedicated to crystallization, melting, glass temperature and other transitions; hence the extensive use of thermal techniques. Other VIs have been and continue to be developed to help support basic material contained in other courses in the polymer program. VIs in the TAS can be divided into two types (Table 1). One consists largely of a demonstration of the effects of changing input variables in classic polymer equations. The other type of VI more closely resembles an instrument, summarizing the effects of instrument and material variables on instrument output, which is usually some form of graph. A single example of both types of VI will be reviewed in detail to show the logic behind their development and the range of input and output responses that are handled. A general overview of the important features of the other VIs will also be included in the following sections. In all cases Labview 5.1® from National Instruments was the computer language system used to construct the VIs.

Table 1
Listing of VI types in TAS

Equation type VIs	Instrument type VIs
Avrami	DMTA
Copolymer	DSC/DTA
WLF	G' and G'' versus frequency
	Viscosity versus shear rate

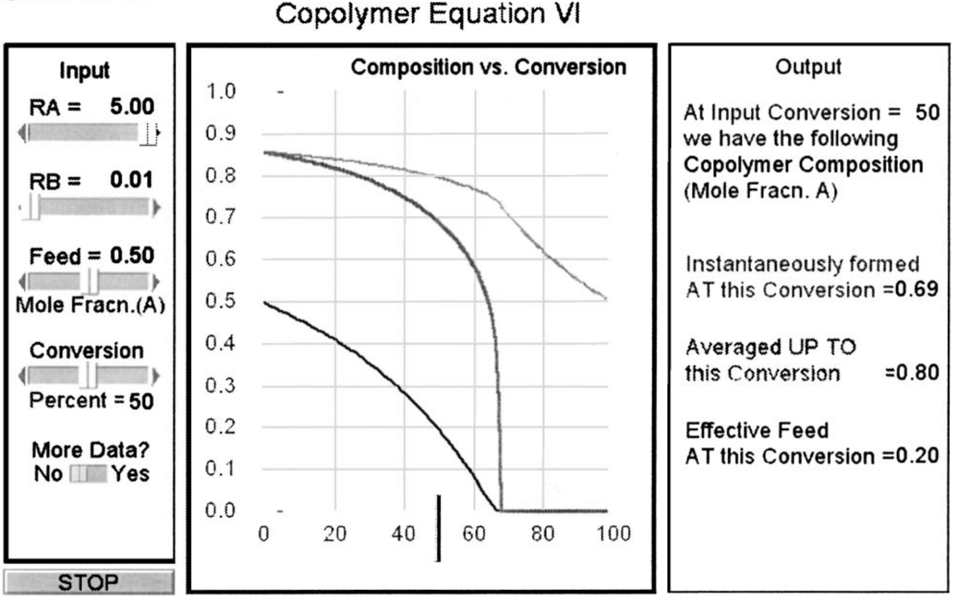
3. Equation VIs

The copolymer equation describes the composition of a copolymer formed from a particular ratio of monomers having different relative reactivities and is written in several ways, a common form being:

$$F_\mathrm{a} = \frac{r_\mathrm{a} f_\mathrm{a}^2 + f_\mathrm{a} f_\mathrm{b}}{r_\mathrm{a} f_\mathrm{a}^2 + 2 f_\mathrm{a} f_\mathrm{b} + r_\mathrm{b} f_\mathrm{b}^2} \tag{1}$$

where F_a is the mole fraction of monomer ‘a’ incorporated into a copolymer composed of monomers ‘a’ and ‘b’, f_a and $f_\mathrm{b}(= 1 - f_\mathrm{a})$ are the mole fractions of monomers in a mixture of monomers (the feed) *at that instant in time when the copolymer is being formed.* The ‘r’s are measures of the relative reactivities of the

EQUATION VIs



Copolymer Equation VI

Input

RA = 5.00

RB = 0.01

Feed = 0.50
Mole Fracn.(A)

Conversion
Percent = 50

More Data?
No Yes

Output

At Input Conversion = 50
we have the following
Copolymer Composition
(Mole Fracn. A)

Instantaneously formed
AT this Conversion =0.69

Averaged UP TO
this Conversion =0.80

Effective Feed
AT this Conversion =0.20

Fig. 2. Copolymer equation VI showing various input and output parameters on the front panel.

growing chain end to monomers ‘a’ and ‘b’. Without going through the gory details, copolymer composition will not generally be the same as that of monomer feed, except for a special case ($r_a = r_b = 1$). It follows that feed composition will change from its initial value (assuming it is a batch reaction) and copolymer composition will also change with time or degree of conversion. Because different copolymer compositions are produced at different times in the reaction (degrees of conversion), it follows that these copolymers will have different properties. Our interest is thermal properties, so we focus on T_g and T_m.

In addition, from probability arguments and using composition and ‘r’ values, equations have been developed that describe the way in which the two different monomers are distributed along the chain; this is the so called sequence length distribution. Consider monomer ‘a’ in a particular chain, do these units tend to be bunched together (blocky), are they randomly distributed, or do they tend to be isolated from each other (alternating)? The product $r_a r_b$ determines which type of copolymer forms.

The copolymer equation VI graphically displays:

1. changes in monomer feed ratio,
2. composition of copolymer produced over a narrow range of conversions (instantaneous) and
3. average copolymer composition.

These outputs are a function of various input values; initial feed ratio, values of ‘r’ for the two monomers and conversion (Fig. 2). At user *specified conversions* output data is also presented numerically. Users can also opt to view additional information; in this case a choice between sequence length distribution of the two monomers and thermal data. In the later case, for a specified conversion we use copolymer composition to compute T_g and T_m. Here T_m is computed using a modified form of the usual Flory type equation for the equilibrium melting point of copolymers:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\left(\frac{R}{\Delta H_f}\right) Lnp \qquad (2)$$

where T_m is the copolymer melting point and T_m^0 is the melting point of a homopolymer of ‘a’. It is assumed that ‘b’ is a non-crystallizable monomer that acts as a defect in the chain; ‘p’ is the probability that an ‘a’ in the chain will be followed by another ‘a’. For a random copolymer that probability equates to F_a, the mole fraction of ‘a’ in the copolymer.

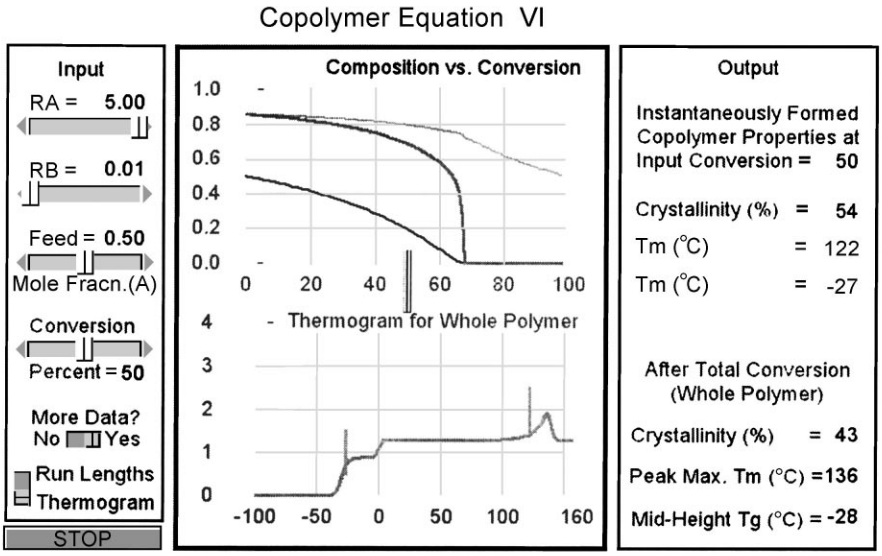
T_g for an amorphous copolymer can be approximated as:

$$T_{g_{\text{copolymer}}} \approx F_a T_{g_a} + F_b T_{g_b} \qquad (3)$$

where T_{g_a} and T_{g_b} are the T_gs of homopolymer 'a' and 'b', respectively. When the copolymer is semicrystalline the situation is more complex. The overall composition of the crystallizable copolymer cannot be used in the above equation; some of the material has crystallized. This crystalline component is rich in crystallizable monomer 'a' and the amorphous phase is therefore depleted in 'a', or richer in 'b' relative to the overall copolymer composition. In order to approximate the composition of the amorphous phase, we need to make some assumptions about percentage crystallinity as a function of composition. There are theoretical approaches to this problem; we chose a computationally easier approach, showing the same general trend of decreasing crystallinity as comonomer content increases.

Even pure homopolymer is assumed to be less than 100% crystalline, in this case we assume it is 95% crystalline. The Flory copolymer melting point is then used as an indicator of crystallinity. It is assumed that crystallinity decreases linearly with melting point from 95% at T_m^0 to 0%, where the melting point of the copolymer approaches T_g. That assumption is reasonable; at T_g chains are unable to move and form crystals. In this case, we use the T_g of homopolymer 'b'. Choice of T_g is probably not critical, the overall trend of decreasing crystallinity with increasing comonomer content is the important point. Changes in crystallinity described in this paragraph mimic those seen in ethylene copolymers [2].

So, for a given copolymer composition, melting point is computed and used to identify percentage crystallinity. All crystalline material is assumed to be pure 'a'. By difference, the amount and composition of the amorphous region is known and used in Eq. (3) to calculate T_g for the amorphous region of the semicrystalline copolymer. Remember, the above calculations are done for a single conversion for a copolymer whose composition versus conversion has been specified by input values of reactivity ratio and initial monomer feed ratio. Calculations for T_m and T_g are performed for all conversions at 1% increments and the results summed to yield an ideal thermogram for the whole polymer produced if the reaction went to completion. Amplitudes for T_m and T_g are approximated as a function of percent crystallinity (amount of each phase). By co-adding individual increments, we are assuming that incrementally produced copolymers are incompatible. This is not necessarily a good assumption but is used here to more clearly demonstrate the result of driving copolymer reactions to completion, namely production of a broad range of



Copolymer Equation VI

Input

RA = 5.00

RB = 0.01

Feed = 0.50 Mole Fracn.(A)

Conversion Percent = 50

More Data? No Yes

Output

Instantaneously Formed Copolymer Properties at Input Conversion = 50

Crystallinity (%) = 54

Tm (°C) = 122

Tm (°C) = -27

After Total Conversion (Whole Polymer)

Crystallinity (%) = 43

Peak Max. Tm (°C) =136

Mid-Height Tg (°C) = -28

Fig. 3. Copolymer Eq. (4) with a modified panel after addition thermal data is requested.

copolymer compositions with a correspondingly broad range of properties. T_g and T_m for any particular conversion are indicated in Fig. 3 with short vertical lines on the thermogram of the whole polymer.

The Avrami equation describes crystallization rates in terms of nucleation and crystallization terms, and is usually expressed as:

$$\frac{W_l}{W_0} = e^{-zt^n} \tag{4}$$

where W_l/W_0 is the fraction of material that has yet to crystallize after time 't'. There is a rate constant 'z' and the Avrami coefficient 'n' that is composed of crystallization and nucleation terms. In the VI there are inputs for 'z', crystallization and nucleation terms. Outputs are three graphs showing plots of this equation versus time and ln time, as well as ln $(-\ln)(W_l/W_0)$ versus log time. A multiple plot approach is used because it is often difficult to visualize how changes of input parameters affect the various outputs, all of which represent crystallization rate data. Slope and intercept for the latter plot are also shown, as are induction times from the other plots as a function of user specified crystallization level.

The WLF equation is classically used to demonstrate time/temperature superposition or equivalency as it is sometimes called. However, the origins of equation development go back to experimenters 'sliding' data along the time axis (ln time) to see if curves taken at different temperatures would overlap. The WLF VI lets users slide data from several temperatures along the ln time axis and generate a master curve. At this point, we can ask questions: what if any relationship exists between the amount shifted along the axis and the temperature at which the original data set was collected? What is being done to the data mathematically when we shift it along the axis?

4. Instrument VIs

With all 'instrument' type VIs, it is assumed that overall trend is what is of prime importance. As a result these are not 'real data' in the sense of being representative of any one polymer but rather are indicative of overall trends in many polymers.

The DTA/DSC VI is a combination of differential thermal analysis (DTA) and differential scanning calorimetry (DSC) in a single module. There are basic experimental differences in the two techniques, but results from both methods are approximately the same. Certainly, when trying to show general trends there is little need to spend time on what are usually minor variations between the two methods. Input variables are copolymer composition and degree of randomness, cooling rate prior to a DTA/DSC run and the heating rate of that run. Melting curve shapes are derived from an assumed Gaussian distribution of lamella thicknesses for T_m, T_g shape is assumed to be a simple integrated Gaussian versus temperature.

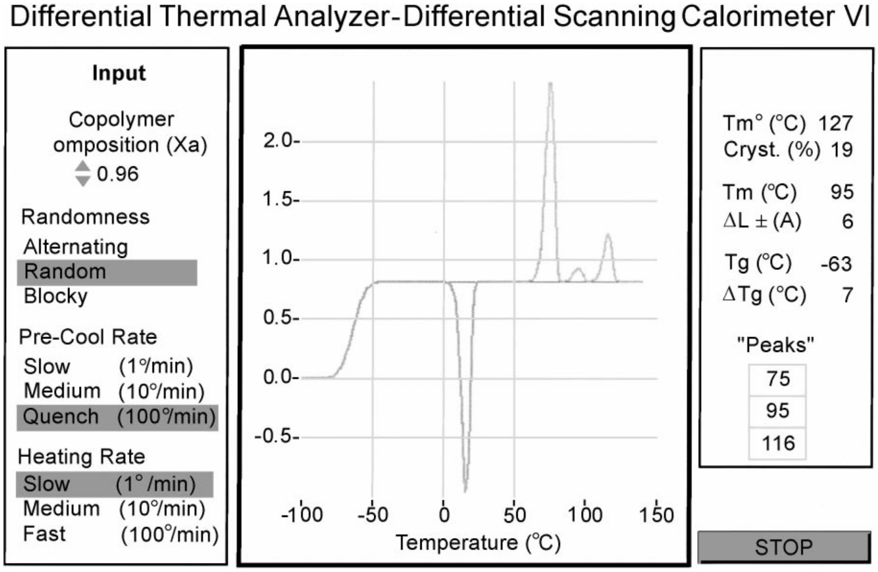
Calculation of copolymer equilibrium melting point T_m, from the Flory equation and corresponding T_g in a semicrystalline copolymer, has been previously described in the copolymer equation section. However, the T_m calculated is an equilibrium melting point and does not account for changes in apparent melting point with changes in cooling rate. If a polymer is cooled quickly thinner lamella crystals are formed compared with those formed on very slow cooling ($\approx$ equilibrium conditions).

The Hoffman–Weeks equation is used for homopolymers to calculate the melting point (T_{m_l}) of lamella crystals of thickness 'l' versus the equilibrium melting point (T_m^0).

$$T_{m_l} = T_m^0\left(1 - \frac{2\sigma_e}{\Delta H_f l}\right) \tag{5}$$

where σ_e and ΔH_f are surface energy and heat of fusion, respectively; values typical of those for polyethylene are used. As an approximation the same approach is used for copolymers, the value of T_m^0 in Eq. (5) is taken as the equilibrium melting point (T_m) calculated from Eq. (2), the Flory equation. Eq. (5) still needs an assumption regarding 'l', as a function of cooling rate. As cooling rate increases, 'l' is assumed to change in the order 200:100:67 Å. Remember, this is a mean 'l' value and a Gaussian distribution of thicknesses is also included.

As with the previously described copolymer VI peak size is taken as a function of percentage crystallinity, which is calculated using the Flory melting temperature. Once again there is a need to modify this assumption because the faster the sample is cooled, the lower is the crystallinity. Changes in crystallinity with increased cooling rate are approximately in the order 10:4:1.



Differential Thermal Analyzer-Differential Scanning Calorimeter VI

Input

Copolymer
omposition (Xa)
0.96

Randomness
Alternating
[✓ Random]
Blocky

Pre-Cool Rate
Slow (1°/min)
Medium (10°/min)
[✓ Quench (100°/min)]

Heating Rate
[✓ Slow (1° /min)]
Medium (10°/min)
Fast (100°/min)

Tm° (°C) 127
Cryst. (%) 19

Tm (°C) 95
ΔL ± (A) 6

Tg (°C) -63
ΔTg (°C) 7

"Peaks"
75
95
116

Fig. 4. DTA/DSC VI showing the response from a crystallizable random polymer cooled quickly and heated slowly. If the sample was rapidly heated after quenching only a single peak is seen at ≈95°C.

Changes in melting and crystallinity described above are valid within the context of the stated assumptions provided the sample is heated quickly enough so that there is no time for reorganization from a non-equilibrium condition. Whatever the cooling rate, it is assumed that if the sample is heated at that rate or higher, no reorganization can occur. However, as heating rate decreases relative to cooling rate, a rapidly cooled sample has opportunity (time) to reorganize to a more 'equilibrium' state on slow heating. The following section shows that differences in heating and cooling rate are treated in two ways.

A fast cooled sample that is reheated slowly is allowed to recrystallize by an amount equal to the crystallinity difference between the levels of crystallinity of the two states (fast cooled versus slow cooled). The temperature at which recrystallization occurs (T_c) is taken as ≈ the mid-point between T_g and T_m for the sample. This recrystallized material is then allowed to melt at approximately midway between T_c and T_m for the original fast cooled sample. In addition, any crystalline material that was originally present in the fast cooled sample is permitted to 'anneal' on slow heating. Approximately 2/3 of the original material anneals to a melting point that is ≈ midway between T_m and T_m^0 for that sample. Of course, the recrystallized material could also anneal, but it was felt that including this option would unnecessarily complicate the thermogram. In all cases, the attempt is to show general trends in thermal analysis of polymers. A number of numerical outputs are also provided and shown in Fig. 4, which represents the response from a typical fast cooled and slowly reheated semicrystalline random copolymer sample.

Dynamic mechanical thermal analysis (*DMTA*) is a general term describing experiments where a material is deformed at some (variable) frequency as a function of temperature. In this case, frequency is kept fixed, sample temperature is raised from below T_g to above T_m and deformation is imagined to be tensile, bending or torsional. Relative modulus and tan δ are output graphically as a function of temperature. Relative modulus is defined here as modulus at any temperature relative to the modulus below T_g; modulus is essentially independent of temperature below T_g. Tan δ represents the relative viscous and elastic contributions to deformation, or can be thought of as a measure of the extent to which mechanical energy is dissipated by viscous elements. Input variables are shown in Table 2. Curve shapes are Gaussian for tan δ and integrated Gaussian for relative modulus. Changes in amplitude, width and position along the

Table 2
Input parameters for DMTA VI

Percentage crystallinity	Molecular weight
Cross-link density	Percentage plasticizer
Blend composition	Number of blend phases

Table 3
Input parameters for G' and G'' versus frequency VI

Molecular weight	Mw/Mn (Mw constant)
Branching/gelation	Temperature

temperature axis are derived from general trends reported by Nielsen [3].

Plotting log G' and G'' versus log test frequency is another approach to presenting dynamic data (Table 3). In this case, the focus is polymer melts and trends are typical of those seen using a cone and plate or flat plate rheometer. Results are consistent with those reported by Colby [4] on styrenic type polymers.*Viscosity versus shear rate VI* is again focussing on polymer melts, in this case results could typically be derived from either a capillary rheometer or from a steady state or dynamic shear rheometer (Table 4). Viscosity shear rate curves are generated using a Carreau type equation of the general form

$$\eta = \eta_0[1 + |\lambda\gamma Y|^a]^{(n-1)/a} \tag{6}$$

where 'n' and 'a' are power law type constants, and '$1/\lambda$' defines the shear rate at which the viscosity curve shows the most pronounced curvature. By and large the data presented summarize information that is abstracted from books by Nielsen [5] and one by Dealy and Wissbrun [6], then compiled and integrated into a common form. Generally agreed on relationships are used throughout, i.e.

$$\eta_0 \propto M \quad \text{or} \quad \eta_0 \propto M^{3.4} \tag{7}$$

depending whether or not molecular weight exceeds some critical value. Molecular weight mixtures are handled empirically as

$$\eta_{\text{mixture}}^{1/3.4} = w_1\eta_1^{1/3.4} + w_2\eta_2^{1/3.4} \tag{8}$$

and show the general trends reported for such mixed systems.

Table 4
Input parameters for viscosity versus shear rate VI

Molecular weight	Mw/Mn (Mw constant)
Long chain branching	Temperature
Molecular weight mixtures	

5. Conclusions

Instrumental VIs deliver two valuable functions. They offer the user the opportunity to discover structure–property–process relationships for themselves. The key word is opportunity, as with real instruments you often have to take what the instrument provides and further treat it some way to find relationships. While generally accepted equations are used in VI development, it would be a surprise if users can directly arrive at those equations from the data. In this regard the VIs give general trends but also point out that theoretical development may arrive at the same experimental answer from a different route. These instrument type VIs also act to summarize a lot of basic information in the polymer area; in many respects these VIs act as review session for the area.

Equation VIs provide different particulars, these VIs are directed more to giving a feel for the relative importance and controlling influence which various parameters in an equation have on the overall output. In some cases equation VIs have been tied to typical data to give more direct meaning to the equations.

These VIs offer a valuable route to low cost information transfer in science and engineering disciplines; they allow users to develop and understand relationships for themselves. More sophisticated VIs than the ones described here can provide the opportunity to test potentially dangerous situations with no danger to the operator or the instrument; pilots have been trained in simulators for years. However, I still want my pilot to have a large number of hours in the air and I want my students to have time in the lab. These VIs are not intended to replace lab time, they are intended to complement and optimize real lab experiences.

The TAS of VIs will be available as a 'stand alone' program on CD or Zip® some time in early 2000. 'Stand alone' implies that Labview® is not required in order for the program to run, both Mac and IBM version can be produced.

Acknowledgements

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