Regression Analysis Studies of Polymer Transitions. I. Volume–Temperature Data on Amorphous Polymers

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Synopsis

An exact procedure for the objective analysis of physical data on polymers, such as volume–temperature, near known or suspected transition points, is presented. Standard computerized linear and polynomial regression techniques are employed for $Y = f(X)$. A set of models typical of known data behavior near polymer transitions has been developed. Several sets of data for testing these models were synthesized, having a built-in random error of 0.075%. Particular emphasis is placed on the residual pattern as a function of X where a residual, RES = Y(observed) $-$ Y(calculated). RES/SE, where SE is the standard error in Y(calculated) is also employed. Residuals for the different models tested against the several sets of synthetic data provide discrimination or recognition patterns to apply when examining unknown bodies of data. We start on unknown data with the simplest possible models, a straight line and a quadratic. These yield residual patterns which guide one to more complex models, which in turn give new residual patterns. The correct model is approached objectively as a limit. We emphasize that these regression techniques can only describe the data but not interpret its physical meaning. These techniques are applied to a detailed analysis of $V{-}T$ data by Wilson and Simha on poly(cylopentyl methacrylate) which show that $V{-}T$ data above T_g follows two quadratics intersecting at 148–149°C. We identify this intersection as the liquid–liquid transition temperature, T_{ll}, in basic agreement with the suggestion of Wilson and Simha.

INTRODUCTION

This series of papers is concerned with computerized regression techniques for handling and interpretation of physical data in the region of known or suspected transitions and relaxations in polymers. The main types of physical data considered are thermodynamic quantities which vary with temperatures such as length L, volume V, and enthalpy H, and their respective derivatives $\alpha' = (1/L)(dL/dT)$, $\alpha = (1/V)(dV/dT)$, and $C_p = dH/dT$. Certain types of kinetic data such as diffusion constant D, preferably D_0 at zero concentration of diluent; and zero shear melt viscosity η_0 are also considered. In such cases the data are plotted as log D_0 or log η_0 as a function of $1/T$; or as a function of $1/(T - T_0)$, where T_0 is a reference temperature.

It is generally known from mechanical and electrical spectroscopy[1–3] that polymers possess a small number of transitions along the temperature scale. For T in Kelvins, these transitions tend to lie at or near: $<0.50\ T_g$; $0.75\ T_g$; T_g; $1.2\ T_g$; $0.85\ T_m$ and T_m; T_g is the glass transition and T_m is the melting point. This has been covered in several recent reviews.[4–8] Except in highly crystalline or

highly crosslinked specimens, T_g receives unambiguous interpretation by C_p—T, L—T, and V—T data are fairly clear at secondary transitions,[9–16] lying below but not above T_g. A transition in the liquid state of amorphous polymers above T_g is the subject of controversy.[7,8] Our regression techniques will be used to locate T_{ll} in poly(cyclopentyl methacrylate).

Semicrystalline polymers are more complex to analyze because crystallinity reduces the absolute intensity of all amorphous phase transitions and may alter their relative intensities.[4–6,17–21] This is especially true of a highly crystalline polymer like polyethylene. For example, Stehling and Mandelkern[20] report L—T data on fractions of linear PE from which they deduce a T_g of $-128°C$. But Davis and Eby,[21] from V—T studies on a heterogeneous specimen of linear PE, arrive at a T_g of about $-30°C$. Both are observing amorphous phase transitions and the 100K difference is not likely to be resolved by regression analysis. Because of problems such as this in crystalline polymers, it is advisable first to treat only amorphous polymers and copolymers.

There are two aspects to be considered: (1) the quality of the physical data which depends on the sample, its thermal history, the apparatus, and techniques; (2) interpretation of the data as regards location of transition temperatures. We propose for (2) the use of highly objective computer techniques to accomplish four closely related objectives:

    a. error-free plotting of the data;

    b. rejection of data points which appear to be clearly in error;

    c. treatment of the data by a small group of statistical procedures;

    d. computer-drawn least-squares regression fitting of the data by one or more straight lines or polynomials, as suggested by c.

Partly, we plan to develop a set of models which permit objective discrimination between alternate choices of interpreting a given body of data.

Statistical procedures for such data analysis are widely available and routinely used by professional statisticians.[22–28] However, the latter are not generally aware of bodies of data of interest to us nor of the physical significance of such data. Two of us (R.F.B. and R.L.M.) have been quite familiar with the literature on polymer transitions and with existing problems and confusion concerning its interpretation. This paper attempts to merge the two required backgrounds and to arrive at a set of recommended statistical procedures designed principally but not exclusively for polymer scientists. The plan to be followed in this paper includes:

    1. Development of two general models to represent physical data in the region of a transition.

    2. Development of five sets of synthetic data representing different models of expected data.

    3. Applying regression analysis to this synthetic data of precisely known characteristics.

    4. Development from this synthetic data of a set of recognition or discrimination patterns to be used with real data of generally unknown characteristics.

    5. Application of these techniques to data found in the literature, starting in this paper with a V—T example, and proceeding in subsequent publications with other types of physical data.

Models for Describing Data

As a result of studying many types of physical data for numerous polymers near known or suspected transitions and relaxations, two general models have been developed. The first is illustrated in Figure 1. It shows only one of a very large number of possible shapes.

Briefly, N_1 data points, at regular or irregular spacing along the T axis, lie on one straight line, L_1, followed by N_c data points on the curved section followed by N_2 data points along straight line L_2. [A quadratic transition function is likely to be an approximation of a more complex function. For a complete mathematical discussion of this problem, and the optimal location of experimental data points, see Park, Ref. 28(b).] Other data points lying below L_1 and above L_2 are ignored. The curved section will have an average radius of curvature, $\overline{R}$, and an actual radius R at any T with $R = f(T)$. Extension of the two straight lines gives a temperature of intersection, T_i. The angle θ measures the sharpness of the intersection. Equations for lines L_1 and L_2 and related quantities are:

$$L_1: \quad Y_1 = A_1 + B_1 T \tag{1}$$

$$L_2: \quad Y_2 = A_2 + B_2 T \tag{2}$$

$$T_i = (A_1 - A_2)/(B_2 - B_1) \tag{3}$$

$$\theta = \tan^{-1} B_2 - \tan^{-1} B_1 \tag{4}$$

$$N = N_1 + N_c + N_2 \tag{5}$$

Following are the variations of Figure 1 most likely to be of interest.
1. Single straight line: $N_c = N_2 = 0, N_1 = N$.
2. Two straight lines: $N_c = 0, \overline{R} = 0$.
3. Three straight lines: $\overline{R} = \infty, N_c = N_{12}$.
4. Polynomial: $N_1 = N_2 = 0, N_c = N, R = f(T)$.
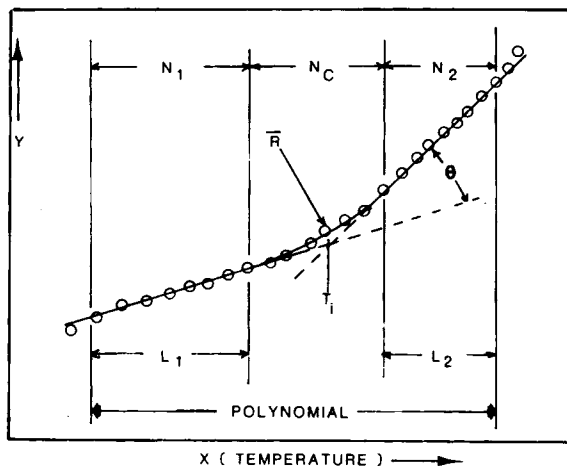5. One straight line and one curved section: let either N_1 or $N_2 = 0$.

Fig. 1. Simple model for $Y = f(T)$ on either side of a transition whose temperature is indicated by T_i. Typically, Y can be volume V above and below T_g; or C_p near the liquid state transition T_{ll} above T_g. N signifies the number of data points over temperature interval L, and $\overline{R}$ is average radius of curvature. All data points, $N = N_1 + N_c + N_2$ may seem to be represented by a polynomial, generally erroneously. θ is the angle used in eq. (4).

In general we consider mainly first and second degree polynomials but occasionally up to fifth degree. Our computer program can handle up to a fifteenth degree polynomial.

As will be seen later, we routinely fit any new unknown body of data to a linear and to a quadratic regression analysis. In general, neither give a satisfactory fit. Objective guides have been developed to decide which variation(s) of the model in Figure 1 best represents the data.

While all examples in this study are based on $Y = f(T)$, it is clear the methods are general to $Y = f(X)$, where X might be velocity, shear rate, cross-sectional area per polymer chain, molecular weight, or other physical parameters for which there is a transition in Y or in dY/dX.

We wish to emphasize that the model shown in Figure 1 using $V-T$ data has long been accepted as characteristic of T_g. Gee[29] has used this model as a formal definition of T_g with the extrapolated intersection point T_i being defined as T_g. A single figure (Fig. 1) in a paper by Bywater and Toporowski[30] shows three V—T plots indicating two intersecting straight lines, three straight lines, and two straight lines connected by a curved section depending on the iso and syndio content of PMMA. Figure 1 type behavior for $L-T$ data below T_g has been reported on numerous occasions by Simha and his collaborators.[9–16]

Our early studies suggested the occasional need of a special, more sophisticated model than that shown in Figure 1, namely, two or more intersecting polynomials, not necessarily of the same degree. As shown schematically in Figure 2, there are N_c (1) data points on the lower curve, N_c (2) on the upper one. In general each will have a different average radius of curvature, $\overline{R}_1$ and $\overline{R}_2$. For simplicity, we treat the case of two quadratics Q_1 and Q_2, since an example of this appears later. We have
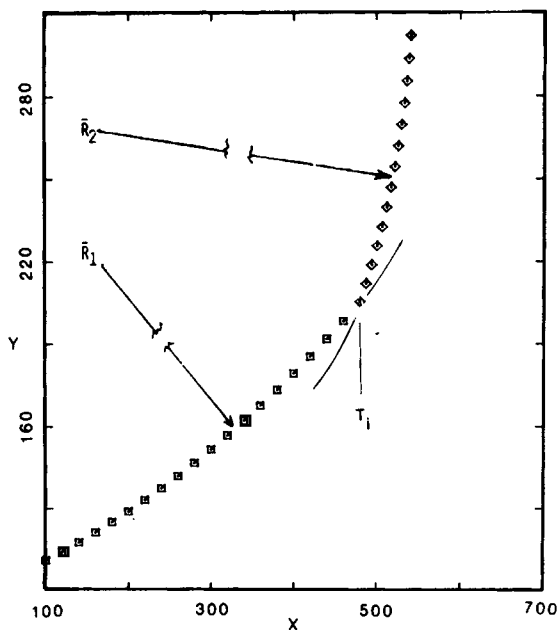

Fig. 2. More sophisticated model consisting of two polynomials, not necessarily of the same degree but commonly both quadratics. $\overline{R}_1$ and $\overline{R}_2$ are average radii of curvature. The first derivative of these polynomials gives a pair of intersecting straight lines, similar to those in Figure 1. (See Fig. 12.)

$$Q_1: \quad Y_1 = A_1 + B_1 T + C_1 T^2 \tag{6}$$

$$Q_2: \quad Y_2 = A_2 + B_2 T + C_2 T^2 \tag{7}$$

The intersection temperature is

$$T_i = \frac{-(B_1 - B_2) \pm [(B_1 - B_2)^2 - 4(A_1 - A_2)(C_1 - C_2)]^{1/2}}{2 (C_1 - C_2)} \tag{8}$$

However, for bodies of data examined thus far (see Figures 12 and 13 later) curvatures are slight with the C_1 and C_2 terms being quite small. Hence eq. (8) is not very reliable.

A preferred procedure is to calculate and plot dY/dT for the entire body of data. If eqs. (6) and (7) hold, two straight lines result, and their intersection yields T_i. An example of this appears later in Figure 12.

The Computer Program

Tabulated data of $Y = f(T)$ are card punched. This information is transferred to punched tape which is used by the computer. A standard statistical program then calculates the following quantities:

a. coefficients of the equation best fitting the data;

b. standard error (SE) in Y(calc), usually designated $\hat{Y}$ (Y hat);

c. coefficient of correlations, R^2, for first (or any) degree polynomial;

d. the residual (RES), Y(observed) $-$ Y(calculated), for each value of T; in computer language, RES $= Y - \hat{Y}$;

e. a chart paper printout of the ratio RES/SE against the consecutive number of each data point (order of increasing T); SE is the standard error in $\hat{Y}$;

f. the data points are plotted on an $X - Y$ recorder, and the regression curve is drawn in automatically.

The following routine was developed by us, although numerous variations are possible:

1. Print out all of the data points to give a large scale (8 × 10 in.) plot of the actual data for visual inspection.

2. Select a portion of the data for detailed analysis, for example, one or several of the three regions, $T < T_g$, $T = T_g \pm 50K$, $T > T_g$.

3. Plot this more limited set of data for visual inspection.

4. Compute and plot a linear least squares first degree line. For the majority of cases to be considered it is an obvious nonfit.

5. Compute and plot a second degree equation. It is usually less apparent but a simple quadratic seldom gives a satisfactory fit near a transition.

6. Compute and plot higher degree polynomials as desired.

7. Inspect the RES/SE plots for the linear and quadratic fits. As will be seen later, some characteristic patterns emerge: If a perfect fit is achieved, the RES/SE points are random about zero and lie within the limits of ±2. If the actual data require two straight lines, the RES/SE have a characteristic pattern for both the first and second degree fits. It will be obvious by inspection of the RES/SE plots that the data follow two straight lines intersecting at a specific data point (or between two data points).

8. With this objective information from the RES/SE plot, one can now ask the computer to fit the data with, for example, two straight lines. Different symbols are used for each set of data.

9. As a final check, one notes the RES/SE plots for the two straight lines should both be random about zero. One can also compare the RES/SE values for the two straight lines with the same for the quadratic or higher polynomial.

Development of Ideal Synthetic Data

Early studies on actual $Y = f(T)$ data quickly revealed three characteristic limitations:

1. Lack of objective, *a priori* knowledge of what fit to expect (except, of course, near T_g).

2. Experimental errors in the data.

3. Lack of sufficient data points, particularly in critical regions of T.

It therefore seemed desirable to synthesize some data of precisely known characteristics, patterned after the model in Figure 1. Five cases, all with the same total number of data points were considered: namely, two straight lines with a curved connecting section, three straight lines, two intersecting straight lines, one straight line, and a quadratic. This body of synthetic data was generated graphically and was essentially error free.

One cannot properly perform a regression analysis on such ideal data because of frequent divisions of quantities, 0/0, as both RES and SE approach zero. All real data contain random errors. The ideal data were consequently modified on a sequential basis by the formula:

$$Y = Y(\text{ideal}) + M(0.5 - \text{RN}) \tag{9}$$

where RN is a random number between 0 and 1 generated by a Texas Instruments TI-58 Programmable Computer software program, a further sophistication would have been to use normally distributed random errors. M is a numerical multiplier which makes the second term on the rhs a reasonable fraction of $Y(\text{ideal})$. At first, the product $M(0.5 - \text{RN})$ was selected to be 1% of the midrange of $Y(\text{ideal})$. One could not distinguish between the cases of two straight lines connected by curvature and a quadratic fit. The multiplier M was then selected to give a percentage of error, midrange, of 0.075%, which is typical of some of the better data in the literature. This was much more satisfactory. One could have the error term in eq. (9) be proportional to X but we chose to have it constant over the entire range of X, as is assumed in the development of regression analysis procedures. A rather trivial problem arises once random errors are introduced. With ideal data, there is a point in common between the several sections (one to two) of Figure 1. Once random errors are introduced, there can no longer be a common point. The "nominal random point" was arbitrarily assigned to the lower or upper segment.

RESIDUAL PATTERNS

Examination of the residual pattern $(Y - \hat{Y})$ or $(Y - \hat{Y})/\text{SE}$, as a function of X is an important aspect of any regression analysis problem.[26] If the correct model has been found for the data, the residuals will be randomly distributed about zero. Any *nonrandom patterns* in the residual indicates either an incorrect model or problems in the data (for example, temperature drift). Such

a drift might appear as residuals being nonrandom about a line other than 0-0.

Figure 3 shows a number of residual patterns, some of which indicate an incorrect model. For example, if the data lie on two straight lines connected or not by a curved section, and a quadratic model is used, the residual pattern shown in the right column of B or C will be found. In this case, the data must be reexamined with a different model.

Hence, by a series of successive approximations, choosing models of increasing sophistication, one tries to arrive in an objective manner at a model which yields residuals random about zero. In practice, real data seldom respond as decisively as the ideal data of Figure 3.

The simple linear model usually gives a clue as to a better model. Figure 4 illustrates in more detail the RES/SE pattern for a first degree polynomial fit to synthetic data consisting of two straight lines connected by a curved section. Using a straightedge, we draw straight lines AB and CD extended to intersect at T_i. The curved section shows the N_c data points of Figure 1. Since points on the curve favor a polynomial fit they may be eliminated by inspection of the RES/SE plot before applying a model consisting of two straight lines. If a two straight line model is correct, the residual pattern for *both* lines should be random about zero. Likewise, the incorrect quadratic models in B and C of Figure 3 provide a guide to a more correct model. The pointed cusp of the quadratic model in B indicates the single intersection region as does the rounded cusp in C or the double cusp in D.

As the correct model is being approached, it is instructive to connect successive points in the RES/SE computer printout by penciled lines. The detailed pattern
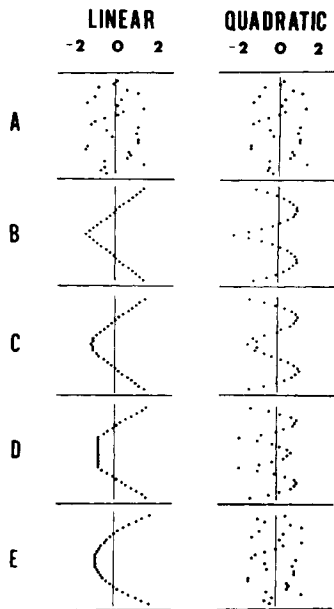

Fig. 3. Residuals/standard error patterns based on linear and quadratic fits to synthetic data (with 0.075% random error) developed according to the following models. (A) One straight line; (B) two straight lines; (C) two straight lines connected by curvature; (D) three straight lines; (E) a quadratic. A residual is defined as Y (observed) $-$ Y (calculated).
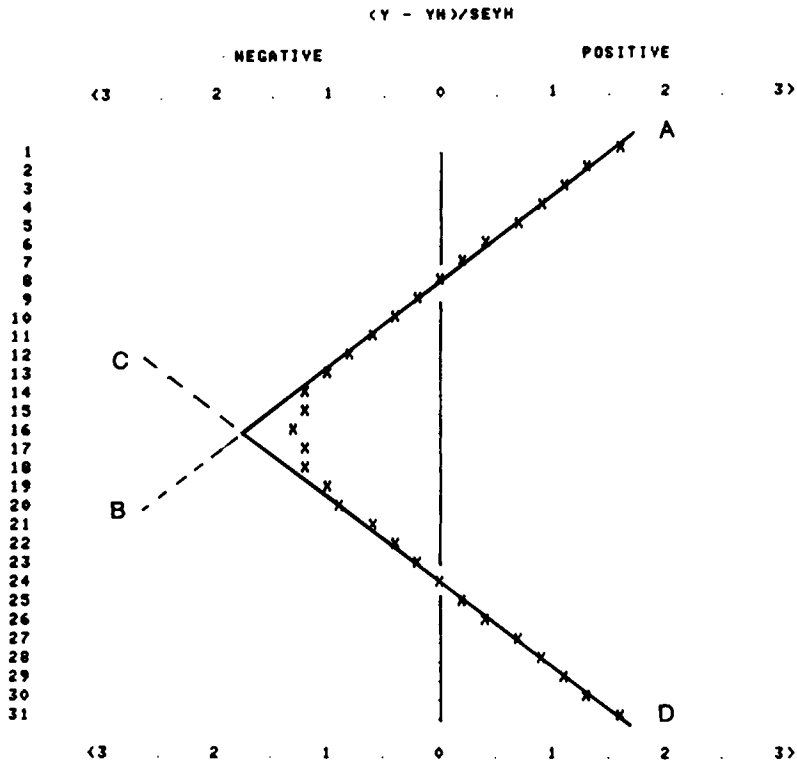
Fig. 4. RES/SE pattern for linear fit to synthetic data consisting of two straight lines connected by a curved section. The apparent transition temperature T_i, is determined from the intersection of lines AB and CD.

is more distinct and the number of crossovers from plus to minus (or vice versa) can be readily counted. The *crossovers* should be about half the total number of data points, except when the number of data points *is small*. Examples appear later in Figure 13. See also page 96 of Ref. 22.

Figure 3 employed only five models out of a potentially much larger set that could have been chosen. A model for two quadratics was not treated via the synthetic data route since the derivative dV/dT yields patterns very similar to those shown in Figure 3. The individual investigator can select other models which appear more suited to the specific nature of the data being considered. The magnitude of the random error and its variation with X can also be selected at will.

Details about Residuals

Distortion of Residuals Patterns

There are two situations in which the RES/SE printout pattern from the computer is distorted:

a. *Y* values lie at nonuniform intervals along the X-axis. Our computer normally prints out RES/SE values for consecutively numbered data points with increasing X. If the temperature intervals between X values are equal, the pattern shown is equivalent to a plot of RES/SE vs. X. More generally, they

are non-equal, and this introduces some distortion. This is not serious for counting traverses, but may be misleading if the printout is used to estimate an intersection temperature as in Figure 4.

b. If the ratio, total data points/total range in X, is very large, the computer gives a distorted pattern of RES/SE because of overcrowding. This is especially true when the pattern is very nonrandom. This observation was made by Keinath[31] and may be a peculiarity of our computer system.

In either case, the distortion is eliminated by preparing an actual plot of RES/SE against X or Y. If $X = T$ or T^{-1}, an RES/SE against X plot is preferable.

Higher Polynomials

Another point to note is the residual pattern behavior on going to polynomial models of higher degrees than quadratic (or if the true function is not a polynomial but is being approximated by the polynomial). This is illustrated using the synthetic data consisting of three intersecting straight lines as in D of Figure 3. When the slope changes between successive lines are small, such data may appear to the eye to be fitted ideally by a simple polynomial. Figure 5 shows a cubic model applied to the synthetic three-straight-line data. However well the visual fit may seem, the residual pattern states unambiguously that the cubic model is incorrect, as seen in Figure 5. Two further points follow about this specific set of synthetic data:

a. The nonrandom pattern persists up to a fourth degree polynomial, changes at the fifth, and loses meaning for higher degrees.

b. The two intersection temperatures are readily located as the minima in the residuals. This is brought out in Table I. Maxima in the table correspond to midpoints of straight line sections. Coefficients and standard errors for the several polynomials are listed in Table II.

We[32] have found this useful in treating a set of actual physical data in which log η_0 is plotted against $1000/T$, where η_0 is zero shear melt viscosity. These data contained random errors larger than 0.075% and showed some curvature between straight line sections. This polynomial treatment on this one set of real data accomplished two important goals: It located intersections of pairs of straight lines, it showed that a higher degree polynomial was not the correct model.

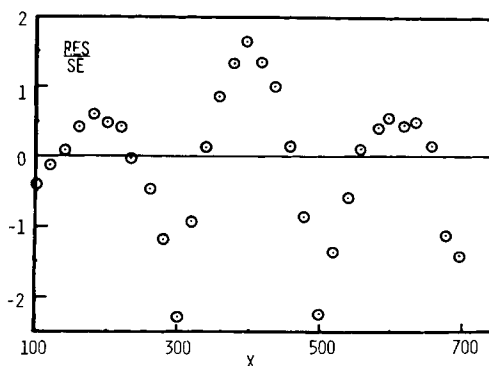There is another important aspect in considering higher degree polynomials

Fig. 5. RES/SE pattern for a cubic model applied to the three-line synthetic data.

TABLE I
Use of Higher Polynomial Models on Synthetic Three-Straight-Line Model

Degree of polynomial	Numerical magnitudes of maxima and minima[a]				
	Max 1[b]	Min 1[c]	Max 2[d]	Min 2[e]	Max 3[f]
2	0.974	−1.7255	0.7442	−1.6892	0.9881
3	0.9756	−1.7218	0.7443	−1.6930	0.9854
4	0.4488	−1.6821	1.2339	−1.6534	0.4248
5[g]	—	—	—	—	—

[a] See Figure 3(D), Quadratic, for nature of RES/SE pattern. The values listed in the table are for the residuals, $Y - \hat{Y}$.
[b] Midpoint of L_1 (180K) (should be 200K).
[c] Intersection of L_1 and L_2 (300K).
[d] Midpoint of L_2 (400K).
[e] Intersection of L_2 and L_3 (500K).
[f] Midpoint of L_3 (600K).
[g] Method breaks down, for 5th and higher polynomials.

as they apply to real data: They can give a false sense of certainty about the choice of a model. As the degree of the polynomial model increases, several things happen:

a. Standard error in $\hat{Y}$ gets smaller before going through a minimum.

b. Coefficients of correlation, R, will increase.

c. The computer program gives nonvanishing numbers for the coefficients of the higher order terms in the polynomial.

d. The number of crossovers should increase as the model becomes more appropriate.

In fact, at degree 3 and higher, the coefficients of successive terms in the polynomial usually begin to alternate in sign. The polynomial approximates the data as a limit. One should be wary of fits in which the signs alternate, and the coefficients of the higher terms become exceedingly small. In connection with polynomial models, the pioneering regression analysis work of Utracki should be mentioned.[33] He examined published precision melt viscosity, η, temperature data which spanned, in some cases 15 orders of magnitude in η. He worked with several simple organic molecules and with plasticized PVC. As models he used theoretical, semitheoretical, and empirical relations which had been proposed in the literature as capable of representing $\eta = f(T)$. His models included exponential and polynomial functions of T. He found that (a) none of these

TABLE II
Coefficients of Polynomial Fits to Three-Straight-Line Model[a]

Term degree	Degree of polynomial			
	2	3	4	5
0	98.22	98.25	89.96	−8.624
1	0.1054	0.1051	0.2241	1.641
2	2.432×10^{-4}	2.441×10^{-4}	-3.047×10^{-4}	-6.849×10^{-3}
3	—	-7.813×10^{-10}	9.994×10^{-7}	1.297×10^{-5}
4	—	—	-6.251×10^{-10}	-8.187×10^{-9}
5	—	—	—	7.702×10^{-14}
Std. error in Y[b]	0.8402	0.8557	—	5.7798

[a] Synthetic data with 0.075% random error.
[b] For a first degree fit, the standard error is 7.2332.

equations described η over the whole range of temperature, (b) standard errors were large, (c) residuals were nonrandom about zero in some ranges. The four compounds studied showed evidence for having one to four transitions. He thus provides additional cases of mathematical models which appeared to describe real data by earlier criteria, but could not always survive the residuals test.

Two Straight Lines vs. Quadratic

One set of models commonly used consists of a pair of straight lines compared to a quadratic. The two straight line case uses five parameters, the A's and B's of eqs. (1) and (2) and the assumed intersection point. The quadratic involves three parameters. This may give an advantage to the two straight line case.

One possible way of judging the relative merits of the three and five parameter models is through the adjusted R^2, as proposed by Hocking:[28]

$$R^2(\text{ADJ}) = 1 - [N/(N - P)](1 - R^2) \tag{10}$$

where N is the number of data points and P is the number of parameters. With two lines, N is the total number of data points. For example, assume a total of eight data points with $R_Q^2 = 0.99$ and $R_{L,L}^2 = 0.995$. From eq. (10), R_Q^2 (ADJ) = 0.984 and $R_{L,L}^2$ (ADJ) = 0.9867. The two line model in this assumed case is actually slightly better.

It is clear from eq.(10) that the adjustment is greater when N and/or R^2 are small. We try to avoid cases where N or R^2 is small.

Another method is to compare two straight lines with a fourth degree equation so that five parameters are involved in both cases.

COEFFICIENT OF CORRELATION, R

Our computer program routinely calculates the coefficient of correlation, R, defined as

$$R = [1 - \sum(y_i - \hat{y})^2/\sum(y_i - \bar{y})^2]^{1/2} \tag{11}$$

where $\bar{y}$ is the mean value of y.

As implied above, we usually relegate R to secondary importance compared with residuals. We find that R may sometimes be quite misleading. For example, using the synthetic data set consisting of three straight lines gives for a quadratic fit, $R^2 = 0.99978$. This quite high value, suggestive of a near perfect fit, results from a large number[31] of quite accurate data points. However, the residual pattern, already shown in Figure 3(D), is decidedly nonrandom. R is mainly of value for regression analysis on simple data sets, such as one straight line or one polynomial.

DERIVATIVES VS. REGRESSION ANALYSIS

Simha and his collegues[9-18] have long used derivatives, dY/dX and d^2Y/dX^2, to locate weak and strong transitions along the temperature axis. His success

stems in large part from tailoring his data acquisition program to the derivative program in either of two ways:

    a. Frequent readings of L or V, say at intervals of several Kelvins.

    b. Large scale plots of L or V vs. T with smoothed values read off at regular intervals of say, 5 Kelvins.

This situation is rare in the literature. Too few data points at nonregular intervals are more likely to be found.

    Our computer calculates dY/dX by the method of running averages first developed for transition studies by Simha et al.[9] We have several options, such as three, five, or seven consecutive running data points. Applied to the synthetic data, dY/dX gives ideal answers. With real data, we have frequently encountered serious problems.

    Our experience has shown that one erroneous data point can cause either of two types of problems: If the point in question is too high, it introduces a false broad maximum in dY/dT; if the point is too low, it introduces a minimum and two apparent maxima. The obvious reason is that such an erroneous datum is used three, five, or seven times as if it were real. This cannot happen as seriously in regression analysis, where such a point is counted only once and tends to show up as a deviant in an RES/SE plot.

    Derivative programs can be quite useful, especially in those cases when regression analysis suggests the presence of one or more polynomial fits to a body of Y—T data. dY/dT appears to be reliable when the number of data points on either side of a suspected transition is several times the number of consecutive data points in the running polynomial used by the computer to calculate dY/dT. An example appears later in Figure 12. Hand- or machine-calculated point-to-point derivations may be employed if the quality of the data is high. Otherwise, there is excessive scatter.

Real vs. Smoothed Data

    Tabulated data of $Y = f(T)$ are frequently smoothed. In such cases the original, raw data are plotted by the authors of the data on large scale and fitted with a smooth curve. Values of Y (smooth) are then read off at regular intervals of 5, 10, or 20K. Such smoothed data may be ideal for some purposes but not for regression analysis for the following reasons:

    1. The smoothing process involves human judgment and the possibility of prejudice.

    2. It is impossible to judge the accuracy of the original data.

    3. Both the SE and the RES approach zero so that the computer in calculating RES/SE is forced to calculate 0/0. It either refuses or gives illogical answers such as $R^2 > 1.0$, or both.

    4. Single "odd" data points may be overlooked.

Smoothed data are therefore the equivalent of the synthetic data without error discussed earlier: a large number of "data points" regularly spaced. Some authors present both the raw and the smoothed data from which a comparison can be made. If the real data follow the Figure 1 pattern of two straight lines and a curved connecting section, a properly executed smoothing operation may not alter this pattern. Hence, the most serious resultant of smoothing is that

real data containing random errors are converted to synthetic or pseudosynthetic data of essentially zero error.

Interpretation of Intersection Temperature T_i

Before discussing analysis of real data, it is important to express our philosophy about interpretation of computer located intersection temperatures, such as T_i in Figure 1. The presence of a T_i does not necessarily prove the existence of a molecular level relaxation or transition. It is desirable to have some additional evidence for a relaxation or transition. At T_g there is no problem since most properties change catastrophically. Property changes at a weak secondary relaxation may be subtle.

The degree of confidence in a relaxation at T_i will increase as the number of data points and accuracy of the data increases, as the sharpness of the slope change increases, and as the RES/SE plot approaches a characteristic recognition pattern. But when these criteria are all strong in V, H, or C_p data, and one deduces that a transition or relaxation is present, it follows that such a transition must also reveal itself in other types of physical measurements. The appropriate measurements may not yet have been conducted, but should be sought.

For example, Ref. 7 shows for polystyrene regression analysis of $C_p - T$ data (Fig. 5), $V - T$ data (Fig. 6), and melt viscosity data (Figs. 8 and 9). Table III lists a number of other physical methods showing evidence for a $T > T_g$ transition in polystyrene. Similarly, Table II and Figure 8 of Ref. 8 illustrate regression analysis of $V - T$ data on poly(methyl methacrylate), showing two intersection temperatures, T_g and $T > T_g$ while Table III lists results on eight other physical methods which reveal these same two transitions.

In some cases, one can also apply a coherency or a consistency test. For example, if $Y = f(T)$ data are obtained as a function of a polymer variable such as molecular weight or composition, and if the T_i's obtained from such data change with said variable in a consistent and logical manner, it is plausible to conclude that each and every T_i is real and not an artifact. We have demonstrated elsewhere (Fig. 21 of Ref. 8) a case where intersection temperatures, $T_i > T_g$, for a series of styrene–butadiene copolymers increased linearly with percent styrene.

TABLE III
Summary of T_i ($\equiv T_{ll}$) Values by Different Statistical Procedures for PCPMA

Model or method	Temp range	T_i (°C)	Figure no. in text	$T_i/T_g{}^d$
Linear	a	ca. 160	6, 7	1.24
Linear	b	ca. 145	8	1.20
Quadratic	b	ca. 150[c]	9	1.22
Two straight lines	b	149	10	1.21
Two quadratics	b	?	12	—
dV/dT	b	148	12 (inset)	1.21

[a] −30–210°C.

[b] 80–210°C.

[c] Crossover of residuals from + to −.

[d] (K/K): Common range of T_{ll}/T_g for many polymers is 1.20 ± 0.05; extreme range is 1.10 to 1.30.[7]

V—T Data on Poly(cyclopentyl Methacrylate) (PCPMA)

As an example for detailed analysis, the set of mercury dilatometer V—T data by Wilson and Simha[15] on PCPMA was selected for the following reasons:

1. It is published in tabular form in a readily accessible journal.

2. 49 smoothed data points at 5K intervals from $-30°$C to $210°$C are available.

3. The data appear quite reliable partly because of smoothing. Yet the smoothing did not obliterate any major transition.

4. The data reveal three apparent transitions: $T_\beta < T_g$, T_g, and $T > T_g$. The authors recognized and discussed the latter two. They ruled out degradation as a source of the slope increase in the α—T plot above T_g and referred to it as a liquid–liquid transition. It is an unusually strong slope change for T_{ll}.

1. Following our recommended procedure, all 49 data points were plotted by the X—Y recorder for general inspection. Since all points seemed in order, this plot is not shown but the data points can be inspected in Figure 6.

2. A linear model fit is shown in Figure 6.

3. The residuals plot RES/SE is given in Figure 7. It appears to consist of four straight line segments, the middle two of which are connected by a curved section, as in Figure 1. Hand-drawn lines AB and CD intersect opposite data point no. 22 at $75°$C, which is the T_g stated by the authors. A deviation from line AB starts opposite point no. 10, at ca. $15°$C. This is T_β, which does not appear in the derivative plot of the authors (their Fig. 4). This gives a T_β/T_g of 0.86 which is somewhat high for the general run of vinyl polymers but not unreasonably above the average of 0.75.[5,6] A more pronounced slope change opposite point no. 39, ca. $160°$C, appears to signify T_{ll} for a T_{ll}/T_g of 1.24. A more exact value of T_{ll} is derived later. T_{ll} is usually near (1.20 ± 0.05) T_g.[7]
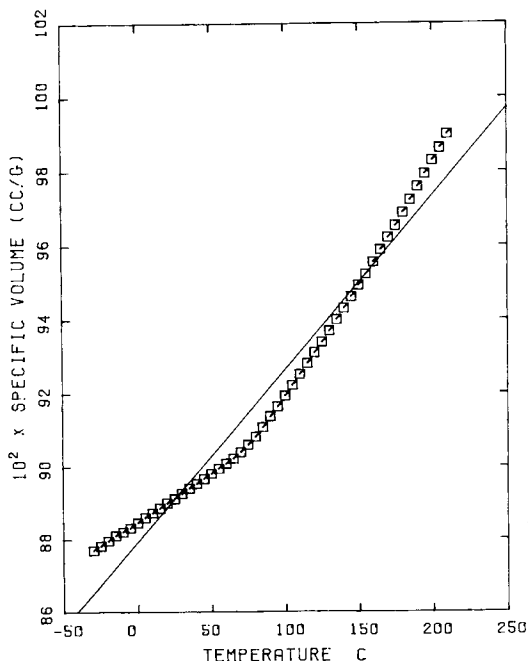

Fig. 6. Linear model fit to all 49 data points for poly(cyclopentyl methacrylate), using the tabulated V—T data of Wilson and Simha.[15]
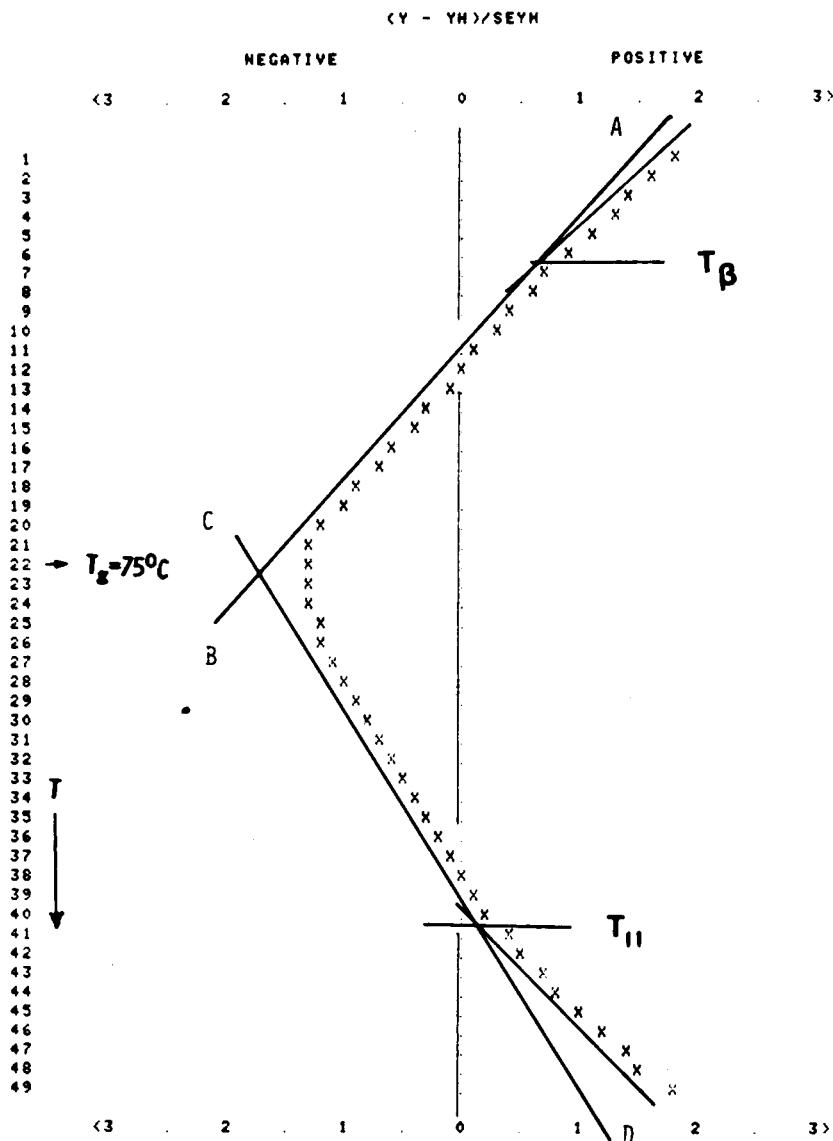
Fig. 7. Computer-printed residuals/standard error in Y(calculated), RES/SE, for the linear model of Figure 6. Temperature is increasing from top to bottom. Four straight lines are drawn along the RES/SE values with intersections near data points nos. 10, 11; 22, 23; and 39, 40, suggesting three transitions. The major transition near 75°C is T_g from intersection of AB and CD.

4. A plot of data above T_g from 80°C to 210°C was prepared with a linear fit, but is not shown.

5. Figure 8 represents the RES/SE printout for this linear fit of 27 data points between 80°C and 210°C inclusive. Comparison with Figure 3 does not yield a clear choice as between C, D, and E linear.

6. We next test the quadratic model shown in Figure 9 which appears to the eye as an excellent fit. However, the outset to Figure 9 giving RES/SE clearly rules out the quadratic model.
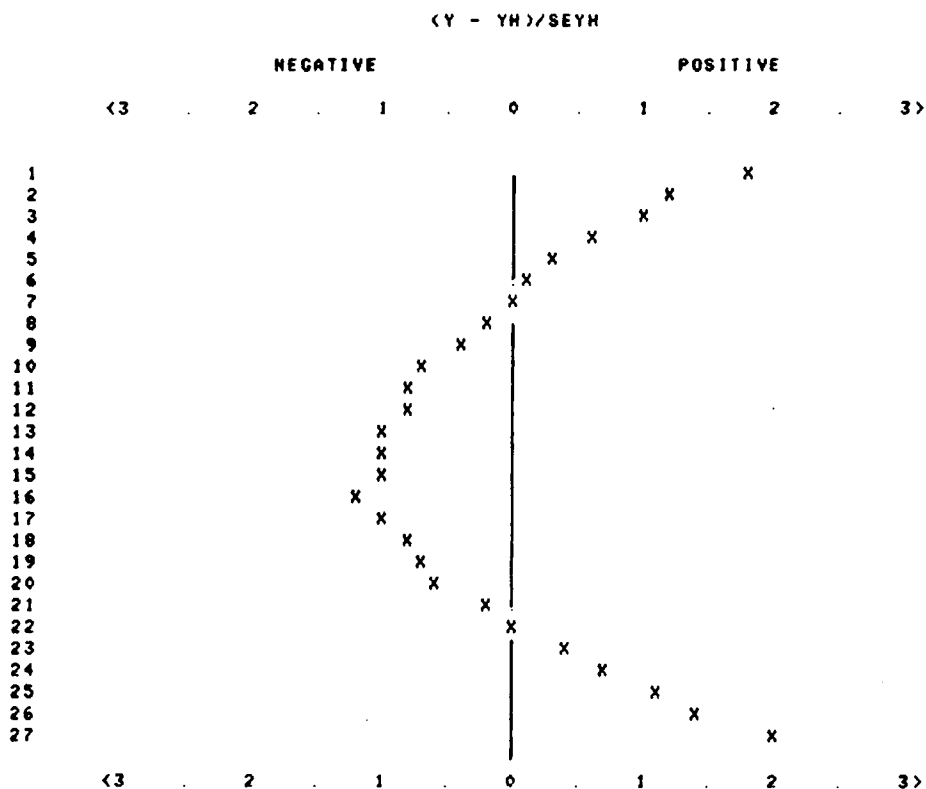
Fig. 8. RES/SE printout for a straight line model to all points above T_g, namely from 80°C to 210°C. The nonrandom pattern is somewhat inconclusive as between models C, D, and E for a linear fit in Figure 3.

7. A model for two straight lines but with points on the curved connecting section removed is shown in Figure 10. Lines L_1 and L_2 intersect at ca. 149°C and appear to give a quite satisfactory fit. Had the quadratic model not been discarded, elimination of data points on the curved section might be a questionable procedure.

8. However, the RES/SE printouts for these two lines, shown on Figures 11(top) and (bottom), respectively, demonstrate distinctly nonrandom patterns, which don't match any discrimination pattern in Figure 3 (linear) except, crudely, E.

9. Figure 12 shows the double quadratic model discussed in connection with Figure 2. As mentioned in the discussion of eq. (8), it would be difficult to locate the intersection of these two quadratics, even with the quadratic coefficients available. The inset to Figure 12 represents dV/dT for these same data, clearly supporting the double quadratic model and indicating an intersection near 148°C.

10. As a check, Figure 13 presents the RES/SE patterns for the lower and upper quadratic fits. With seven and five crossovers, random patterns are confirmed. Tests for the number of crossovers are available. See Ref. 22.

The existence of an intersection temperature T_i above T_g is thus amply confirmed. It is most readily demonstrated by the two straight line model or by
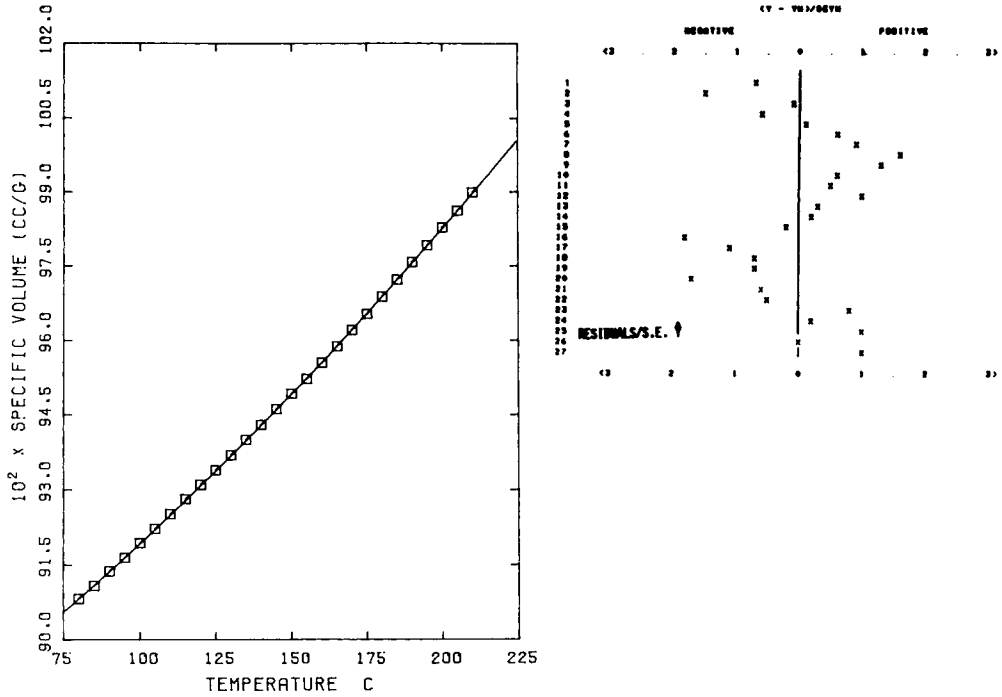
Fig. 9. Computer drawn quadratic fit which gives the nonrandom RES/SE pattern shown in the outset, thus ruling out a quadratic.

dV/dT. However, its presence is indicated by the other devices used, as summarized in Table III.
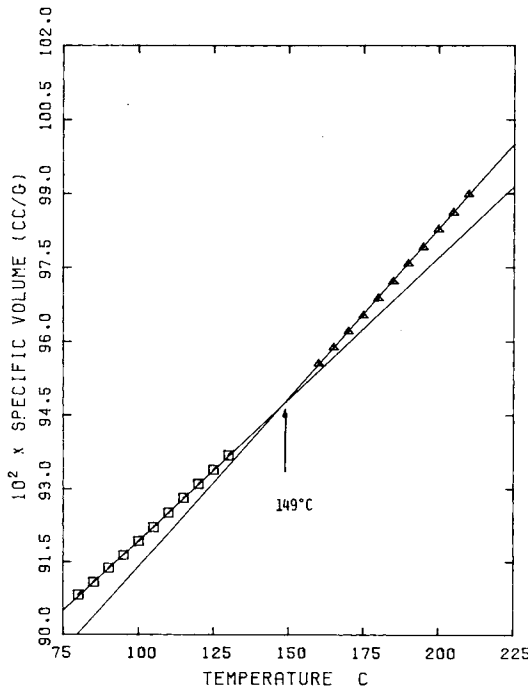

Fig. 10. A two-straight-line model fitted to data, with points on curved section not included. A T_i value near 149°C suggests a transition.
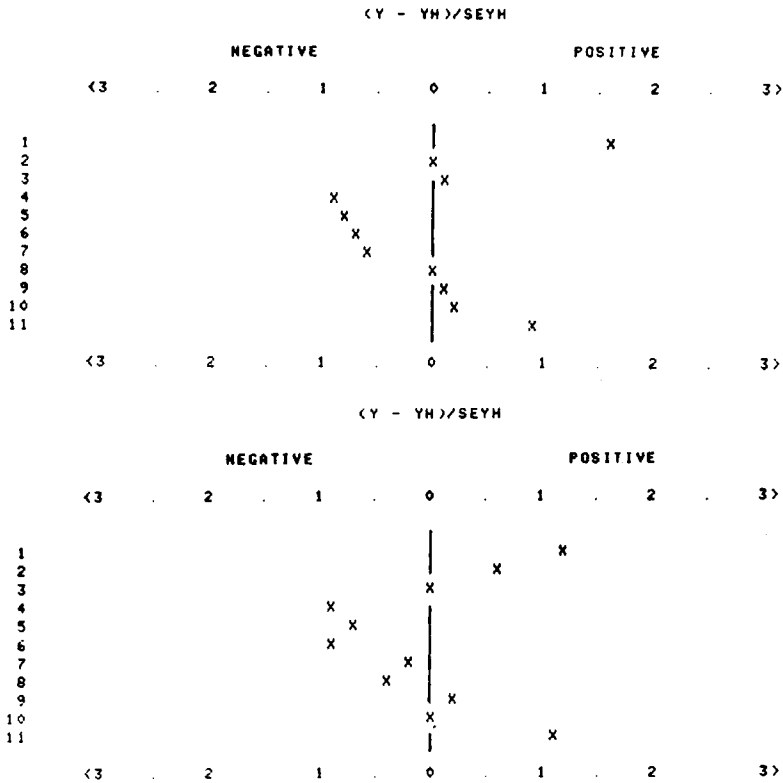
Fig. 11. Top, RES/SE printout for the lower straight line L_1 of Figure 10; bottom, the same for the upper line L_2. Distinct nonrandom patterns rule out the two-line model.

Meaning of T_i Values

The regression analysis program just presented for PCPMA gives a rather detailed description of the tabulated data reported by Wilson and Simha.[15] Three intersection temperatures are suggested. The slope change near 75°C is so strong that this must be T_g for this amorphous polymer. This is fully confirmed by the α—T plot of the authors (Fig. 4 of Ref. 15) in which α jumps from its glassy state value of 3×10^{-4} deg^{-1} below 75°C to about 6×10^{-4} deg^{-1} above.

Concerning the weak transition near 10°C, we properly should have applied regression analysis in the temperature range of -30°C to about $+40$°C. However, since most vinyl polymers have a β process near $0.75\ T_g$,[5,6] there is little reason to question the identity of this T_i value.

TEST FOR T_g

In the more general situation, especially with data on a newly synthesized polymer, one may not know the value of T_g a priori. A set of data lying on either side of the 75°C intersection in Figure 7, say from 25°C to 125°C, should be examined, first by the linear and the quadratic models and next by two straight lines, possibly omitting the points on the curved section. These lines should intersect at or near 75°C. The slope of line 1 (L_1) is the expansivity, $\beta = dV/dT$.
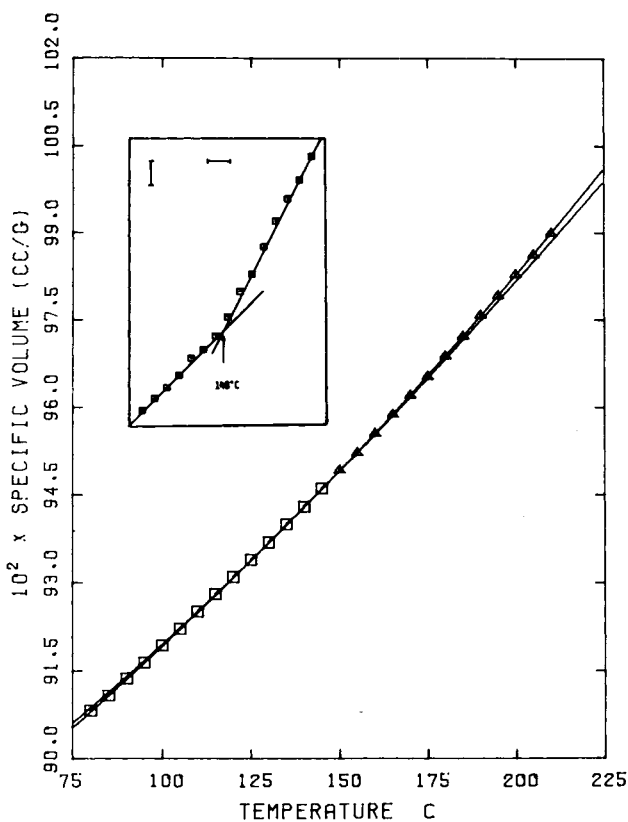
Fig. 12. Double quadratic as in the model of Figure 2. The inset shows the computer calculated first derivative, dV/dT, confirming the double quadratic model and locating the T_i at 148°C. Inset scale markers: vertical, 1×10^{-5} cc·g^{-1}·deg^{-2}; horizontal, 10K.

β_1/V_i, where V_i is the extrapolated volume at T_1, gives α_1. If T_i is T_g, this value of α_1 is α_g and normally is close to 2×10^{-4} deg^{-1}. Similarly from L_2 we get β_2 and α_2. If T_i is T_g, $\alpha_2 = \alpha_l$ and normally would be near 5–6 $\times 10^{-4}$ deg^{-1}. By the Simha–Boyer rule,[34] $\Delta\alpha T_g$ should be about 0.11, where $\Delta\alpha = \alpha_l - \alpha_g$. Also, $\alpha_l T_g \simeq 0.16$.[34] If the polymer in question has a strong secondary β relaxation below T_g, α_g will be greater than 2×10^{-4}, $\Delta\alpha T_g < 0.11$, but $\alpha_l T_g$ still should be close to 0.16.[34] These criteria for T_g have been shown graphically in Figure 10 of Ref. 6, which also includes the examples for semicrystalline polymers. If the polymer is amorphous and if $\alpha_l T_1$ is much less than 0.16, then T_i is not T_g. Failure to apply these numerical criteria may cause an incorrect assignment of T_g, especially for semicrystalline polymers.

The main area of controversy concerns not T_g but the liquid state above T_g, for which polymer scientists generally expect V to increase as a smooth power function of T. This view has been strongly expressed by Patterson et al.,[35] who state, without supporting evidence, that density ρ should decrease above T_g as T^3. These authors ascribe past efforts by one of us (R.F.B.) to find intersecting straight lines in $V\text{—}T$ data above T_g as "unwarranted and fruitless." This controversy belongs elsewhere and indeed has been so treated.[7,8]

Since we confirm by regression analysis the finding of Wilson and Simha by dV/dT of a sharp slope increase above T_g in PCPMA, and since such a finding
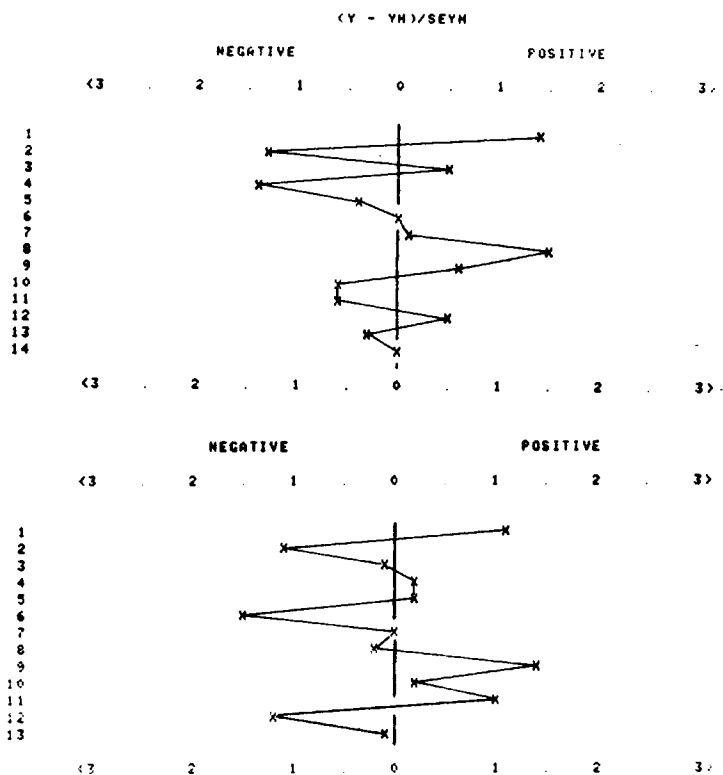
Fig. 13. Top, RES/SE random pattern for the lower quadratic Q_1; bottom, the random pattern for the upper quadratic Q_2. Consecutive RES/SE points are connected in each case by light construction lines to emphasize crossovers of the 0,0 locus.

appears to flaunt conventional wisdom, one should repeat the question of Wilson and Simha about possible effects arising from thermal decomposition.

Methacrylates are known to degrade thermally to monomer. Monomer in a dilatometer could have either or both of two effects: (a) If it volatilized, an exponential increase in volume should be observed arising from increased rate of production of monomer and increased vapor pressure, both with increasing T. (b) If the monomer remained dissolved in the polymer, thermal expansion would increase because of the greater free volume associated with the monomer. But again the slope change should be exponential as the rate of production of monomer increased with T. Since the volume increase above T_i is as a mild quadratic only slightly greater than linear, we agree with Wilson and Simha that thermal decomposition is not the cause of T_i near 150°C. They based their conclusions on other considerations.

In addition, we have examined other types of physical evidence for a $T > T_g$ transition in a-PMMA,[8,36] i-PMMA,[36,37] and poly(cyclohexyl methacrylate).[8]

We have included this discussion to elaborate on the distinction between what the experimental data tell us, namely, $V = f(T)$, as contrasted with how this might be interpreted. Both have been the subject of confusion and controversy in the past. We feel that the methods advocated herein can answer precisely what the physical data say. Regression analysis cannot tell what the data mean. Except for an unpublished DSC trace, we have not located other physical evidence for T_{ll} in PCPMA.

OTHER REGRESSION ANALYSIS STUDIES

While these regression analysis techniques were being developed, they were tested on other sets of data as follows:

1. C_p—T data on polyisobutylene;[38] atactic PS;[7] poly(pentene-1) and poly-(hexene-1);[8] and several styrene–butadiene elastomers.[8]
2. V—T data on anionic PS[7,8] and PMMA's of varying tacticity.[36]
3. η_0—$1/T$ on several atactic polystyrenes[7,39] and polyisobutylene.[38]
4. Diffusion of organic penetrants through amorphous polymers.[40]
5. P—V—T data on polymers.[8,37,41,42]

None of these studies were as sophisticated as the present one on PCPMA.

In addition to the above studies dealing with transitions, we have used regression analysis to obtain linear correlations of various polymer physical properties with cross-sectional areas per polymer chain as follows: Mooney–Rivlin constants;[43] chain entanglements;[44] surface fold energy;[45] chain stiffness;[46] and tensile strength.[47]

We applied regression analysis to isobaric P—V—T data for the liquid state of poly(n-butyl methacrylate), as shown in Figure 13 of Ref. 8. A T_{ll} transition was evident at pressures of 1–200 bars but was completely suppressed at higher pressures. Isothermal V—P plots on PS, PIB, PVAc, and i-PMMA were able to reveal T_{ll} and other liquid state transitions but did not require regression analysis.[37,41] Development of a linear form of the Tait equation for isothermal V—P data does rely on regression analysis and residuals.[42]

FUTURE PLANS

The second paper in this series involves a detailed regression analysis study, already completed, on multiple trasitions in poly(vinylidene fluoride), based on unpublished length-temperature data of Mandelkern, Martin, and Quinn.[48] This polymer, with 45% crystallinity, is much more tractable than polyethylene, although its multiple transition behavior is similar, as will be emphasized.

We have plans for a paper on C_p—T and H—T data analysis. This does not involve any new principles of regression analysis but will emphasize physical differences over V—T data and will provide a guide to the available literature.

Other potential papers include a detailed study of V—T data on PS, isothermal V—P data on selected polymers, and V—T data on liquid hydrocarbons as analogs of PE.

SUMMARY

1. Computerized standard statistical procedures for linear and polynomial regression analysis have been organized into a routine for the analysis of physical data on polymers in the region of known or suspected transitions such as the glass temperature T_g, sub–glass temperatures, and liquid state transitions above T_g.

2. While the methods are general to $Y = f(X)$, emphasis in this paper is on $X = T$ and Y = volume or length. Other variables with temperature or T^{-1} include heat content and specific heat, zero shear melt viscosity η_0, and diffusion constant D_0. These have been examined elsewhere or may be discussed in subsequent papers in this series.

3. For simplicity, this paper considers data on amorphous polymers only, although a treatment of semicrystalline polymers follows.

4. To assist in interpretation of unknown data, several models have been proposed: (a) one straight line, (b) two straight lines, (c) two straight lines connected by a curved section, (d) three straight lines, (e) quadratic, (f) two intersecting quadratics, (g) variations of the above. Sets of synthetic data for (a)–(e) were developed, containing a random error of 0.075% to simulate high quality real data.

5. This synthetic data has been subjected to regression analysis to generate a set of discrimination patterns useful in testing real data of unknown characteristics.

6. Main reliance is placed on residual patterns when checking a model against real or synthetic data. A residual, RES = Y(observed) − Y(calculated) [designated $Y - \hat{Y}$], and/or RES/SE, where SE is the standard error in $\hat{Y}$, is printed out or plotted out against running values of X.

7. A major goal has been to develop more objective procedures than simple visual inspection, thus permitting the analysis of unknown data in a manner freer from potential bias on the part of the investigator.

8. Other standard statistical quantities are used where indicated such as coefficient of correlation and derivatives, dY/dX, d^2Y/dX^2.

9. Real data present more problems in analysis than do synthetic data for various reasons: (a) less accuracy, (b) too few data points in the region of a transition, (c) systematic errors such as a time or temperature drift, (d) general complexity of real vs. model behavior.

10. This regression program attempts to define the course of a real body of data, $Y = f(X)$, regardless of imperfections in the data. Interpretation of the physical meaning of this data is beyond the scope of regression analysis. Personal intervention is required.

APPENDIX: SOURCES OF SPECIFIC VOLUME DATA

For the convenience of readers Table IV lists key sources of specific volume–temperature data, not all of which were used in this paper. This is not presented as an exhaustive literature search. We have on occasion obtained from the original authors their tabulated $L-T$ or $V-T$ data, even though they published their results in graphical form. None of these sets of data was used herein. References to other published data may be found in the Simha–Boyer papers.[34] We cite a few $P-V-T$ papers which give relative volumes only or which give $P-V-T$ specific volumes at only a few temperatures. These are cited in our $P-V-T$ studies.[37,41] In general, tabulated data are no longer published because of the pressure on journal space. Some journals, such as *Macromolecules*, provide for making such data available in supplementary form.

TABLE IV
Some Sources of Tabulated V—T Data on Amorphous Polymers[a]

Polymer	Temperature range (°C) From	To	No. of temperatures	Ref.
1. Polyethylene (branched)[b,c,d]	19.1	198.0	8 (above T_m)	e
2. Polyethylene (linear)[b,c,d]	19.5	199.7	7 (above T_m)	e
3. Polyethylene (high mol. wt.; linear)[b,c,d]	18.7	199.5	6 (above T_m)	e
4. Polystyrene (atactic)[b]	7.7	75.4[f]		
	115.4	195.6	6	g
5. Poly(orthomethyl styrene)[b]	29.1	81.9[f]	8	
	139.4	197.7		g
6. Poly(vinyl acetate)[b]	−30	100[h]		h
7. Poly(methyl methacrylate)[b,c] (atactic PMMA)	17.2	159	13	e
8. iso PMMA	−35	200	48	i
9. iso PMMA[b]	8.8	190.2	12	j
10. Poly(cyclopentyl methacrylate) (PCPMA)	−30	210	49	i
11. Poly(cyclohexyl methacrylate) (PCHMA)	−30	220	51	i
12. PCHMA[b,c]	18.6	198.9	17	e
13. Poly(n-butyl methacrylate)[b,c]	12.2	199.5	16	e
14. Polydimethylsiloxane[b,c]	25	70	4	k, l

Note: Hellwege et al.[m] give PVT data in the form of relative volumes for polymers corresponding to 1, 2, 4, and 7 above as well as hard PVC. Specific volumes are given at one pressure and a few temperatures. Beret and Prausnitz[n] present PVT data as relative volumes at a few temperatures for Polymers 6 and 14 above and also polyisobutylene. Kubota and Ogino[o] give PVT data as relative volumes for Polymer 14 above at five temperatures from 29 to 60°C.

[a] Atmospheric pressure unless noted; see footnote b.

[b] Also V_{sp} values at elevated pressure.

[c] Supplementary material, including full sized tables available from American Chemical Society. See end of each reference for details.

[d] Included because of data on molten polymer.

[e] O. Olabisi and R. Simha, *Macromolecules*, 8, 206 (1975).

[f] Data on either side of T_g omitted because of time effects.

[g] Ref. 14.

[h] Smoothed data. J. E. McKinney and M. Goldstein, *J. Res. Natl. Bur. Stds.*, 75A, 331 (1974).

[i] Ref. 15. Smoothed data.

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[l] Similar data on six different molecular weights.

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