

NEW DATA PROCESSING TECHNIQUES IN FT-IR SPECTROSCOPY

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Abstract - Spectroscopic methods have been developed for measuring the structural conformational compositions of polymers. The number of spectroscopically distinguishable conformations is determined using a factor analysis approach based on the examination of a range of samples with different compositions. The spectra of the pure structures are obtained from the spectra of the mixtures using a deconvolution technique based on the ratioing of the absorbances. Calibration of the absorptivities is accomplished using an internal technique requiring the fractions of the conformations to sum to unity. Finally, a least-squares curve-fitting technique is used to fit the spectra of the mixtures using the spectra of the pure components. In this manner, a sensitive quantitative method for the determination of the structural composition in polymers has been developed and has been applied to investigate structure property relationships.

INTRODUCTION

It is the objective of most studies of polymer structure to develop the basic understanding necessary to optimize the structure to produce improved properties (Ref. 1,2 & 3). One of the instrumental techniques often used is infrared spectroscopy. However, classical infrared spectroscopy suffers from low sensitivity and the number of applications was correspondingly limited. A major development has been the application of interferometric techniques to infrared instrumentation leading to what is termed as Fourier transform infrared (FT-IR) spectroscopy. The increased energy throughput and the multiplex advantage lead to substantial increases in sensitivity. Additionally, the availability of a dedicated computer leads to utilization of powerful data processing techniques which further improve the resolution of structural differences by infrared spectroscopy.

The purpose of our work is to put forth an analytical method or algorithm using vibrational spectroscopy by which the structural components in a polymeric system can be evaluated, spectroscopically separated, and finally quantitatively analyzed. The problem bears distinct similarity to the spectroscopic separation and analysis of an n-component mixture system where n is initially not known. The application of the algorithm and its approach has been tested for binary mixtures of hexane and cyclohexane and recently applied to PET. In general, the method should be applicable to all n-component mixtures where the number of components and their individual spectra are unknown. Of course, n shall be as small as possible because the difficulties increase with n.

Critical to the analysis is the development of a means to calibrate infrared spectra (on an absorbance scale) of individual components of an unknown mixture. This, however, must be accomplished without the benefit of the spectra of the pure components since for polymers, no pure systems are available. It has to be done solely with the spectroscopic information available in the mixture spectra themselves. The quantitative ratio methods (Ref. 4) have been applied to both the model hexane/cyclohexane system and PET.

The components of the algorithm include factor analysis, quantitative application of the ratio method, and least-squares curve-fitting of infrared (IR) spectra.

Confronted with the task of analyzing a series of unknown mixtures, the infrared spectroscopist has had several options to follow. He might identify specific strong bands that belong to a suspected component, obtain a pure spectrum of the suspected component, and then remove from consideration those bands of the mixture spectrum due to the identified component. The process is repeated for the remaining bands in the mixture spectra. This process has progressed to the state where computerization of the technique is available (Ref. 5).

Once knowledge of the component spectra in a mixture is achieved, a series of calibration curves are produced. These standard curves relate concentration to absorbance using Beer's law. By interpolation, the concentration of the components of the mixture are graphically or

numerically obtained. The advent of computerized infrared spectroscopy has allowed the spectroscopist to digitally subtract out components from a mixture. The convenience of computerized spectroscopy coupled with Fourier transform methods yields excellent sensitivity and spectral registration.

An analogy can be drawn between the composite infrared spectra arising from n-component mixtures of simple organic solvents and the composite spectra resulting from differing chain conformations in amorphous polymer glasses. Spectra assignable to individual components of the mixture should produce the mixture spectrum upon linear co-addition. In order to study the amorphous phase, it will be necessary to analyze mixture spectra for the number of basis spectra or the number of conformations. It will also be necessary to obtain the individual component spectra properly scaled in order that a quantitative analysis of the mixture be performed. This would require a method of internal calibration of the component spectra for measuring the amounts of polymer conformations. Pure component spectra for any given chain conformation cannot be externally measured since the pure sample is unobtainable.

The quantitative analysis of chain conformational mixtures, would therefore, seem to pose an intractable problem. However, a number of methods which have recently been applied to infrared spectroscopy allow a systematic approach to investigating mixtures. Factor analysis is a method for determining the number of components in a series of mixtures. Antoon, D'Esposito, and Koenig have shown the utility of the method applied to infrared spectra (Ref. 6). The absorbance ratio method has been utilized to deconvolute mixture spectra into component spectra (Ref. 7 & 8). Necessary to this study where external calibration of component conformer spectra is obtainable, a refinement of the ratio method leads to a method of internal calibration (Ref. 4). Least-squares curve-fitting of component spectra to mixture spectra as shown by Antoon, Koenig and Koenig, (Ref. 10) provides a method more quantitatively accurate and reproducible than peak intensity or area measurements of absorbance.

The integrated use of the above techniques have been utilized to study the amorphous and semicrystalline phases of poly(ethylene terephthalate). Factor analysis was used to determine the number of spectrally discernable components in a series of PET films possessing varied thermal histories. The two rotational conformations of the glycol linkage of the polymer repeat differ in dihedral angle. The gauche conformer has an angle of 60° with methylene units rotated out of the plane containing the terephthalate carbon atoms. The predicted slightly more stable trans conformer adopts a 180° dihedral angle and is the chain extended conformation. X-ray crystallographic study of PET by Daubeney, Bunn and Brown (Ref. 11) and a later study by Kilian, Halboth, and Henckel (Ref. 12) show that the trans conformer is exclusively the crystalline conformer. Tomashpol'skii and Markova reached a similar conclusion using electron diffraction analysis (Ref. 13).

The quantitative ratio method was used to separate the conformational spectra and provide the necessary internal calibration of the component conformer spectra. Least-squares curve-fitting of these gauche and trans PET spectra was performed to measure the amount of the conformers in PET samples. The amount of trans conformer in the crystalline phase for annealed PET films is subtracted from the total amount of trans content if spectroscopic distinction cannot be made between the two. Crystallinity measurements utilizing a density gradient column are therefore necessary. In this manner, a conformational analysis of the amorphous phase of semicrystalline PET can be made.

EXPERIMENTAL APPROACH

Method of factor analysis

Factor analysis is a mathematical procedure for determining the number of linearly independent components in a set of mixtures. This procedure has been useful in analyzing ultraviolet-visible spectra (Ref. 14) and mass spectrometric data (Ref. 15). Recently in our laboratory, infrared spectra of mixtures have been investigated using the techniques of factor analysis. Studies performed by Antoon, D'Esposito, and Koenig involved binary and tertiary mixtures of ortho, para, and meta xylenes (Ref. 6). The curing kinetics of epoxy resin systems have also been subjected to factor analysis (Ref. 16). Presented with a series of PET film spectra, each film possessing a different thermal history, factor analysis performed on this set of mixture spectra should provide the number of spectroscopically separable conformational components.

Consider a matrix, A, dimensioned m by v where m represents a given mixture spectrum and v the absorbance value for the spectrum m at each measured frequency or spectral element (in cm^{-1} for infrared data). This represents a simple listing in matrix form of the mixture spectra of this A matrix. The rank will be equivalent to the number of linearly independent basis column vectors (basis spectra) which make up the A matrix (series of mixture spectra).

The task of determining the rank of A is accomplished by first multiplying A by A^T (A transpose) yielding a matrix, C, termed the covariance matrix. This is shown in Fig. 1. The dimensions of the covariance matrix are abridged to m by m. For a set of 10 mixture spectra,

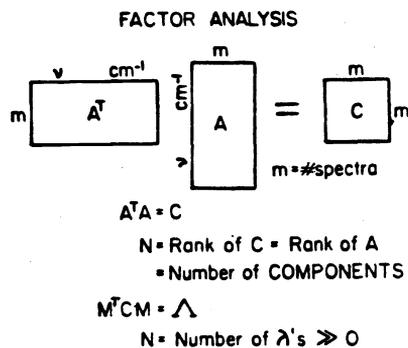


Fig. 1. Method of factor analysis: A - spectral matrix; B - covariance matrix; Λ - eigenvalue matrix.

the covariance matrix will therefore, have the dimensions of 10 by 10. Matrix algebra holds that the rank of the C matrix is equal to the rank of the A matrix, the desired result. The rank of the C matrix, hence the rank of the A matrix, is identical to the number of non-zero eigenvalues of the C matrix.

The C matrix is diagonalized and its eigenvalues (A matrix) computed using standard algorithms. The eigenvectors can also be calculated. In practice, random noise in the spectra will contribute small positive eigenvalues. However, the magnitude of these eigenvalues is sensitive to the signal-to-noise ratio of the spectra. This procedure has been installed as a Fortran program where the input consists of the mixture spectra file names and the output lists the determined eigenvalues of the C matrix. A plot of the common logarithm of the eigenvalues versus component index has been shown by Ohta (Ref. 17) as useful in determining the number of non-zero eigenvalues.

Determination of component spectra using the ratio method

An absorbance ratio method has been applied to mixtures of simple organic solvents by Hirschfield (Ref. 7) and also to polymer systems by Antoon, D'Esposito, and Koenig (Ref. 8). Ratioing infrared spectra in these studies allowed the component spectra to be determined without chemical or physical separation. It has been shown that not only does the method provide a means of spectrally separating the components, but it can also determine the relative concentrations of the components without external calibration (Ref. 4).

Consider a binary mixture system. Equations 1 and 2 describe two possible spectra resulting from such a mixture. M_1 and M_2 represent the mixture spectra each composed of a pure component absorbance, a_1 , multiplied by a concentration factor, c_1 . The equations are written assuming equal and constant pathlengths and are straight-forward from the Beer-Lambert law.

$$M_1 = a_1 c_1 + a_2 c_2 \quad (1)$$

$$M_2 = a_1 c'_1 + a_2 c'_2 \quad (2)$$

$$M_2/M_1 = a_c c'_1 + a_2 c'_2 / a_1 c_1 + a_2 c_2 \quad (3)$$

They apply to each spectral element (at every frequency throughout the infrared spectrum). Equation 3 defines the ratio spectrum of M_1 and M_2 when taken over all spectral elements. In regions of the ratio spectrum where the spectral contribution of component 2, a_2 , is absent (at a frequency equal to ν_1), the ratio is simply the ratio of the concentration factors for component 1. Similarly, the ratio of the concentrations for component 2 are obtained in regions of the spectrum where a_1 is absent. Equations 4 and 5 detail these two cases and serve to define the ratio coefficients R_{ν_1} and R_{ν_2} (R_1 and R_2 for simplicity) which are the experimentally obtainable quantities for a binary mixture system. Since the concentration factors are defined as volume fractions, they must add to unity for each mixture.

$$\text{For } \nu_1 \quad M_2/M_1 = a_1 c'_1 / a_1 c_1 = c'_1 / c_1 = R_{\nu_1} = R_1 \quad (4)$$

$$\text{For } v_2 \quad M_2/M_1 = a_2 c'_2 / a_2 c_2 = c'_2 / c_2 = R_{v_2} = R_2 \quad (5)$$

$$c_1 + c_2 = c'_1 + c'_2 = 1 \quad (6)$$

Combining equations 4, 5 and 6, a solution for the concentration coefficients as a function of R_{v_1} and R_{v_2} yields equations 7.

$$c_1 = 1 - R_2 / R_1 - R_2 \quad c_2 = R_1 - 1 / R_1 - R_2 \quad c'_1 = R_1 c_1 \quad c'_2 = R_2 c_2 \quad (7)$$

Also having the mixture spectra M_1 and M_2 , the unmixed and internally calibrated pure component spectra A_1 and A_2 are obtained as shown in equations 8 and 9 respectively.

$$A_1 = (1/1 - R_2)(M_2) - (R_2/1 - R_2)(M_2) - (R_2/1 - R_2)(M_1) \quad (8)$$

$$A_2 = (1/1 - R_1)(M_2) - (R_1/1 - R_1)(M_1) \quad (9)$$

It is important to emphasize that A_1 and A_2 are properly scaled to one another. This allows their direct use for least-squares quantitative analysis.

There are a number of restrictions on the use of the quantitative ratio method. Already mentioned is the requirement of equal sample pathlength or thickness. If they are not equivalent but known very accurately, their ratio can be used to correct the ratio spectrum, (Equation 3). Adherence to the Beer-Lambert Law and the linear addition of component spectra in a mixture spectrum are also prerequisites. As it was first reported (Ref. 7), there should exist many "flat" areas in the ratio spectrum defined by equation 3 at values corresponding to the ideal ratio coefficients. It is reasonable to accept that baseline slope and band overlap will modify this situation. Antoon, D'Esposito, and Koenig (Ref. 8) have shown in a computer simulation that due to these effects, the experimental numerical magnitude of the larger ratio coefficient will be slightly depressed. The smaller ratio coefficient will be slightly higher in magnitude than perfect spectra would give. For this reason, the extreme values of the ratio spectrum where absorption bands occur are used. Baseline correction to remove background and slope is performed on spectra prior to ratioing to help remove these artifacts.

The ratio method can be expanded to include as many components as required. Equations similar to equations 1 through 9 can be written for n-component, though, experience using infrared spectral mixtures beyond five components seems impractical. The number of mixture spectra necessary will always be n where n is the number of components. N-1 ratio spectra will have to be obtained to obtain the n(n-1) ratio coefficients.

It becomes easier to solve for the concentration factors for large numbers of components by writing the ratio method in matrix form. Consider a set of n mixture spectra each composed of n components. In analogy to equations 1 and 2, equations 10 result.

For $i = 1$ to n ;

$$\begin{aligned} M_1 &= c_{11}a_1 + c_{12}a_2 \dots c_{1n}a_n \\ &\vdots \\ &\vdots \\ M_n &= c_{n1}a_1 + c_{n2}a_2 \dots c_{nn}a_n \end{aligned} \quad (10)$$

Equations of this form are analogous to the matrix equation 11. The column matrix, M_v , represents the mixture spectra while the square matrices C_v and F_v represent the concentration factors and the pure component absorbances, respectively. The subscript v refers to the fact that such a matrix can be defined for every spectral element.

$$M_v = C_v F_v \quad (11)$$

If each of the mixture spectra is divided by M_1 (but not M_1 itself), the necessary n-1 ratio spectra are defined. N ratio coefficients are defined in each ratio spectrum, the total being n(n-1) unique coefficients. Division of M_1 by itself leads to n "1"s. Equation 12 shows the matrix formulation of the ratio coefficients, r_{ij} for an n component system.

$$\begin{array}{r}
 R_{11}=1 \quad R_{12}=1 \quad \dots \quad R_{1n}=1 \\
 \\
 R \equiv \begin{array}{ccc}
 R_{21} & R_{22} & R_{2n} \\
 \vdots & & \\
 R_{n1} & R_{n2} & R_{nn}
 \end{array}
 \end{array} \quad (12)$$

The task to perform is to use the experimentally determined r_{ij} 's in equation 12 with equation 11 to solve for the C matrix since it contains all of the concentration information. For a given mixture, the concentrations will assume a row matrix and can be calculated as shown in equation 13 through 15 where c is a row matrix of the concentration factors for each mixture, j, and b is also a row matrix of 1's.

$$c_{ij} R^T = b \quad (13)$$

$$c_{ij} = b(R^T)^{-1} \quad (14)$$

$$C_{ij} = r_{ij} c_{ij} \quad (15)$$

Equation 15 details the calculation of the desired C matrix. Having obtained it, the calculation of the F matrix is readily obtained using equation 16. Clearly, the elements of C^{-1} give the scaling coefficients which when performed and summed over each mixture spectrum, lead to the generation of each pure component spectrum.

$$F = C^{-1}M \quad (16)$$

Least-squares composition determination

The third step in the analysis of mixture spectra is to determine the relative amounts of each component in each mixture using the pure component spectra. The component spectra themselves can be externally measured or internally calibrated as is necessary for chain conformational mixtures in polymers. A least-squares curve-fitting method available in this laboratory (Ref. 10) represents a method for achieving this. The fitting equation employed is shown in equation 17.

$$\sum_{i=1}^N R_{i,j} = \sum_{j=1}^M x_j \left(\sum_{i=1}^N \omega_i R_{i,j} R_{i,k} \right) \chi_j \quad (17)$$

$$S_i = \sum_{j=1}^M \chi_j R_{i,j} \quad (18)$$

The number of spectral elements (data points) in each spectrum is N. The number of component spectra used in the fitting procedure is M. $R_{i,k}$ represents the absorbance data for the i^{th} spectral element of the k^{th} component spectrum. S_i is the data for the spectral range of the mixture spectrum. A statistical weighing factor, ω_i is equal to $1/S_i$. χ_j is the multiplier for each component spectrum which is optimized by the program. It is from these χ_j values which represent the volume fractions for each component that the complex mixture spectra are analyzed.

Described have been the three techniques that have been systematically applied not only to model mixtures but also to annealed PET films which contain a mixture of chain conformations. Figure 2 illustrates the computer-assisted method for both unknown mixtures and mixtures of amorphous polymer conformations in outline form.

RESULTS

Determination of conformational sequence resolution

The first determination required is the number of conformational sequences which are detectable under the conditions of the spectroscopic measurements. When the resolution of the frequency was 2 cm^{-1} and the signal-to-noise ratio improved by coadding of 100 scans, the question to be answered is whether only isolated trans and gauche isomers are detectable or whether pairs or longer sequences are contributing spectroscopic differences which can be

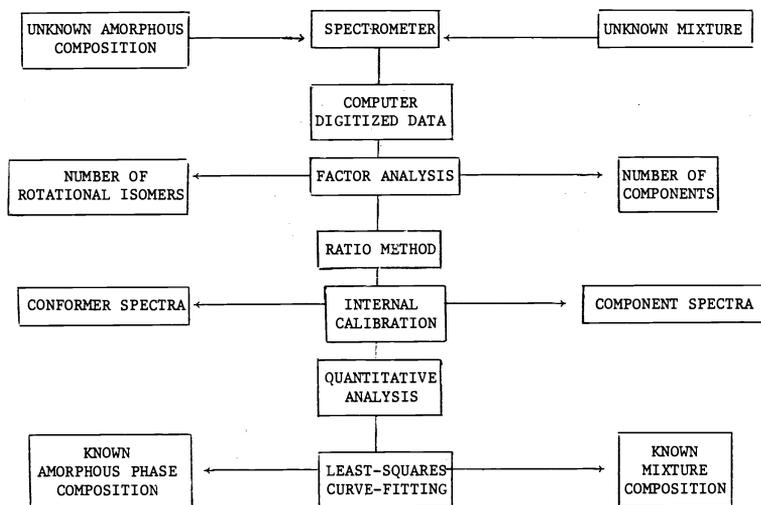


Fig. 2. The computer-assisted method for both mixtures and mixtures of amorphous polymer conformations in outline form.

resolved and detected under the measurement conditions. Additionally, since PET is a semi-crystalline polymer, the spectra of the trans isomer in the crystalline phase may be resolvable from the trans isomer in the disordered phase.

Factor analysis was used to make this determination. As indicated above, factor analysis required a series of mixtures with a range of concentrations of the components. For PET, this variation in relative concentrations was accomplished by annealing samples sequentially at an elevated temperature and examining the spectra after specified time intervals. Figure 3 shows the spectra (in the absorbance mode) for samples annealed at 230°C for the times indicated. Superimposed on the spectra are designations of those bands which have been assigned to the trans and gauche isomers from previous studies. The expected increase in the intensity of those bands associated with the trans isomer is observed as well as the decrease in the gauche isomers. The results of the factor analysis indicate that only two spectral components are being observed.

The presence of only two spectral components in the PET system is consistent with the observation of a trans and a gauche isomer. No intramolecular coupling is observed so pairs and longer sequences are not resolvable at this spectral resolution. Similarly, the spectra of the trans isomer in the crystalline and disordered phases must be sufficiently similar as not to be resolvable under these experimental measurement conditions. Subsequently, we established that the similarity of these two spectra is consistent with a small or negligible difference in the intermolecular forces between the trans isomer in the crystalline or disordered phase.

Determination of spectra of trans and gauche isomers of PET

The spectra of the two components, in this case, the trans and gauche isomers can be obtained from the spectra of the polymer by absorbance subtraction or the ratioing of the absorbances. The latter method is preferred particularly in those circumstances where characteristic bands of the components are available. For PET, these assignments are available and suggest that the absorbance ratios be based on the 973 cm^{-1} band for the trans isomer and the 898 cm^{-1} for the gauche isomer. The spectra obtained using the ratio method are shown in Fig. 4 for the gauche and trans isomers. These spectra have been scaled to 100% of each of the isomers and represent the specific absorbance spectra of each of the isomers. The ratio method was used for a number of different film pairs and the results were reproducible within the experimental error. This result verifies the observation of only two components by factor analysis.

These determined pure spectra of the trans and gauche isomer support the previous assignments based on experimental and theoretical results. The spectrum of the trans isomer has been calculated and is in good agreement with the observed spectrum given here. The spectral differences between the trans and the gauche isomer are rather striking when comparisons are made. These differences reflect the expected sensitivity of vibrational spectroscopy to conformational isomers.

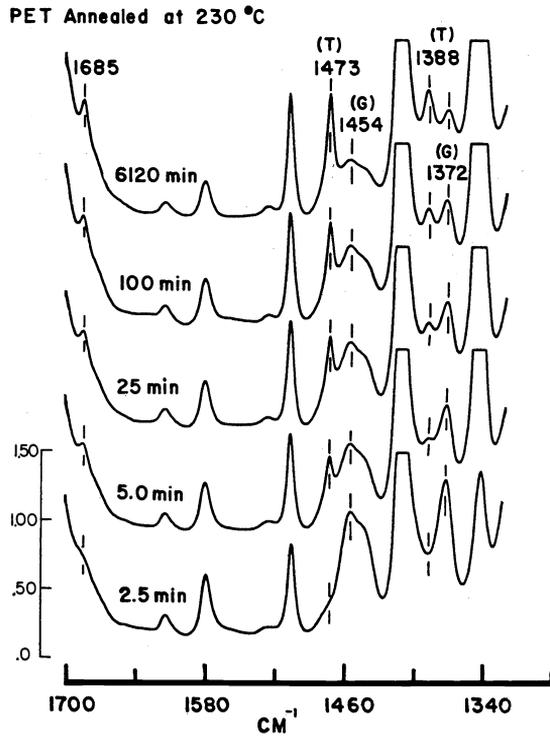


Fig. 3. Infrared spectra of PET films annealed at 230°C for various annealing times.

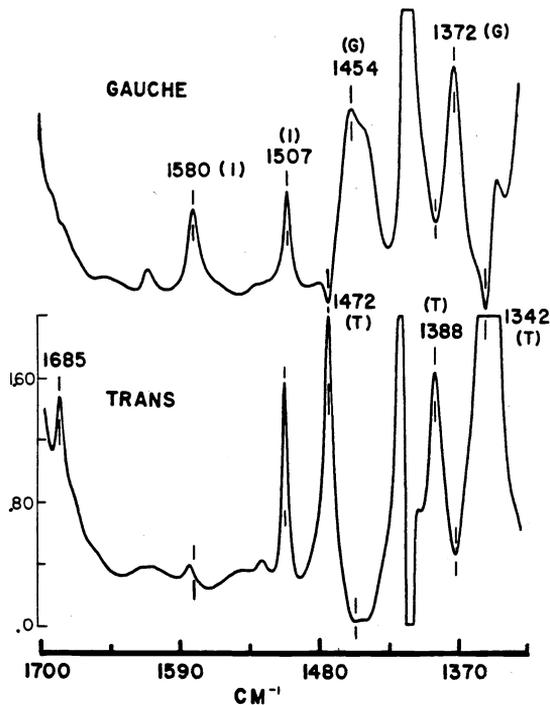


Fig. 4. Calculated spectra of pure trans and pure gauche isomers of PET.

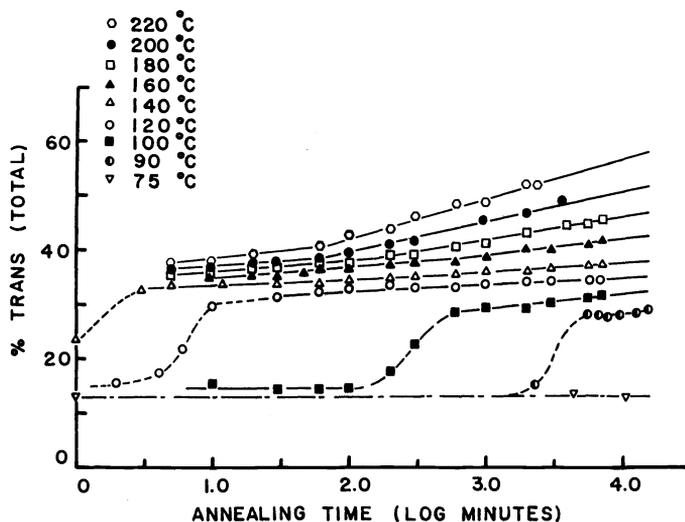


Fig. 5. The total trans isomer content versus annealing for various temperatures.

Quantitative determination of the conformational isomeric composition in PET

Using the pure spectra of the trans and gauche isomers it is possible to quantitatively determine their relative concentration in films of PET. We have used the least-squares curve-fitting technique to carry out the frequencies for the quantitative analysis. The results of this analysis for films of PET which were crystallized from the glassy state by annealing at various temperatures are shown in Fig. 5 for the trans isomer. The results for the gauche isomer are simply the difference since the total amount must be unity. The shapes of the curves are consistent with expectations, that is, for the lower temperatures a longer induction time, a slower rate of transformation and a lower limiting value at long times.

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