Communications to the Editor

On the Validity of a Commonly Employed Infrared Procedure Used To Determine Thermodynamic Parameters Associated with Hydrogen Bonding in Polymers

For more than two decades, infrared spectroscopic data obtained in the N–H stretching region of the spectrum of polyamides and polyurethanes have been employed to estimate the thermodynamic parameters associated with hydrogen bond formation.[1-7] In essence, previous authors have tacitly assumed that the N–H stretching region is composed of just two major contributions, attributed to "free" and hydrogen-bonded N–H groups, each of which may be measured by using an *average* absorption coefficient (a constant relating band area to concentration of functional groups present). Using this assumption, Schroeder and Cooper[3] devised an elegant procedure for determining the fraction of hydrogen bonded N–H groups at any temperature, which eliminates the necessity for curve resolving.

Essentially, these authors argued that the change in total area in the N–H stretching region observed upon raising the temperature is related to the fraction of bonded N–H groups that transform to "free" N–H groups. Although the two bands assigned to these groups have very different absorption coefficients, Schroeder and Cooper mathematically demonstrated that given the above assumption, and also assuming that absorptivity is not a strong function of temperature, it is not necessary to resolve the N–H stretching region, but rather just follow the change in total area as a function of temperature, employ measured absorption coefficients of the two bands, and use the information via an equilibrium scheme to obtain thermodynamic parameters. On the surface this appears to be a perfectly reasonable approach, but as we will attempt to show in this communication there is a serious flaw in this argument.

For illustrative purposes we will use the experimental results obtained from an amorphous polyamide (a polyamide synthesized from hexamethylene diamine and a mixture of terephthaloyl and isophthaloyl dichlorides, kindly supplied by E. I. du Pont de Nemours and Co. Thermal analysis reveals a T_g of about 135 °C and there is no evidence of a crystalline melting point). Figure 1 shows the FTIR spectra obtained for this sample in the N–H stretching region, from 3150 to 3500 cm^{-1}, recorded as a function of temperature. It should be emphasized that the spectra were obtained on the same sample and are displayed in absolute absorbance units, so that the obvious change in total area with increasing temperature is readily visualized. The weak, poorly resolved band at about 3444 cm^{-1} may be confidently assigned to "free" N–H groups. This is in agreement with previous results[2,3,6,8] and does not appear to be the subject of debate. This band *appears* to be increasing in relative intensity with increasing temperature, albeit marginally. However, this *apparent* increase predominantly arises from the fact that the broad hydrogen-bonded peak shifts to higher frequency with increasing temperature and the greater overlap of the two curves causes an increase in the peak height value at 3444 cm^{-1}.

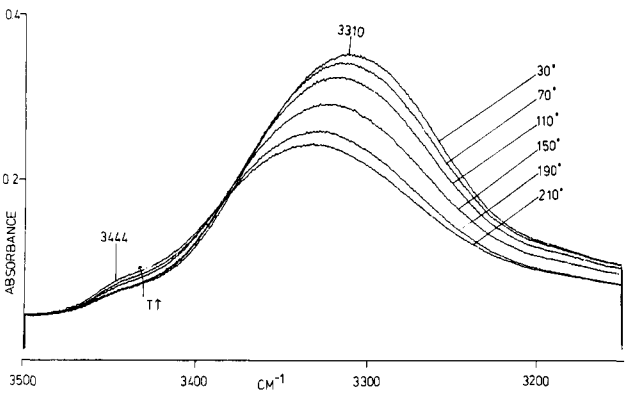

Figure 1. FTIR spectra from 3150 to 3500 cm^{-1} recorded as a function of temperature.

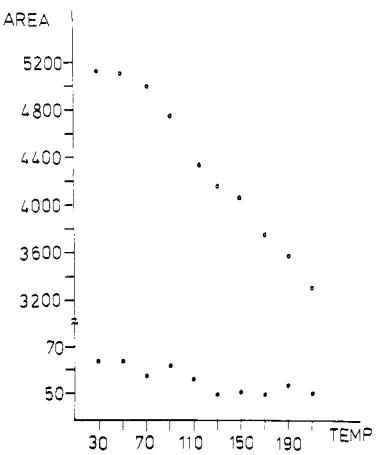

Figure 2. Plot of area vs. temperature for the bonded (○) (top curve) and "free" (●) (bottom curve) N–H bands.

Using a curve fitting procedure,[9] we have measured the area of the "free" N–H band and subtracted it from the total area of the N–H stretching region shown in Figure 1. The results are displayed graphically in Figure 2. The total area of the "free" N–H band is essentially constant, within experimental error. Certainly, there is no significant increase in the relative intensity of this band with increasing temperature. In contrast, the broad hydrogen-bonded N–H band shifts to higher frequency with increasing temperature and concurrently its area decreases dramatically.

This observation is central to our arguments and needs further elaboration. The broad band centered at 3310 cm^{-1} for the sample recorded at 30 °C is assigned to the hydrogen bonded N–H groups. The broadness of this band (in large part) reflects a wide distribution of intermolecularly hydrogen-bonded distances and geometries in the amorphous polyamide. As the temperature is raised, the peak position of the broad hydrogen-bonded band shifts to higher frequency and there is a considerable decrease in the total area of this band. In fact, there is a reduction of about 35% of the area of the hydrogen-bonded N–H band over a temperature range of about 30–210 °C. How then are we to explain this significant change in total area?

To reiterate, it has been tacitly assumed in previous studies that an *average* absorption coefficient may be employed for the hydrogen-bonded N–H stretching vi-

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bration and that this absorption coefficient does not change as the band shifts to higher frequency with increasing temperature. It is important to emphasize that this is completely different from the other stated assumption, that an absorption coefficient measured at a specific wavenumber does not vary significantly with temperature. An obvious initial approach to explain the reduction in area of the hydrogen-bonded N–H band with increasing temperature is to assume that as the hydrogen-bonded N–H band shifts to higher frequency a new *average* absorption coefficient is applicable. For example, if we consider the two spectra obtained at 30 and 210 °C (Figure 1) the peak maxima, ν_1 and ν_2, respectively, are separated by about 22 cm^{-1}. The ratio of the two areas (minus the contribution from the "free" N–H band) is $A_{210}/A_{30} = 0.645$. Accordingly, this would imply that the *average* absorption coefficient at 3310 cm^{-1} is about 1.6 times that at 3332 cm^{-1}. Whereas the above is conceptually simple, and has been presented to illustrate the general principle, it is, in fact, far too simple. The broad hydrogen-bonded peak spans a range in excess 200 cm^{-1}. In effect, the observed band is a superposition of numerous curves representing a range of strengths of hydrogen bonded N–H groups. The absorption coefficient of each of these bands may be very different, but presumably will vary in a systematic fashion with hydrogen bond strength and hence frequency.

We are currently in the process of developing a simple model to explain the change of absorptivity with the strength of the hydrogen bond. Very briefly, we are assuming that at any given temperature, T_1, there is a Gaussian distribution of hydrogen-bonded N–H groups of varying strengths centered about a mean position, ν_1, which corresponds to the average strength of the intermolecular interaction. Intuitively, this appears to be a reasonable assumption. One can readily envisage that at a given moment in the amorphous polyamide there will be N–H groups at varying distances and geometries from complimentary carbonyl groups. At some elevated temperature, T_2, the *average* strength of the hydrogen-bonded N–H groups will decrease leading to a distribution of identical form to that occurring at T_1, the only difference being the mean position, ν_2, which reflects the reduction of the *average* strength of the hydrogen bonds present at T_2.

If the broad hydrogen-bonded peak observed in the experimental spectra (Figure 1) reflected only the normalized weight fraction distribution of hydrogen-bonded species present, then we would anticipate identical curves of the same area centered at different frequencies corresponding to a particular temperature. This is not what is observed and the reduction in area observed experimentally upon increasing the temperature from T_1 to T_2 is assumed to be due to the variation of absorption coefficient, $a(\nu)$, with hydrogen bonding strength or frequency. This naturally assumes that any increase in the concentration of "free" N–H groups with increasing temperature (over the range of 30–210 °C) is insignificant. This appears justified by the curve fitting results displayed in Figure 2.

Can we theoretically justify a strong variation of absorption coefficient with frequency? The intensity, I_i, of a given normal vibration may be expressed in terms of the Beer–Lambert law

$$I_i = a_i bc \tag{1}$$

where a_i is the absorption coefficient, b is the path length, and c is the concentration of the species.

From the theory of infrared intensities,[10] I_i is also proportional to the square of the change in dipole moment, $(\partial\mu/\partial Q)^2$, with normal coordinate, Q:

$$I_i = C(\partial\mu/\partial Q)^2 \tag{2}$$

The dipole moment is related to the bond distance, r, and the effective charge, q, via

$$\mu = qr \tag{3}$$

It is well-known that the N–H bond length increases upon hydrogen bonding. This, of course, explains the decrease in frequency upon hydrogen bonding as the force constant of the N–H stretching vibration decreases. The effective charge, q, would also be expected to change with the strength of the hydrogen bond. As a result, changes in the parameters given in eq 3 will lead to a change in μ. As intensity is proportional to $(\partial\mu/\partial Q)^2$, it would be anticipated that the absorption coefficient should be a strong function of frequency.

Our preliminary studies suggest that it is possible to calculate the variation of the absorption coefficient with hydrogen bonding strength (and hence infrared frequency) from the experimental spectra. In fact, our initial calculations show a very strong dependence of the absorption coefficient with frequency. We will present these results in a future publication.

There are a number of important conclusions that arise from the experimental results and theoretical arguments presented in this work.

(1) The commonly employed procedure to determine the fraction of hydrogen bonded N–H groups in polyamides and polyurethanes at a given temperature from the N–H stretching region of the infrared spectrum is invalid because it does not take into account the strong dependence of the absorption coefficient upon band frequency (and, in turn, the strength of the hydrogen bond).

(2) As the fraction of hydrogen-bonded N–H groups at elevated temperatures has been underestimated in previous studies, the corresponding values of ΔH and ΔS acquired from van't Hoff plots are subject to unacceptable errors.

(3) The reduction in area of the hydrogen-bonded N–H band with increasing temperature is not simply a result of hydrogen-bonded N–H groups transforming to "free" N–H groups but is primarily due to the reduction in the value of the absorption coefficient as the overall strength of the hydrogen-bonded N–H groups diminishes.

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Registry No. (Hexamethylenediamine)·(terephthaloyl dichloride)·(isophthaloxyl dichloride) (copolymer), 66536-08-1; poly(imino-1,6-hexanediyliminocarbonylphenylenecarbonyl) (SRU), 58814-83-8.

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Michael M. Coleman,* Daniel J. Skrovanek, Steven E. Howe, and Paul C. Painter

Material Science and Engineering Department
The Pennsylvania State University
University Park, Pennsylvania 16802

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Conformational Energy Contributions to Energy Storage in Deformed Macromolecules

The stretching of a macromolecule by an external force results in an increase in the free energy of the macromolecule. Since this increase equals the work done on the polymer by the external force, it is usually referred to as energy storage.[1,2] Such free-energy storage in polymers deformed by shear and elongational flows has played an important role in models of turbulent drag reduction by polymeric additives by providing a mechanism through which energy transferred to the viscous sublayer can be dissipated even at very high Reynolds numbers.[2] Previous treatments[2-6] which used the Gaussian model for the free polymer chain addressed only the entropic contributions to free-energy storage, i.e., computed the reduction in the number of possible configurations of a macromolecule distorted by the flow, assuming that all the configurations are isoenergetic in the absence of the flow.

In this communication we estimate the importance of effects associated with the energetics of the conformational states of a macromolecule by using the rotational isomer state model[7] to analyze the free-energy storage in a deformed polyethylene-like chain. We assume that the polymer is free draining, i.e., that the flow interacts with all the monomers in the chain (no hydrodynamic screening effects[8]). Since for steady-state potential flow the frictional forces between the polymer segments and the flow field can be described by a potential,[9] we can associate a potential energy with each macromolecular conformation. Thus, assuming that a steady state is reached in the presence of the flow, the segment distribution will be given by the appropriate Boltzmann distribution. The analysis of the free-energy storage in semiflexible polymers in steady extensional flows is complicated by the fact that the potential energy associated with the monomer–flow interaction is a function of the vector $\vec{r}$ from the center of mass of the macromolecule to the monomer and the angle it makes with the extension axis of the flow.[10] (We hope to report the results of Monte Carlo calculations based on the exact model, in the near future.[11])

Here we consider a simpler model for the monomer–external field interaction which is appropriate for the stretching of the polymer by a homogeneous quadrupolar field[12]

$$v = -\frac{\alpha}{2}(3\cos^2\vartheta - 1) \qquad (1)$$

where α is a constant (independent of the location of the monomer) and ϑ is the angle the monomer makes with the extension axis. In this case, the steady-state distribution function is identical with the one obtained for a polymer chain dissolved in a nematic solvent.[13] In particular, the partition function Z for a polyethylene-like chain (the backbone bonds lie on a tetrahedral lattice) has been given in ref 13 as a matrix product

$$Z = \sum_{u,v=1}^{36} \mathbf{g}(u)\mathbf{W}^{N-3}(u,v) \qquad (2)$$

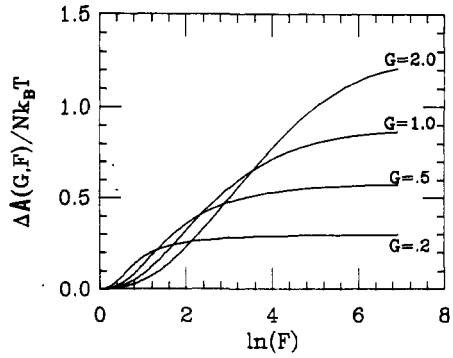

Figure 1. Free-energy storage per monomer (in units of k_BT) is plotted against the monomer–field interaction energy ln F for G = 0.2, 0.5, 1, and 2.

where $\mathbf{W}$ is a (36) × (36) matrix and $\mathbf{g}$ is a (36) vector, both evaluated in ref 13 (N is the number of monomers in the chain). The elements of the matrix consist of products of the factors F and G where $F = \exp(\alpha)$ is the Boltzmann factor containing the potential energy of the monomer–field interaction and $G = \exp(-E/k_BT)$ is the Boltzmann factor corresponding to the gauche state of a trimer[13] (E is the relative energy of the gauche with respect to the trans configuration). Notice that $F = 1$ at zero field and that the chain is purely entropic for $G = 1$, since $E = 0$ means that the gauche and trans states are randomly distributed.

Taking the negative of the logarithm of the partition function, we obtain the Gibbs potential for a chain stretched by the external force.[14] This expression contains the (negative) energy of interaction with the external field that has to be subtracted in order to obtain the free-energy storage. The latter is given by the difference of Helmholtz free energies[14] in the presence and absence ($F = 1$) of the flow

$$\Delta A(G,F) = -k_BT \ln \frac{Z(G,F)}{Z(G,1)} + k_BT\langle n_z\rangle \ln F \qquad (3)$$

where $\langle n_z\rangle$ is the average number of monomers having a projection along the external field axis. Both ln Z and $\langle n_z\rangle$ have been computed by diagonalizing the $\mathbf{W}$ matrix and taking the limit $N \to \infty$ in which only the largest eigenvalue contributes.[7]

In Figure 1 the dimensionless free-energy storage per monomer is plotted as a function of ln F (interaction energy per monomer). As we have previously mentioned, the purely entropic behavior over the complete range of ln F is given by the $G = 1$ curve. The initial (small ln F) regime of all the other curves is also entropic; it corresponds to the redistribution of trans and gauche configurations in order to increase the projected chain length along the external-field direction— at *fixed* ratio of trans to gauche configurations.[15] In this regime the energy storage is a decreasing function of G (at constant F), since it is proportional to the unperturbed dimensions of the polymer which *decrease* with increasing G.[7] The nonentropic effects become important at higher values of ln F at which curves with $G < 1$ ($G > 1$) fall below (above) the $G = 1$ curve. Here the stretching due to redistribution is saturated and further stretching involves changing the ratio of gauche to trans configurations. This conformational energy effect tends to reduce the available free-energy storage capacity for chains with $G < 1$ (such as polyethylene) and to increase it for chains with $G > 1$ (which, qualitatively describes the behavior of poly(oxyethylene)).

As expected, the free-energy storage saturates at high values of ln F that correspond to a fully stretched state

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