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Hydrogen Bond Network Formation

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SUMMARY: The signs of the dynamic dichroism of the NH stretch and the amide I bands in nylons were found to be counterintuitive. Experiments show that polymer chains tend to align in the direction of an applied tensile strain. The CH stretching bands in nylons exhibit the expected negative dynamic dichroism indicating chain alignment in the strain direction. The ΔA′ peaks for the NH and amide I bands are positive. The ΔA′ peak for the NH band is also unusual in that it has a derivative shape. This can be explained by band shifts brought about by anisotropic changes in the intermolecular spacing in the glassy polymer. Above T_g the derivative shape disappears but the ΔA′ peak for both the NH and amide I absorption remain positive. We postulate that the positive ΔA′ peaks of the NH and amide I bands result from a hydrogen bonding network where stress is transmitted through a network consisting of covalent chains connected by hydrogen bonds.

Introduction

Dynamic IR or strain modulated dichroism studies were initiated by Noda and Marcott in the 1980's. In their early studies1) they employed a dispersive instrument where the mechanical sample deformations were done in a Dynastat (Northern Industrial) and the small dichroism signals isolated and quantified using lock-in amplifiers. We have reported on the duplication of their early instrumentation2). Here we report on some studies of hydrogen bonding in polyamide samples.

Experimental

The spectrometer used for making the dynamic IR measurements was constructed following the teachings of Noda, Dowrey and Marcott1) and has been described in an earlier publication2). In the present study the spectral region between 2750 and 3450 cm^{-1} was examined in ca. 300 steps using entrance and exit slits to the 0.5 meter Spex Monochromator set at 2.5 mm (spectral resolution of ca. 14 cm^{-1}). CaF_2 lenses and windows were employed along with a 56.7 kHz CaF_2 photo elastic modulator, PEM (Hinds), and an InSb detector (Infrared Associates). For the amide I band, the region between 1550 and 1750 cm^{-1} was examined in ca. 150 steps. In this spectral region a 37 kHz ZnSe PEM (Hinds) was employed with a MCT detector (Infrared Associates). A 20 Hz mechanical deformation was imparted to the sample with a peak to peak tensile strain of 2 ppt using a Dynastat dynamic mechanical tester (Northern Industrial). For a given spectrum, data were collected by taking 10 readings at each step and scanning through the entire spectral region 16 times. The 160 voltage readings were then simply averaged.

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In these IR studies, the polymers were examined as thin coatings on 75 μm corona treated Teflon® FEP film. The nylon-6 and the copolymer of nylon-6 and 6,9-nylon were obtained from A. Siegmann and M. Zilberman of The Technion in Israel. A 7% (wt/wt) solution was prepared in a mixture of formic acid and tetrahydrofuran (ca. 50/50 volume/volume) and the solution doctored onto the Teflon® FEP film. The films were dried at 80°C in a vacuum oven for 3 to 4 hours. The oven was then turned off and the samples allowed to remain in the oven overnight with a N_2 bleed. The Zytel®330 sample was prepared from a 5% solution in n-methylpyrrolidone. After doctoring onto the Teflon® FEP substrate, the samples were dried in a 65°C vacuum oven overnight. The oven temperature was then raised to 120°C and the sample dried an additional 12-16 hours. Thin film strips [3-4 cm. long, length/width ≅ 3] were used in the tension experiments. The test specimens were mounted in the Dynastat and annealed by heating to 130°C and then slowly cooled to room temperature before taking data.

Results

The absorbance and dynamic dichroism data for the NH band at 3300 cm^{-1} and CH stretch bands between 2800 and 3000 cm^{-1} in 6-nylon are shown in Figure 1. The data for the CH bands are as expected. In general, one would expect that the polymer backbone would tend to align in the direction of the tensile strain. Since the CH bonds and the dipoles associated with their stretching vibrations are normal to the polymer backbone, conventional wisdom would expect their dichroism to be negative and hence their in-phase dynamic dichroism, ΔA′, peaks to be negative. This is observed. The ΔA′ data for the NH band was not expected. Since the orientation of the NH bond with respect to the polymer backbone is very similar to that of the CH bonds, one expected a negative ΔA′ peak. The peak is positive. The ΔA′ peak is also quite large and has some of the characteristics of a derivative

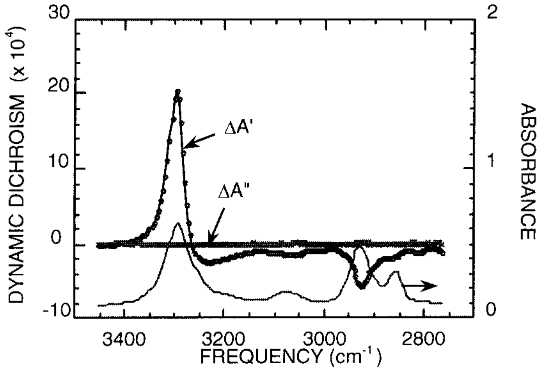

Figure 1. In-phase (ΔA′) and quadrature (ΔA′′) dynamic dichroism and absorbance for nylon-6 NH and CH bands at 30°C.

curve. The complexity of the NH band has been well documented by Coleman[3] so the supposedly "simpler" amide I or carbonyl band was also examined. Room temperature data for the amide I band are shown in Figure 2. The absorption consists of two bands - - one at ca. 1660 cm^{-1} assigned to the free carbonyls and the second at 1645 cm^{-1} assigned to the hydrogen bonded carbonyls[3].

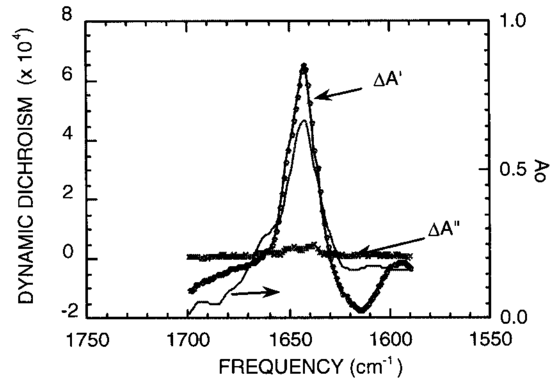

Figure 2. In-phase (ΔA′) and quadrature (ΔA") dynamic dichroism and absorbance for nylon-6 amide I band at 30°C.

The ΔA′ peak appears primarily associated with the hydrogen bonded carbonyls. The fact that it is positive "agrees" with the positive ΔA′ peak of the NH band. One also notes that it has some characteristics of a derivative shape.

Since nylon-6 is semicrystalline one sought to eliminate the potential morphological complications introduced by the crystallites and turned to samples thought to be largely, if not totally, amorphous. A copolymer sample of nylon-6 and 6,9-nylon was obtained from A. Siegmann and M. Zilberman. Its examination with dynamic IR yielded much the same results as found with nylon-6. These are shown in Figure 3 and 4. Again the ΔA′ peaks for the CH bands were negative as seen with nylon-6. The ΔA′ peak of the NH band is large, positive and has characteristics of a derivative curve.

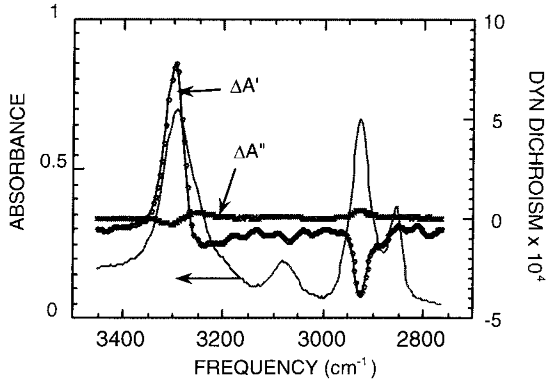

Figure 3. In-phase (ΔA′) and quadrature (ΔA′′) dynamic dichroism and absorbance for nylon-6/6,9 copolymer NH and CH bands at 30°C.

The data for the amide I band was also very similar to that observed with nylon-6 as seen in Figure 4. Data were also collected as a function of temperature from 30° to 100°C.

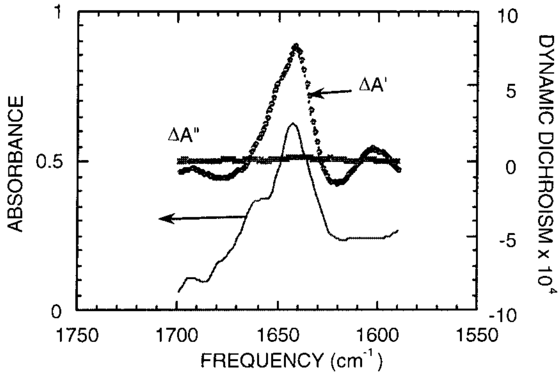

Figure 4. In-phase (ΔA′) and quadrature (ΔA′′) dynamic dichroism and absorbance for nylon-6/6,9 copolymer amide I band at 30°C.

These are shown in Figures 5 and 6.

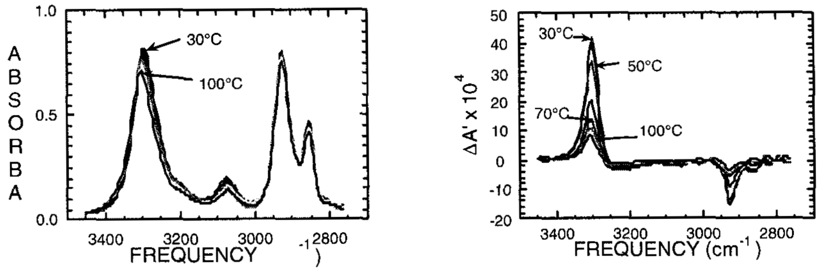

Figure 5. Temperature dependence of the absorbance and in-phase dynamic dichroism for the NH and CH bands in nylon-6/6,9 copolymer

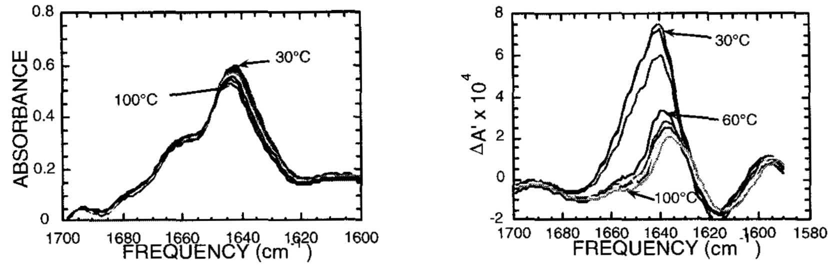

Figure 6. Temperature dependence of the absorbance and in-phase dynamic dichroism for the amide I band in nylon-6/6,9 copolymer

The absorbance data for both the NH and CO bands indicate a slight loss in hydrogen bonding but the magnitude of the changes are quite small and monotonic. The ΔA′ data exhibit large changes but both the NH and CO bands remain positive. In these experiments ΔA′ should be proportional to the amplitude of the strain, the stress optical coefficient and the shear modulus4). Since the shear modulus undergoes a dramatic decrease at T_g one would expect that the magnitude of the ΔA′ peaks would have much the same character. In Figure 7 the magnitude of the ΔA′ peaks are determined from their integrated intensities normalized by their integrated absorbance. The data in Figure 7 indicate a T_g in the vicinity of 55°C. We suspect that T_g is strongly dependent on the moisture content of the sample but the latter was not determined. One also notes that the T_g is marked by a peak in quadrature component of the dynamic dichroism. The reason for the sign change between ΔA′ and ΔA′′ is not clearly understood at this time. One also notes that magnitudes of the ΔA′ peaks are reduced only by a factor of ca. 2 in passing through T_g. For polystyrene and other amorphous polymers, the change is much larger4).

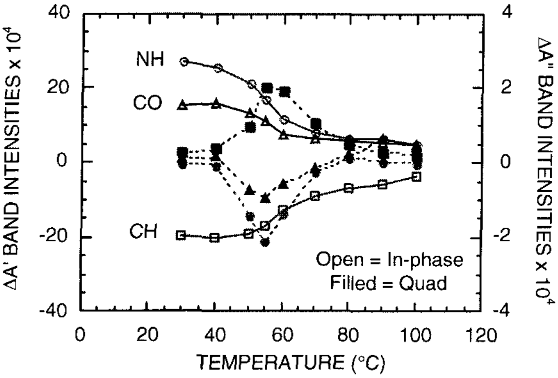

Figure 7. Dynamic dichroism band intensities as a function of temperature for nylon-6/6,9 copolymer sample.

Zytel®330 is an amorphous nylon resin with a T_g in the vicinity of 134°C (the latter will change according to moisture content)[5]. Figure 8 contains data for the NH and CH bands. The general results are very similar to that found with the other two nylon samples. The ΔA′ peak for the CH bands are negative and the ΔA′ peak for the NH band is positive and has a derivative shape.

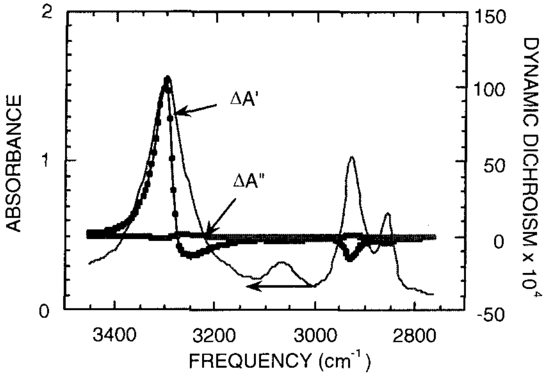

Figure 8. In-phase (ΔA′) and quadrature (ΔA′′) dynamic dichroism and absorbance for Zytel®330 NH and CH bands at 30°C.

As before, the ΔA′ peak for the CO band is positive as shown in Figure 9.

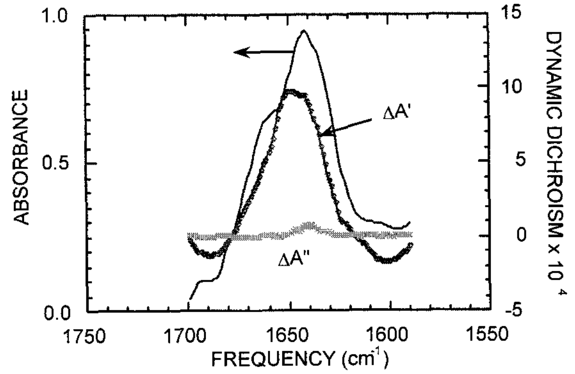

Figure 9. In-phase (ΔA′) and quadrature (ΔA′′) dynamic dichroism and absorbance for Zytel®330 amide I band at 30°C.

The temperature dependence of the ΔA′ peaks for the NH and CO bands exhibit an interesting difference from the previous two nylon samples.

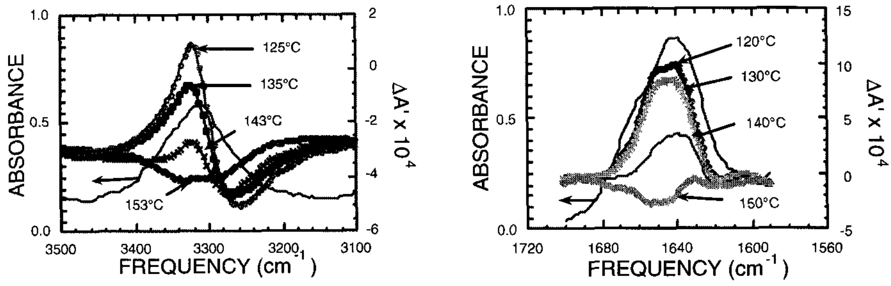

Figure 10. Temperature dependence of the in-phase dynamic dichroism (ΔA′) of the NH and amide I bands in Zytel®330

As before, the magnitude of the ΔA′ peaks decrease at T_g but in this instance they both become negative at about 150°C (20°C above T_g).

Discussion

Below T_g the sign of the ΔA′ peaks for the NH and CO bands in our three nylon samples appear to be counter intuitive. They are positive while the peaks for the aliphatic CH stretching vibrations are negative and we would have expected all three bands to show the same dichroism. This change in sign does not appear to be a manifestation of the crystallinity since the nylon-6 sample is known to be semicrystalline while the other two samples are either amorphous or very nearly so and the data for all three are very similar. The shape of the NH absorbance peak and the derivative character of the NH ΔA′ peak indicate complexity that hinders analysis. On the other hand, the ΔA′ peaks for the CO bands are clearly associated with the hydrogen bonded moieties. To rationalize these data one postulates that the hydrogen bonds are acting as intermolecular links in the transferring of stress in the sample. This is illustrated in Figure 11. The stress is postulated to be transferred from chain-1 to chain-2 through the hydrogen bond. In such a situation, the CO and NH bonds would tend to align in the direction of stress and thus produce a positive dichroism. The above is not to imply that the hydrogen bonds are permanent links. Our concept is that hydrogen bonds are dynamic features, constantly being made and broken. At any given instance, however, a substantial number of interactions should be active and thus account for the positive ΔA′ peaks.

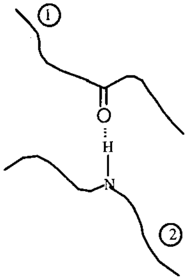

Figure 11. Schematic representation of interchain coupling through hydrogen bonds.

Based on melt viscosity data, one speculates that at high enough temperatures this mechanism of intermolecular stress transfer through the hydrogen bonds would no longer be operative. With the two aliphatic nylon samples, this temperature was not reached at 100°C even though this was 30-40°C above T_g. In Figure 10 one notes that the ΔA′ peaks for both the NH and CO bands in Zytel®330 become negative at 150°C. This is the dichroism one would expect in the absence of hydrogen bonding.

The derivative character of the ΔA′ peaks for the NH band deserves comment. This same band shape has been observed in a number of instances where one notes:

1. This ΔA′ peak shape is observed only with bands strongly associated with hydrogen bonds (the OH band in polyvinyl alcohol; the NH and CO bands in polyureas, polyurethanes and other nylons)

2. It is usually observed only with glassy specimens
3. The larger positive lobe is always on the high frequency side
4. The magnitude of the $\Delta A'$ peak can be quite substantial (10^{-3} vs. 10^{-4})

One speculates that this unusual shape of the $\Delta A'$ peak is brought about by band shifts.

The usual interpretation of the $\Delta A'$ measurement is that it is an indicator of the realignment of dipoles in response to an external perturbation (in this case a mechanical strain). The problem is that, with mechanical strains on the order of 1 ppt, $\Delta A'$ is very small and the required sensitivity of the instrumentation forces the consideration other factors. Two such factors are sample thinning[5] and band shifts. Although $\Delta A'$ is directly measured in the present experiments it can be thought of as the subtraction of two independent measurements, $A'_{\parallel}$ and $A'_{\perp}$. $A'_{\parallel}$ and $A'_{\perp}$, themselves, can be thought of as the difference between two absorbances, the absorbance at maximum stress minus the absorbance at rest. For $A'_{\parallel}$ one considers just those moieties whose dipoles are aligned in the strain direction. At zero strain one will observe some absorption. In the glassy state, a tensile deformation has a chance to increase the intermolecular spacing in the strain direction. This increase in intermolecular spacing results in a decrease in the strength of the hydrogen bonds in this direction and a band shift to higher frequencies for the NH and CO bands. If one assumes a band Grünheisen parameter of 0.1 to 0.2 and a Poisson's ratio of 0.42[6)] then a 1 ppt strain can result in band shifts of 0.05 to 0.1 cm^{-1}. Such band shifts are quite small but the measurements are capable of detecting very small changes in absorbance and these very small shifts might be detected. For example, if one considers a Gaussian absorption band with a peak absorbance of one and a width of 50 cm^{-1}, a band shift of just 0.05 cm^{-1} would result in a difference derivative peak of 10^{-3}, an easily detectable quantity. In addition to a band shift the strain will also result in sample thinning (10^{-3}) and thus a decrease in absorbance (10^{-3}). Finally, if one postulates a reorientation of dipoles into the strain direction, there will be an absorbance increase. The sum of these three factors will result in an $A'_{\parallel}$ with a derivative shape with a larger positive component on the high frequency side. $A'_{\perp}$,the in-phase dynamic absorption in the normal direction, just measures the dipoles that are aligned normal to the stretch direction. At zero strain there is a given absorbance. At maximum strain there will be sample thinning and also a decrease in absorbance due to the reorientation of dipoles If there is compression of the intermolecular spacings in the normal direction, the strain will lead to the opposite band shift seen parallel to the strain. The overall result will be a band with a derivative shape exactly opposite to that postulated for the parallel direction. Since $\Delta A' = A'_{\parallel} - A'_{\perp}$ the result will be similar to $2A'_{\parallel}$. A more likely scenario is that the strain will lead to very little compression of the intermolecular spacing in the normal direction due to the anisotropy of the intermolecular forces (i.e. Lennard-Jones potential). In this case $A'_{\perp}$ will just reflect sample thinning and dipole reorientation and $\Delta A'$ will have a derivative shape with a large positive lobe on the high frequency side. In Figure 12 one notes that the derivative shape is most strongly evident in $A'_{\parallel}$ and not in $A'_{\perp}$.

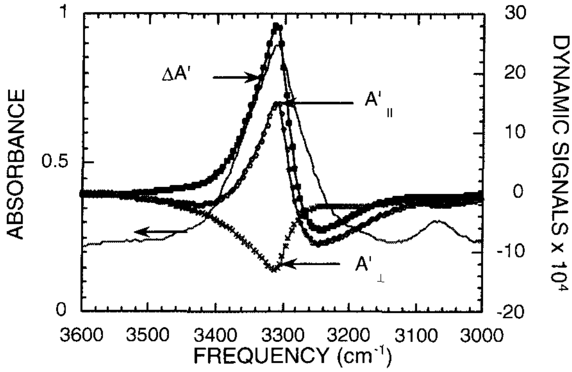

Figure 12. In-phase dynamic absorbance ($A'_{\parallel}$ and $A'_{\perp}$) and dynamic dichroism ($\Delta A'$) of the NH band in Zytel®330.

For most polymer infrared bands, the Grüneisen parameters are sufficiently small(7) so that band shifts in dynamic IR experiments need not be considered. For bands strongly associated with hydrogen bonding one would expect greater sensitivity to intermolecular spacing and this is in harmony with our observations.

Finally, one must comment on the effect of the band shifts on our postulating the network formation through the hydrogen bonds. In our view, changes in intermolecular spacing and the resulting band shifts can only take place in the glassy polymer (i.e. when Poisson's ratio differs from 0.5). Above T_g, the relaxation processes in amorphous polymers will insure constant intermolecular spacing and we observe very little derivative character of the $\Delta A'$ peaks. In all three polymers studied, the $\Delta A'$ peaks for the NH and CO bands remained positive above T_g. Thus, in the absence of band shifts their reorientation was normal to the reorientation of the CH bonds and in harmony with our postulation of the network formation.

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