Fourier Transform Infrared Study of a Poly(diacetylene)

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Received June 27, 1985

ABSTRACT: Fourier transform infrared spectra of the poly(diacetylene) poly-4BCMU are presented as a function of temperature. Two endotherms are observed in thermograms and these are correlated to spectroscopic changes. The lower temperature endotherm is related to a melting of the one-dimensionally ordered hydrogen bonded chains that are parallel to and help stabilize the stiff rodlike backbone conformation of this polymer. Although there appears to be some degree of disorder introduced into the conformation as a result, most of the change in conjugation length apparently occurs during the second thermochromic transition.

Introduction

Poly(diacetylenes) with urethane substituent groups, for example, those referred to as poly-3BCMU and poly-4BCMU, display thermochromic transitions in both solution and the solid state.[1-12] The planar conformation of the stiff, conjugated polymer backbone $=((R)CC{\equiv}CC(R))=$ of these poly(diacetylenes) is stabilized by intramolecular hydrogen bonds between the side chains ($R = (CH_2)_3OCONHCH_2COO(CH_2)_3CH_3$ for poly-3BCMU and $R = (CH_2)_4OCONHCH_2COO(CH_2)_3CH_3$ for poly-4BCMU). It has been established that in solution the transition from a planar to a nonplanar conformation is associated with a disruption of the ordered hydrogen bonded chains that parallel the backbone of these polymers. Beyond that, there is considerable disagreement concerning the nature of the conformational transition. Patel et al.[5] originally considered a nonplanar conformation to be a result of rotations around the single bond of the polymer backbone. Lim and Heeger[11] point out, however, that this would not lead to a rod-to-coil transition, because the single bonds are parallel. Wenz et al.[9] applied a range of techniques and interpreted their results in terms of a conformational transition to a wormlike chain. They also argued that the spectral shift associated with this transition is not just a single-chain phenomenon but also related to aggregation between rodlike chains. More recent results by Heeger and co-workers[10,11] seem to rule out this aggregation interpretation. These authors also argue that a coiled conformation could be related to a trans-cis isomerisation.

Unlike solution studies, where only one conformational transition is observed, two endotherms are observed in thermal studies of cast films of poly-3BCMU and poly-4BCMU.[1,3,8] The lower temperature endotherm has been assigned to an intermolecular melting phenomenon, while the higher temperature endotherm was associated with intramolecular melting. Fourier transform infrared (FTIR) results presented in these papers and also in a separate study[6] appear to indicate, however, that the intramolecular hydrogen bonds melt during the *lower* temperature transition, although the results were not interpreted in this way.

In both solution and solid-state studies an infrared methodology developed by Schroeder and Cooper[13] has been used to interpret the data. This leads to an estimate that the hydrogen bonds contribute between 14 and 20 kcal/mol toward the stabilization of the planar polymer conformation. Although these numbers are consistent with those obtained for other polymers, such as nylons and polyurethanes,[14,15] they are anomalously high compared to similar low molecular weight materials.[16] Recent work in this laboratory has demonstrated that the method used to obtain these numbers is erroneous.[17,18] We have determined that the infrared absorption coefficient for the N-H stretching mode varies enormously with the degree of hydrogen bonding and that the spectra cannot be interpreted as the sum of two contributions, free N-H and hydrogen bonded N-H. Instead, a range of hydrogen bonded states is observed, each characterized by an individual absorption coefficient, and this distribution varies systematically with temperature.

In view of this reassessment of the application of infrared spectroscopy to the measurement of hydrogen bonding in polymers and in view of the inconsistent assignment of the lower temperature endotherm observed in poly-3BCMU and poly-4BCMU to intermolecular melting, we have performed a detailed FTIR study of these polymers. Here we will present an analysis of the spectrum of films of poly-4BCMU and its variation with temperature. Equivalent studies of films and solutions of poly-3BCMU will be considered in a separate publication.

Experimental Section

Samples of poly-4BCMU were similar to those used in other studies.[1-8] The as-received samples were washed with acetone to remove residual monomer. Films for infrared analysis were prepared by casting from 1% (w/v) chloroform solutions onto a KBr window. We found that the cast films used in initial work also contained some residual monomer and possibly low molecular weight material. Further acetone washing of such films produced a yellow solution. For the results presented here we therefore used the initial precipitates obtained by adding hexane to a chloroform solution (3 parts to 2, respectively). When these precipitates were redissolved and cast from new chloroform solutions, they gave films that did not dissolve in or discolor acetone.

DSC measurements were made on either of two Perkin-Elmer instruments, a System-4 or DSC-2. All thermograms were obtained at a rate of 20 °C/min and within the temperature range −120 to +175 °C. The sample size was 12 mg of polymer in most runs, 6 mg in some.

FTIR spectra of poly-4BCMU chloroform-cast films were recorded as a function of temperature, which was controlled by a programmable heat cell. The temperature was raised to the appropriate level at the completion of each scan set, approximately 3 min. The temperature changes between each set were as follows: 20 °C between 30 and 90 °C, 5 °C between 90 and 150 °C, and 10 °C between 150 and 160 °C. This allowed more spectra to be recorded in the temperature range in which the polymer transitions occur. The heating rate used was the maximum capable for the controller. Two minutes of equilibration time was required

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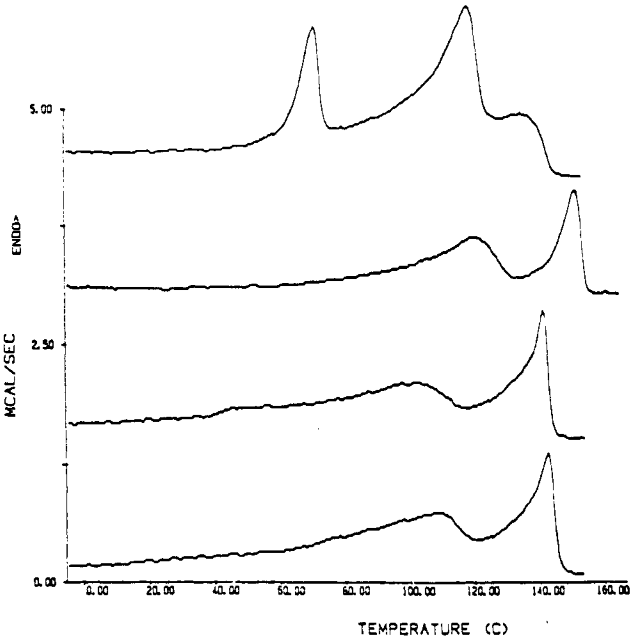

Figure 1. Initial-heating DSC thermograms for various PDA-4BCMU sample preparations, top to bottom: (1) as-polymerized single crystals; (2) washed single crystals; (3) hexane precipitate (from chloroform solution); (4) chloroform-cast film.

before collecting sets separated by 5 °C. Proportional time was required for the other changes. Similar experiments were performed with oriented samples. Orientation was achieved by stroking films with the tattered end of a paper matchstick in a slowly diminishing atmosphere of chloroform.

All spectra were recorded with a Digilab FTS/15-E spectrometer at a resolution of 2.0 cm^{-1}. The reported traces are the product of not less than 64 coadded interferograms.

Results and Discussion

For the purpose of our discussion it is convenient to consider the infrared spectroscopic results in the context of the thermal transitions observed by differential scanning calorimetry (DSC). DSC studies of poly-3BCMU have previously been reported in the literature,[3,19] but these principally involved the detection of endotherms as a function of polymer conversion. A thermogram of the as-received poly-4BCMU single crystals is shown in Figure 1. Although these samples were reportedly washed, three endothermic transitions, near 69, 115, and 135 °C, can be observed. The 69 °C transition is due to the melting of cocrystallized monomer.[3,19] Samples washed with acetone show just two transitions, shifted to higher temperature (125 and 150 °C). The character of the low- and high-temperature polymer endotherms appears to switch as a result of washing, however. In the as-received samples, the transition near 115 °C is strong and relatively sharp, while the high-temperature transition is broader and weaker. In thermograms of the washed samples, and also those obtained by precipitation or as a cast film from chloroform solutions, the lower temperature transition becomes weaker and broader than the higher temperature transition. It is likely that this is due to the removal of cocrystallized monomer from the original polymer lattice, which would allow a relaxation and change in morphology. Unfortunately, the as-received samples were not in a form suitable for spectroscopic analysis and we could not pursue this point. The infrared spectra we will present were obtained on films cast from chloroform and should therefore be correlated to the thermogram shown at the bottom of Figure 1. It is important to note that thermograms of these samples were also obtained upon cooling from elevated temperature and two exotherms were observed, indicating that we are indeed observing two distinct transitions and not a melting–recrystallization–melting phenomenon.

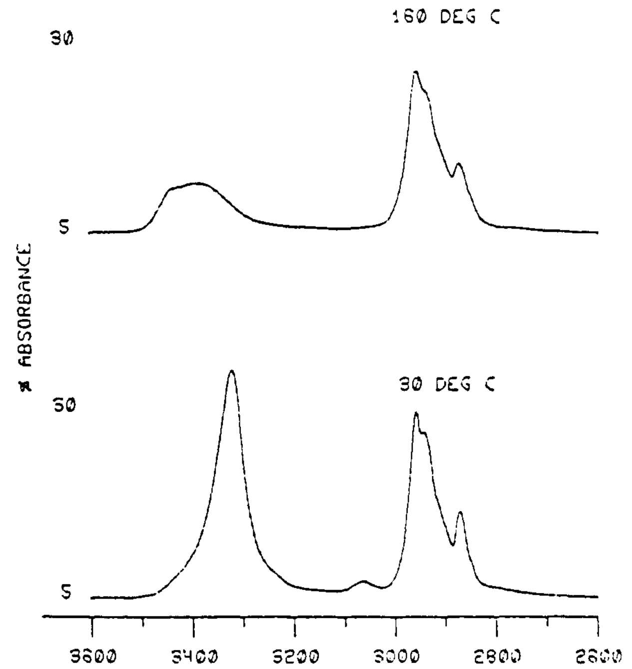

Figure 2. FTIR spectra of a PDA-4BCMU cast film recorded at 30 and 160 °C, between 3600 and 2600 cm^{-1}. Spectra are arbitrarily offset.

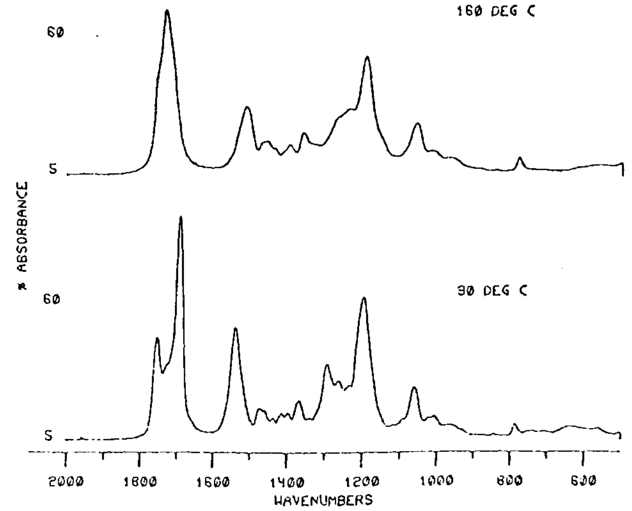

Figure 3. FTIR spectra of a PDA-4BCMU cast film recorded at 30 and 160 °C, between 2000 and 500 cm^{-1}. Spectra are arbitrarily offset.

The infrared spectrum of poly-4BCMU is dominated by bands due to the side chain. The type of change that occurs with temperature is illustrated in Figures 2 and 3, which compares the spectra of cast films held at 30 and 160 °C. Figure 2 displays the N–H stretching region of the spectrum. At room temperature a strong sharp band centered near 3319 cm^{-1} can be observed, while at 160 °C two much weaker N–H stretching modes near 3350 and 3435 cm^{-1} are all that remain. These changes can be (qualitatively) related to the degree of hydrogen bonding, as we will discuss below. Dramatic changes can also be observed in the 2000–500-cm^{-1} region of the spectrum, as shown in Figure 3. We will principally be concerned with the modes observed between 1800 and 1600 cm^{-1}, assigned to the ester and urethane carbonyl groups, because these

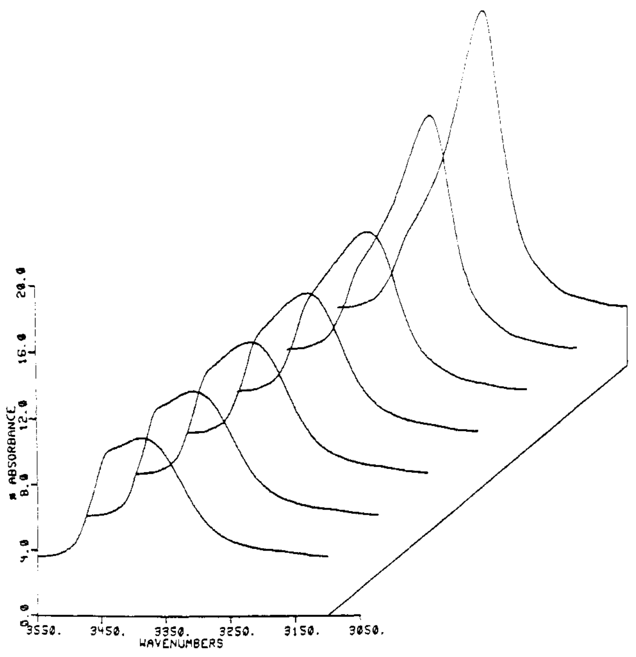

Figure 4. FTIR spectra of a PDA-4BCMU cast film recorded at 10 °C intervals from 90 to 150 °C, between 3550 and 3115 cm^{-1}. Spectra are equally offset at an angle of 43°.

are most easily interpreted in terms of the degree of hydrogen bonding.

The N–H stretching mode is extremely sensitive to hydrogen bonding. The 3319-cm^{-1} band can be assigned to highly ordered, regularly arranged hydrogen bonds. "Free" N–H groups absorb infrared radiation near 3435 cm^{-1}, and a shoulder in the spectrum of the sample held at 160 °C can be observed at this wavenumber. Clearly, there are states intermediate between these extremes. This can be clearly seen in Figure 4, where a pseudo-3D plot of the N–H stretching region of the spectrum as a function of temperature is displayed. A band assigned to some sort of hydrogen bonded N–H group shifts to higher wavenumber and decreases dramatically in intensity with increasing temperature.

Although these results seem clear and straightforward, in previous studies of the spectra of materials such as nylons and polyurethanes it has been implicitly assumed that the spectrum can be interpreted in terms of a simple equilibrium between bonded and nonbonded groups.[13-15] This methodology has also been applied to the characterization of poly(diacetylenes).[6,8,19] Recent work in this laboratory[17,18] and the results presented above indicate that this interpretation is simplistic. For a homopolymer two "end points" or spectral extremes are observed. One is indeed characteristic of non-hydrogen-bonded groups, but the other is characteristic of highly ordered, well-aligned hydrogen bonded chains, such as those found in crystalline nylons or, in this case, one-dimensionally ordered poly-4BCMU. In between these extremes there is a range of states consisting of N–H groups that are less strongly hydrogen bonded. As the strength of the hydrogen bond decreases, the N–H stretching mode shifts to higher frequency and decreases dramatically in intensity. Accordingly, the infrared analysis based on a two-state model gives numbers for the enthalpy of hydrogen bond formation and the number of hydrogen bonded groups that are just plain wrong. As far as this study is concerned the question now becomes can the various spectral contributions be separated in order to correlate the infrared results to the thermal transitions detected in the DSC experiments?

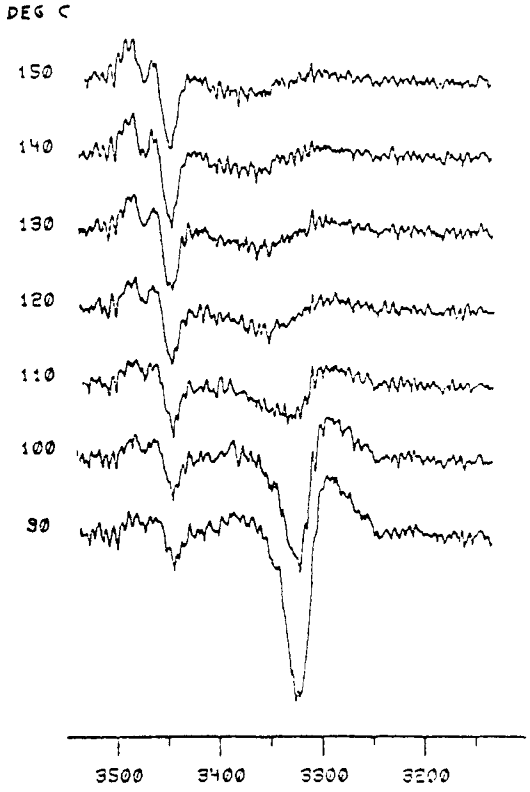

Figure 5. Second derivative of FTIR spectra of a PDA-4BCMU cast film recorded at 10 °C intervals from 90 to 150 °C, between 3550 and 3115 cm^{-1}. Spectra are arbitrarily offset and on absolute scales.

In principle, this can be done by curve-resolving. Unfortunately, this is often a subjective process and the results of such an analysis have to be treated with a great deal of circumspection. We use a computer program that least-squares fits a spectral profile to a number of specified bands.[20] Initial values of variable such as frequency, peak height, width at half-height, and a factor that defines the degree of Gaussian or Lorentzian character of the band shape are used as input to the program. Clearly, a reasonable initial estimate of these parameters and, most importantly, the number of bands present in the region of interest are a necessity for obtaining a meaningful result. In this work we were able to obtain this information through the use of spectral subtraction and the calculation of derivatives, at least for the spectra obtained at the temperature extremes of this study. At these temperatures the spectra are dominated by bands due either to highly ordered hydrogen bonded chains or to bands assigned to weakly or non-hydrogen-bonded groups. The major problem occurs at the transition point, where it is very difficult to judge whether a particular band has disappeared. Because the transitions are sharp, however, this is only a problem in analyzing spectra obtained in a very narrow temperature range and is, in fact, a clear indication of the transition zone.

The second derivatives of the spectra shown in Figure 4 are presented in Figure 5. Minima in these plots correspond to the position of bands in the original spectra. Relatively sharp bands, such as those due to ordered hydrogen bonded N–H groups at 3319 cm^{-1} and free N–H groups near 3435 cm^{-1}, give clearly defined second-derivative minima. Naturally, broad bands do not have a sharp second derivative, but between the ordered and free peaks the presence of a weak broad band that shifts to higher wavenumbers with increasing temperature can clearly be

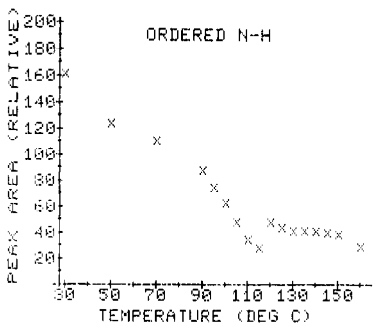

Figure 6. Peak area of the curve-resolved "ordered" N–H stretching band vs. temperature, from 30 to 160 °C.

discerned. This band represents a distribution of N–H groups, less strongly hydrogen bonded than those in the ordered structure and presumably representing a dynamic situation of formation and breaking of inter- as well as intramolecular bonds. At lower temperatures this band overlaps the stronger, sharper band due to intramolecularly ordered hydrogen bonded groups, and its presence can only be inferred from looking at the series of second-derivative plots.

The spectra were fitted to three bands, which we will define as ordered hydrogen bonded, disordered hydrogen bonded, and free N–H groups. The most questionable part of the procedure is, as mentioned above, the determination of the point at which the last trace of the sharp ordered band disappears. The area of this curve-resolved band is plotted as a function of temperature in Figure 6. It can be seen that there is a gradual decrease in intensity between 30 and 90 °C, but the rate of change increases dramatically between 90 and 110 °C. This parallels the changes observed in the thermogram shown at the bottom of Figure 4. In spite of the problems associated with the exact quantitative determination of curve-resolved band areas, it is clear that the first thermal transition is associated with the loss of "ordered" hydrogen bonded N–H groups.

This conclusion is supported by an analysis of the bands observed in the carbonyl stretching region of the spectrum, between 1800 and 1600 cm^{-1}. The intensities of these modes are also affected by the electronic changes induced by hydrogen bonding but far less so than the corresponding N–H bands.[17,18] Consequently, the changes in hydrogen bonded states are better defined. Spectra obtained at 20 °C intervals between 30 and 150 °C are shown in Figure 7. The strong, relatively sharp bands near 1754 and 1693 cm^{-1} are readily assigned to vibrations of the ester carbonyl and the ordered, hydrogen bonded carbonyl of the urethane group, respectively. Between these two outposts of well-assigned bands, two others can be discerned that increase in intensity and shift in frequency with increasing temperature. These appear near 1731 and 1712 cm^{-1} in the spectra of samples held at 150 °C. On the basis of dilute solution studies of compounds that model the side chains of poly-4BCMU and poly-3BCMU, the 1731-cm^{-1} band can be assigned to the free or non-hydrogen-bonded urethane carbonyl.[5] By analogy with the results obtained in the N–H stretching region, we have assigned the band near 1712 cm^{-1} to urethane carbonyls that are hydrogen bonded in an irregular pattern. There is another possibility. It is well-known that modes due to carbonyl groups in ordered structures are split as a consequence of dipole–dipole interactions.[21] The number of bands that should appear in the spectrum then depends upon the number of chemical groups within the Bravais unit cell and the symmetry of this unit cell. For poly-4BCMU (and poly-3BCMU) the chemical repeat unit coincides with the translational repeat unit, so only interactions between those urethane carbonyls on side chains on opposite sides of the main chain would lead to a splitting. Because of their distance apart, interaction terms between such groups are negligibly small. Dipole–dipole interactions between adjacent urethane groups linked by hydrogen bonds parallel to the chain direction certainly occur and contribute significantly to the shape of the dispersion curve. Because these carbonyl groups are related by a translational symmetry element, however, only the totally in-phase vibrations of these groups are permitted by the selection rules. Accordingly, the band due to the ordered hydrogen bonded urethane carbonyl group should not be split by intramolecular interactions and an assignment of the band near 1712 cm^{-1} to an irregularly hydrogen bonded carbonyl is preferred. As we will see, the intensity changes that occur with temperature are also consistent with this assignment.

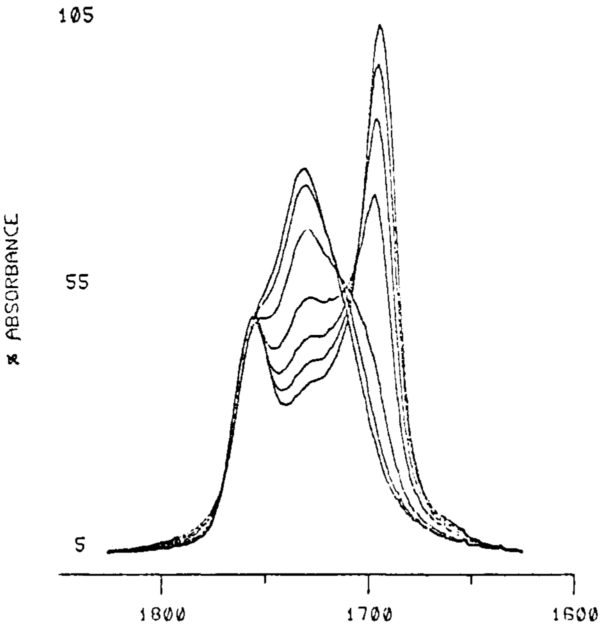

Figure 7. FTIR spectra of a PDA-4BCMU cast film recorded at 20 °C intervals from 30 to 150 °C, between 1825 and 1625 cm^{-1}. Spectra are overlayed.

As with the N–H stretching modes, the number of bands in this region of the spectrum was defined by using second-derivative determinations, as illustrated in Figure 8 for the spectrum obtained at 30 °C. Three bands are clearly defined and a fourth suggested by a prominent shoulder. The presence of this fourth band is much more clearly defined in the spectra obtained at higher temperatures (see Figure 7, above). Accordingly the spectra obtained at temperatures up to 90 °C were fitted to four bands. This is illustrated in Figure 9, where the profile obtained by adding the four curve resolved peaks is compared to the original spectrum. As might be expected, the strong bands near 1754 and 1693 cm^{-1} are precisely matched (the lines are superimposed), but there are some small errors in determining the weaker bands near 1712 and 1731 cm^{-1}. The main problem is again the determination of the point at which the band assigned to ordered linear arrays of hydrogen bonds melt. For this reason, a least-squares fit to both three and four bands was obtained for spectra obtained at temperatures above 90 °C. The fit to four bands for the spectrum obtained at 150 °C is shown in Figure 10. It is clear that the band included at 1693 cm^{-1} is determined to be of very weak intensity if, in fact, it is real at this temperature. Either way, it does

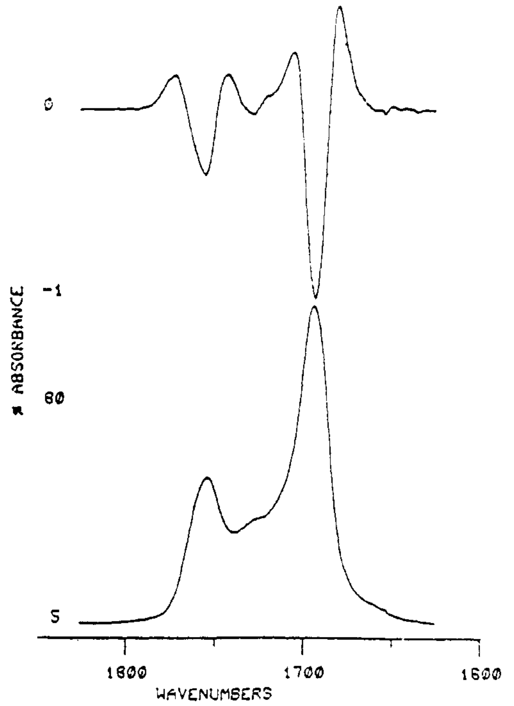

Figure 8. FTIR spectrum of a PDA-4BCMU cast film recorded at 30 °C (bottom) and its second derivative (top), between 1825 and 1625 cm^{-1}. Spectra are arbitrarily offset.

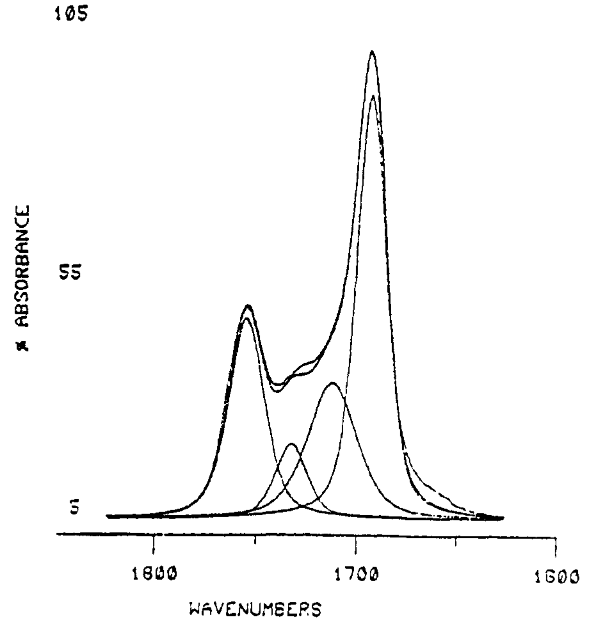

Figure 9. FTIR spectrum of a PDA-4BCMU cast film recorded at 30 °C, a curve-resolved FTIR spectrum, and four individual curve-resolved peaks, between 1825 and 1625 cm^{-1}. Spectra are overlayed.

not affect the qualitative nature of the conclusions we will draw concerning the nature of the first thermal transition.

The areas of the curve-resolved bands near 1693, 1712, 1731, and 1754 cm^{-1} are shown as a function of temperature in Figure 11–14, respectively. As with the N–H stretching region, the band due to ordered hydrogen bonded groups decreases gradually with increasing temperature, followed by an abrupt change over the range of the first thermal transition. To reiterate, these spectroscopic changes parallel those observed in the DSC experiments over this temperature range. The area of the band assigned to urethane carbonyls hydrogen bonded in an irregular fashion (near 1712 cm^{-1}) depends upon whether we include

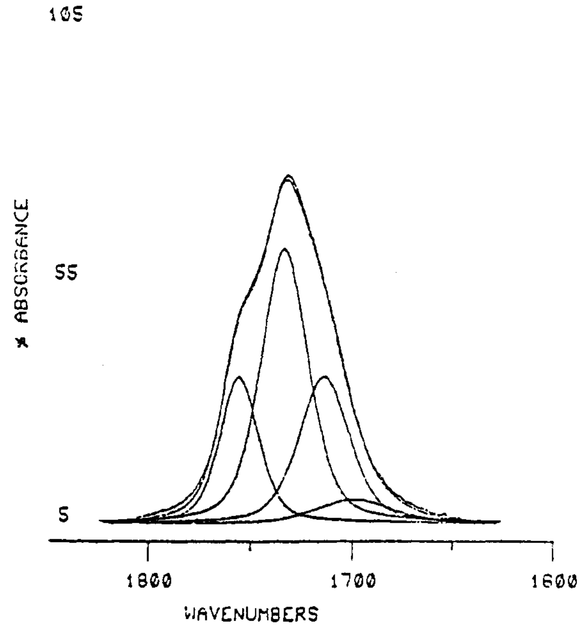

Figure 10. FTIR spectrum of a PDA-4BCMU cast film recorded at 150 °C, a curve-resolved FTIR spectrum, and four individual curve-resolved peaks, between 1825 and 1625 cm^{-1}. Spectra are overlayed.

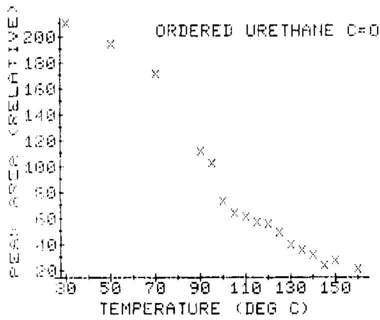

Figure 11. Peak area of the curve-resolved "ordered" urethane carbonyl band vs. temperature, from 30 to 160 °C.

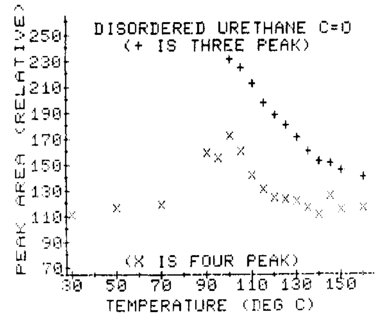

Figure 12. Peak area of the curve-resolved "disordered" urethane carbonyl band vs. temperature, from 30 to 160 °C.

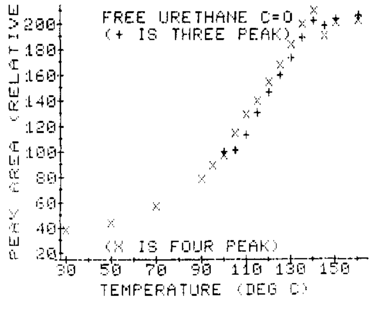

Figure 13. Peak area of the curve-resolved "free" urethane carbonyl band vs. temperature, from 30 to 160 °C.

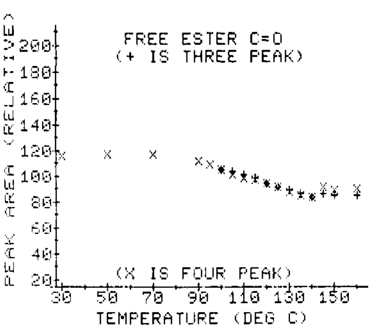

Figure 14. Peak area of the curve-resolved "free" ester carbonyl band vs. temperature, from 30 to 160 °C.

a band at 1693 cm^{-1} in the least-squares fit of spectra obtained at temperatures above 90 °C. Both are shown. When a fit to three bands is determined the area of the 1712-cm^{-1} mode is increased by the area of the band otherwise included near 1693 cm^{-1}. The areas of the bands assigned to free (non-hydrogen-bonded) urethane carbonyls and the ester group are not affected by this choice of procedures, however (Figures 13 and 14).

The plots of intensity as a function of temperature show two distinct effects. The first has already been described; bands due to the one-dimensionally ordered hydrogen bonded side chains melt at the first thermal transition. The second is apparent from Figure 11. The band due to "disordered" hydrogen bonds increases during the first transition and then decreases continuously through the second transition. This trend is qualitatively clear even though uncertainties in curve-resolving affect the absolute intensity of this band. The states that we are labeling as "disordered" hydrogen bonded presumably describe a dynamic equilibrium of forming and breaking hydrogen bonds that at this point could be intermolecular as well as intramolecular. It should be noted, however, that this increase in the intensity of the carbonyl band assigned to such groups is not mirrored in the N–H stretching region. This is due to the dramatic intensity changes that hydrogen bonding induces in this latter region of the spectrum.[17,18] The increase in the number of disordered hydrogen bonded N–H groups is more than offset by the exponential decrease in intensity that accompanies a reduction in the strength of the hydrogen bond. Finally, it should be noted that the band assigned to "free" urethane carbonyls increases continuously over the range of both transitions, while the band due to the ester carbonyl changes only slightly and possibly not at all, because the accuracy of determining the area of this band decreases with increasing temperature and the resulting increasing intensity of the overlapping "free" urethane carbonyl group.

Although the origin of the first transition seems clear from this study, the nature of the second transition, which gives a sharper and better defined endotherm in DSC studies, is not. The color of the cast films, observed in transmission and described in terms of ISCC–NBS standards of lightness saturation and hue,[22] changes from dark moderate red with a glossy sheen to a medium moderate brownish-orange over the temperature range of the first transition. The second thermal transition is characterized by a change from the orange to a medium vivid yellow. This suggests that there is still a degree of electron delocalization and hence main-chain order, even though the stabilizing contribution of the ordered intramolecular hydrogen bonds has been broken. We obtained some experimental support for this observation somewhat by accident. Partially oriented films were produced by

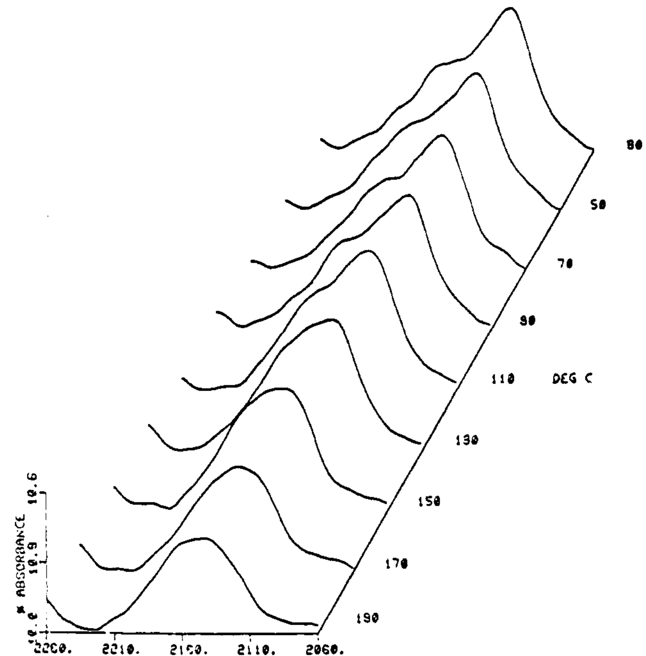

Figure 15. Smoothed FTIR spectra of a partially oriented PDA-4BCMU cast film with the IR beam polarized parallel at 20 °C intervals, from 30 to 190 °C, between 2260 and 2060 cm^{-1}. Spectra are equally offset at an angle of 60°.

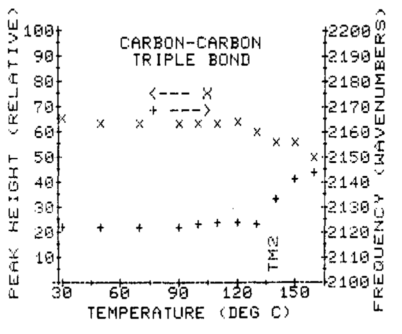

Figure 16. Peak height and peak maximum frequency for the carbon–carbon triple bond stretching band of a particularly oriented PDA-4BCMU cast film versus temperature, from 30 to 160 °C.

stroking cast solutions as the solvent evaporated. Our initial aim was to examine the dichroic properties of the hydrogen bond as a function of temperature. This particular study provided no new information, but we did notice the enhancement of a weak infrared band at 2122 cm^{-1}, which was more prominent in spectra obtained with the infrared beam polarized parallel to the orientation direction. This is illustrated in Figure 15, which shows the bands in this region of the spectrum as a function of temperature. These modes are extremely weak and in order to obtain even halfway decent spectra we had to prepare thick films and co-add a large number of interferograms. The weak intensity of these bands is precisely what we would expect for poly(diacetylene) carbon–carbon triple bonded stretching modes, which only appears in the infrared as a result of a breakdown in selection rules. In the spectra of unoriented films, this region of the spectrum appears to consist of the superposition of at least two bands. In the spectra of oriented films obtained with parallel orientation of the IR beam, the lower frequency mode near 2122 cm^{-1} is intensity enhanced and more clearly defined. As the temperature is increased there is little change in either the peak height or frequency of this and until a temperature of 130 °C is reached, well above the first thermal transition. This data is plotted in Figure 16, and it is clear that changes in this region of the spectrum correlate to the second thermal transition.

The frequencies of bands observed in this region of the infrared spectrum do not correspond to those observed in the Raman, where the intensities are resonance enhanced.[23] Consequently, the frequency of the observed Raman line depends upon the excitation energy, because of a selective enhancement of modes associated with a particular conjugation length. In contrast, the infrared spectra shown in Figure 15 reflect the total distribution of conjugation lengths, with the modes associated with the longest conjugation lengths absorbing at the lowest frequencies. Accordingly, the second transition observed in the DSC experiments is most likely related to a major change in the conjugation length of the polymer backbone. Unfortunately, these data do not allow us to distinguish between the rival mechanisms proposed for the rod-to-coil transition (formation of a wormlike chain or trans–cis isomerism of the double bond).

Conclusions

There are two major conclusions and one word of warning that can be drawn from this study. The lower temperature endotherm observed in thermograms of poly-4BCMU filsm is related to a melting of the one-dimensionally ordered hydrogen bonds that are parallel to and help stabilize the stiff, rodlike backbone conformation. Although there is presumably some disorder introduced into this conformation as a result, most of the change in conjugation length apparently occurs during the second thermochromic transition. Finally, the N–H stretching region of the infrared spectrum cannot be used to determine the degree of hydrogen bonding; in previous studies such estimates have been related to an average conjugation length. This is because the methodology used to determine such numbers is based on describing the spectra in terms of an equilibrium between two contributions, hydrogen bonded and free. The results presented here clearly illustrate that there is a distribution of hydrogen bonded strengths that varies with temperature. Furthermore, the absorption coefficient of each species and hence its intensity is dramatically affected by the strength of the hydrogen bond. A new methodology needs to be worked out for determining the degree of hydrogen bonding in polymeric materials.

Acknowledgment. We gratefully acknowledge the support of the NSF Polymers Program.

Registry No. Poly-4BCMU (homopolymer), 68777-93-5; poly-4BCMU (SRU), 76135-61-0.

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