Probing the complex hydrogen bonding structure of urethane block copolymers and various acid containing copolymers using infra-red spectroscopy

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Infra-red spectroscopy has long been used to characterize the hydrogen bonding structure in polymeric materials. However, the concept that is often used in interpreting infra-red data is that characteristic absorption bands are simply due to free and one type of hydrogen bonded moieties. With more sophisticated data analysis software (for example, Fourier deconvolution), it can be shown that the infra-red spectra of model urethane block copolymers and various ethylene/acrylic and methacrylic acid copolymers indicate a much more complex hydrogen bonding structure than has been previously and generally identified. For example, in model urethane block copolymers composed of a poly(propylene oxide), diphenyl methane-4,4'-diisocyanate (MDI), and varying amounts of butanediol as the chain extender, the infra-red data show that several distinctive absorption bands due to hydrogen bonds of various strengths are present and are a function of hard segment length. The data is indicative of hydrogen bonding in ordered and disordered (possibly interfacial) regions of the polymer. In ethylene/acid copolymers, varying the amount and type of acid gives infra-red spectra which indicate complex hydrogen bonded structures are present. Both cyclic dimers and open 'long' and 'short' range hydrogen bonded structures are suggested by the data. The implications of the detailed knowledge obtained about the hydrogen bonded structures are discussed.

(Keywords: hydrogen bonding; urethane block copolymer; infra-red spectroscopy; ethylene/acrylic acid copolymers; phase separation)

INTRODUCTION

Hydrogen bonding has been the topic of many scientific studies over the past several years[1,2]. The importance of hydrogen bonded structural units has been addressed, for example, in biological systems[3], solution[4], inert gas matrices[5] and polymers[6–8]. Infra-red spectroscopy has been the analytical technique of choice for studying hydrogen bonding due to the sensitivity of molecular vibrations, particularly fundamental stretching modes, to perturbations due to the interaction. From infra-red spectra, it has classically and generally been assumed that the absorption bands due to free and hydrogen bonded groups can be observed[9–11]. From the data, a variety of information such as heat of dissociation and hydrogen bond lengths can be obtained. However, very few studies have been made which deal with detailed information available about hydrogen bonding in various materials.

McLachland and Nyquist[12] have correlated the shift in the hydrogen bonded carbonyl stretching frequency to long range hydrogen bonded structure (i.e. *n*-mer determination) and have alluded to the presence of more than one type of hydrogen bonded species that they have studied[12]. Also, Otocka and Kwei[13] have observed several absorption bands in the carbonyl stretching region of ethylene/acrylic acid copolymers. Recently, interest in the details of the hydrogen bonding structure in polyamides and polyurethanes has been shown[14–16].

This paper will discuss the use of computer techniques such as Fourier deconvolution[17,18] and derivative spectra[19–21] to assist in probing the complex hydrogen bonding structure from infra-red spectra of model polyurethanes and various ethylene/acid copolymers. It will be shown that the hydrogen bonding structure in polymeric materials can be more complex than has generally been observed and documented.

EXPERIMENTAL

Materials

The model polyurethanes are based on a 2000 molecular weight poly(propylene oxide), diphenyl methane-4,4'-diisocyanate (MDI) and 1,4-butanediol. The materials were made by synthetic procedures previously described[22]. The films for spectroscopic analysis were cast from DMF solution and treated in the same manner as described in a previous publication[22].

The ethylene/acid copolymers contain either 6.5 or 9.0% acrylic or methacrylic acid. The films for spectroscopic analysis were prepared by hot pressing the films at 150°C for 10 s under pressure.

Infra-red spectroscopy

Infra-red spectra were recorded using a Nicolet 60SX Fourier transform infra-red spectrophotometer equipped

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with a caesium iodide beam splitter and t.g.s. detector. The spectra were collected at 2 or 4 cm^{-1} resolution and 256 scans were signal averaged. The variable temperature infra-red measurements were performed using a Beckman variable temperature unit (VLT-2) with automatic temperature controller (CTC-250). The temperature was maintained to within ±1°C of the reported value. A copper–constantan thermocouple was used for making the temperature measurements.

FOURIER DECONVOLUTION AND DERIVATIVE SPECTRA

The use of derivative spectra to assist in interpreting spectroscopic absorption band contours is not a new technique[19–21]. However, it appears from the literature that use of derivative spectra is rarely made to assist in interpreting infra-red spectra. As a result, structural information about a material can be lost. In the second derivative spectra, the minimum peaks correspond to peak maxima in the absorbance spectrum. From the second derivative spectra better frequency accuracy can be achieved. Second derivative spectra are used here to assist in confirming the results of the Fourier deconvolution to be described below.

The technique of Fourier deconvolution has also been used for several years to aid in the interpretation of infra-red spectra. (For an example of an application see reference 23.) The use of Fourier deconvolution allows the resolution of the spectrum to be effectively improved by removing what is essentially the natural line shape of an absorption band from the experimentally obtained contour. The following is a brief description in mathematical terms of the Fourier deconvolution technique. The reader is referred to the references cited for a more complete description of the mathematics and theory of the technique[17,18].

The experimental spectrum, $E(\tilde{\nu})$, can be written as a convolution product (denoted by $*$) as follows.

$$E(\tilde{\nu}) = G(\tilde{\nu}) * E'(\tilde{\nu}) \tag{1}$$

where $G(\tilde{\nu})$ is a line shape function and $E'(\tilde{\nu})$ is 'a spectrum' resulting from the deconvolution. The actual deconvolution is performed on the interferogram (i.e. the data as recorded using interferometric techniques). To deconvolute, one takes the Fourier transform of equation (1).

$$\begin{aligned} I(x) &= \int_{-\infty}^{\infty} E(\tilde{\nu})\exp(-i2\pi\tilde{\nu}x)\,\mathrm{d}\tilde{\nu} \\ &= \int_{-\infty}^{\infty} G(\tilde{\nu})\exp(-i2\pi\tilde{\nu}x)\,\mathrm{d}\tilde{\nu} \qquad (2) \\ &\quad \times \int_{-\infty}^{\infty} E'(\tilde{\nu})\exp(-i2\pi\tilde{\nu}x)\,\mathrm{d}\tilde{\nu} \end{aligned}$$

or

$$I(x) = \mathcal{F}^{-1}\{G(\tilde{\nu})\}I'(x)$$

where $\mathcal{F}^{-1}$ is the inverse Fourier transform. The interferogram corresponding to the deconvoluted spectrum is given by

$$I'(x) = 1/(\mathcal{F}^{-1}\{G(\tilde{\nu})\})[I(x)] \tag{3}$$

The Fourier transform is then computed on the interferogram and the deconvolution spectrum is generated. A Lorentzian lineshape function is used as the deconvolution function in our case and is given by a general expression:

$$E_0(\tilde{\nu}) = \frac{\sigma/\pi}{\sigma^2 + \tilde{\nu}^2} \tag{4}$$

where $E_0(\tilde{\nu})$ is the intrinsic line shape function of $E(\tilde{\nu})$. The σ parameter is the half bandwidth. For the specifics of the relationship between $E_0(\tilde{\nu})$ and $G(\tilde{\nu}) * E'(\tilde{\nu})$ the reader is referred to reference 17.

To demonstrate the technique, Lorentzian band shapes have been generated for one and a sum of two bands. The curves are shown in *Figure 1* along with the Fourier deconvoluted spectra. One observes how the bandwidths are greatly reduced, resulting in resolution enhancement which gives more accurate relative intensity measurements. Two parameters are necessary for the deconvolution procedure: the bandwidth parameter, 2σ (the full width at half height), and the resolution enhancement factor, K. Specifics on the definition of the latter can be found in the cited references[17,18]. (The program used was that written by Nicolet Instruments for their 60SX data system based on D. Cameron's algorithm, see reference 17.)

In this paper, the Fourier deconvoluted spectra and second derivative spectra will be used to show the complexity of the hydrogen bonding structure in model polyurethane and ethylene/acid copolymers. However, as with any mathematical treatment of data, the results need to be evaluated based on the original data and limitations of the techniques. Both deconvolution and second derivative spectra have been used in a complementary fashion in the resolution enhancement of the spectroscopic data.

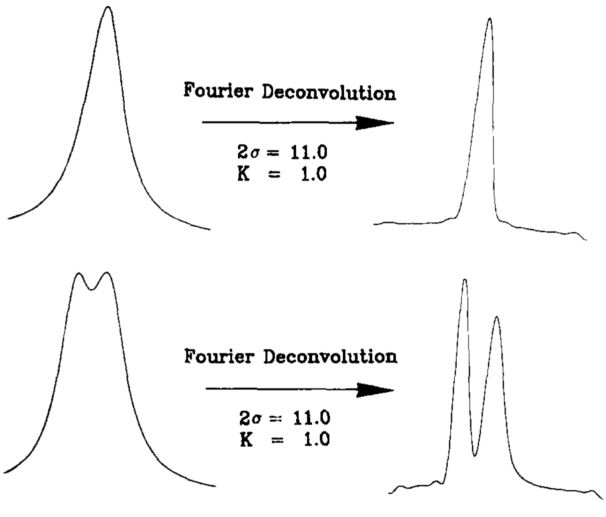
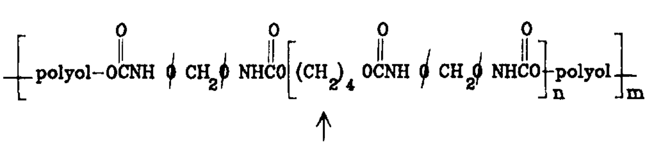


Figure 1 Synthetic curves for one and a sum of two Lorentzian functions before and after Fourier deconvolution

RESULTS

Model polyurethanes

The model polyurethanes are materials that contain well defined hard and soft segment structures as shown in *Figure 2*[22]. The polymers consist of the soft segment which is a 2000 molecular weight poly(propylene oxide) and the hard segment composed of various chain length MDI/1,4-butanediol segments. Recently, we have reported, among other analyses, variable temperature infra-red experiments on the B0, B1, B2 and B4 model polymers[22]. *Figure 3* again presents the variable temperature experiments on the model polymers in the carbonyl stretching region. The original goal was met by correlating the changes in hydrogen bonding in the various hard segment length polymers with the observed physical and mechanical properties of the polymer. However, during the analysis of the data, it was observed that the frequency of the hydrogen bonded carbonyls for the B0 and B1 polymers is different to the frequency for the B2 and B4 polymers. Also, the fit of the theoretical and experimental contours using curve fitting analysis at higher temperatures (greater than 125°C) for the B2 and B4 was not as good as that at lower temperatures using two curves (one for the free and one for the hydrogen bonded carbonyls). This suggests that additional absorption bands are present or appear at the higher temperatures and were observed to be intermediate between the frequency of the free and hydrogen bonded carbonyl stretching absorption frequency.



$$\left[\text{polyol}-O\overset{O}{\overset{\|}{C}}NH\ \phi\ CH_2\phi\ NH\overset{O}{\overset{\|}{C}}O \left[(CH_2)_4\ O\overset{O}{\overset{\|}{C}}NH\ \phi\ CH_2\phi\ NH\overset{O}{\overset{\|}{C}}O\right]_n \text{polyol}\right]_m$$

butanediol (chain extender)

polyol: P2000, 2000 molecular weight poly(propylene oxide)

n=0 (B0); n=1 (B1); n=2 (B2); n=4 (b4)

Figure 2 Repeat unit structure of the model polyurethanes

Coleman *et al.*[14–16] have recently published work on Nylon 11 and a simple polyurethane which shows the complexity of the carbonyl stretching region. They quantified the amount of free and hydrogen bonded carbonyls that were present as a function of temperature. It is not the intention here to quantify the amount of free and hydrogen bonded carbonyl groups for the polyurethanes but rather to show the complexity of the hydrogen bonding in polyurethanes as assisted by Fourier deconvolution and derivative infra-red spectra and to propose an interpretation of the data. Much of the previous work has assumed a simple bonded or free moiety (see for example references 24–26).

Figure 4 shows the infra-red spectra for the four model polyurethanes recorded at room temperature, the Fourier deconvoluted, and the second derivative spectra. One can observe how the results of the two techniques confirm the presence of an absorption band and improve the accuracy of the frequency determined for the band. *Table 1* summarizes the vibrational absorption frequencies in the carbonyl stretching region. As can be observed from the data, for the B0 and B1 polymers, the lowest frequency absorption associated with the hydrogen bonded carbonyl groups is at 1708 cm^{-1}. For the B2 and B4 polymers, the lowest frequency absorption occurs at

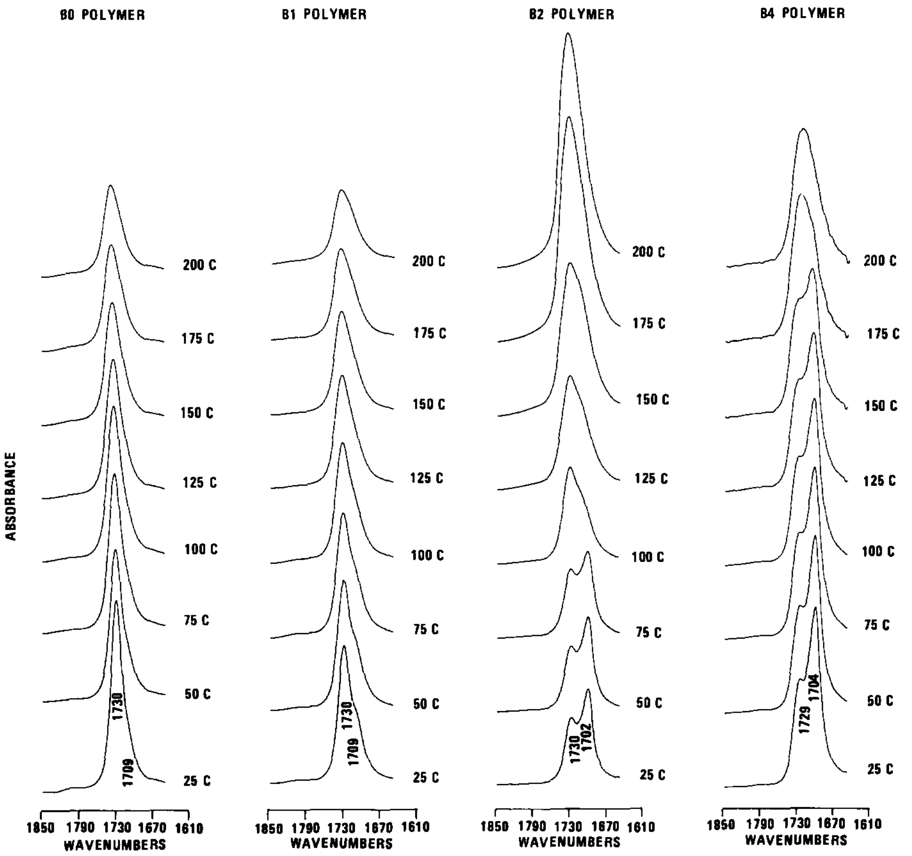


Figure 3 Variable temperature infra-red spectra in the carbonyl stretching region for the model polyurethanes (4 cm^{-1} resolution, 256 scans)

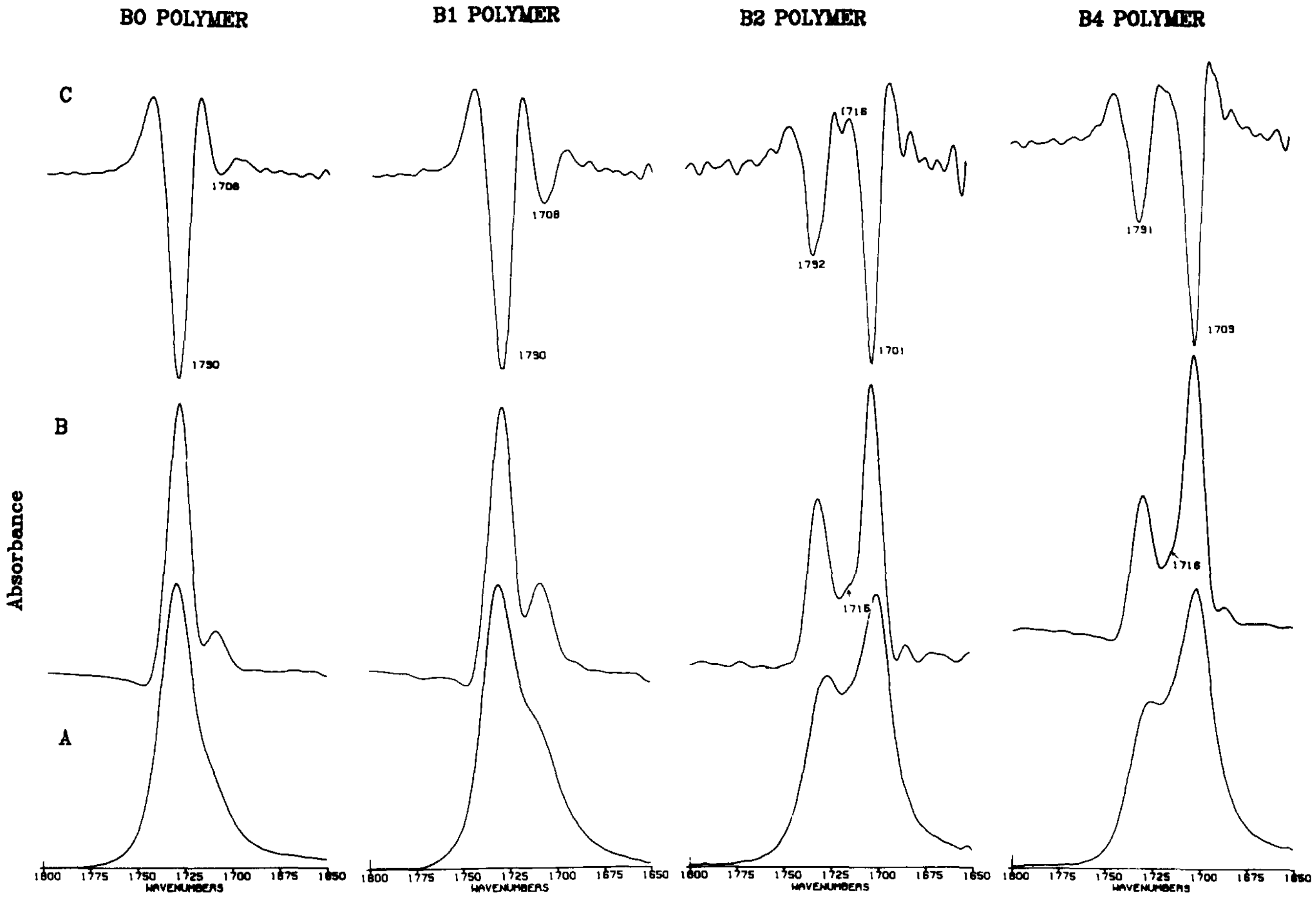


Figure 4 (A) As recorded, (B) Fourier deconvoluted (bandwidth = 16.0 cm^{-1}, $K = 1.8$), and (C) second derivative room temperature infra-red spectra for the model polyurethanes (4 cm^{-1} resolution, 256 scans)

Table 1 Frequency and assignment of carbonyl stretching bands in the model polyurethanes

	Vibration frequency and assignment			
		Interchain disordered hydrogen bonded carbonyl stretching		'Intrachain' controlled ordered hydrogen bonded carbonyl stretching
Polymer	Free carbonyl stretching	'Short range'	'Long range'	
B0 (r.t.)	1730		1708	
B0 (50°C)	1731	1711		
B0 (100°C)	1732	1715		
B0 (175°C)	1736	1720		
B1 (r.t.)	1730		1708	
B1 (50°C)	1731	1711		
B1 (100°C)	1730	1716		
B1 (175°C)	1736	1722		
B2 (r.t.)	1732	1716		1701
B2 (50°C)	1732	1716		1701
B2 (100°C)	1732	1716		1701
B2 (175°C)	1734 (1738)	1722		
B4 (r.t.)	1731	1716		1703
B4 (50°C)	1731	1716		1703
B4 (100°C)	1738	1716		1703
B4 (175°C)[a]	1737	1724	1711	

[a] Bands at 1691 and 1678 were also observed

1701 cm^{-1}. The B0 and B1 polymers have been shown to be very phase mixed[22], and the hard segment chain contains only two or four urethane or carbamate linkages. Conversely, the B2 and B4 polymers are elastomers and there are six and ten urethane linkages, respectively, per hard segment chain.

Coleman *et al.*[15,16] in their recent work have assigned bands in a simple aliphatic hard segment urethane to free carbonyls, ordered and disordered hydrogen bonded carbonyls. However, they did not have the advantage of having model polymers and did not suggest the source or cause of the ordered or disordered hydrogen bonded materials except to say the ordered structure was associated with crystalline melting, as would be expected. From the spectroscopic data of the model polyurethanes, several factors can affect the molecular ordering of the material: the extent of phase segregation, the hard segment chain length, chain conformation and chain packing. Thus, order can be defined as the combination of these effects which can be detected by characterization techniques such as small angle X-ray scattering (SAXS), microscopy and differential scanning calorimetry (d.s.c.). A disordered structure would still be hydrogen bonded, yet phase structures may not be detected by SAXS and microscopy.

The chain length, conformation and packing would predominately influence the extent of intrachain ordering. From the data, it appears that the ordering, as evidenced by the absorption band at 1701 cm^{-1}, appearing for the B2 polymer (and not the B1 polymer) suggests that the two additional carbamate linkages in the B2 *versus* B1 polymer contribute significantly to the ordering due to intrachain effects. However, the solubility of the B2 chain in the polyol is reduced resulting in a more phase segregated material that also can contribute to the order.

The B4 polymer exhibits longer range order as determined by small angle X-ray scattering and microscopy[22]. *Figure 5* shows some representative Fourier deconvoluted infra-red spectra of the model polymers at room temperature and selected temperatures as found in *Figure 3*. Obviously, for the B2 and B4 polymers two types of carbonyls are observed at frequencies intermediate to the free and ordered hydrogen bonded carbonyls. *Table 1* summarizes the frequencies and the assignments for the polymers. In the model systems (B2 and B4) with the ordered structures, disordered materials are also present.

It can be concluded that the 1716 cm^{-1} absorption is associated with a hydrogen bonded structure in a disordered phase that occurs in the B2 and B4 polymers. (Representation shown in *Figure 6*.) The absorption frequency is similar to that in the B0 and B1 polymers which exhibit little phase segregation and ordering. The absorption bands at 1716 and 1724 cm^{-1} for the B2 and B4 polymers, respectively, are associated with hydrogen bonded structures in a disordered phase that are similar to the species that absorb at lower temperatures at 1708 cm^{-1}. The shift in the 1708 cm^{-1} band for the B0 and B1 polymers to higher frequency is likely associated with a decrease in the 'long range' interchain hydrogen bonding (e.g. going from a structure that is disordered with several carbamate groups interacting to one that has much fewer groups interacting and is potentially even more disordered).

The analogy is based on the interpretation made by McLachlan and Nyquist[12] for model carbamate molecules in solution. The 1716–1724 cm^{-1} band is associated with hydrogen bonds that are 'short range' and in a disordered phase. The frequency corresponding to a change from 'long' to 'short' range order is not rigorously defined.

In fact, the absorptions in the 1708–1724 cm^{-1} region

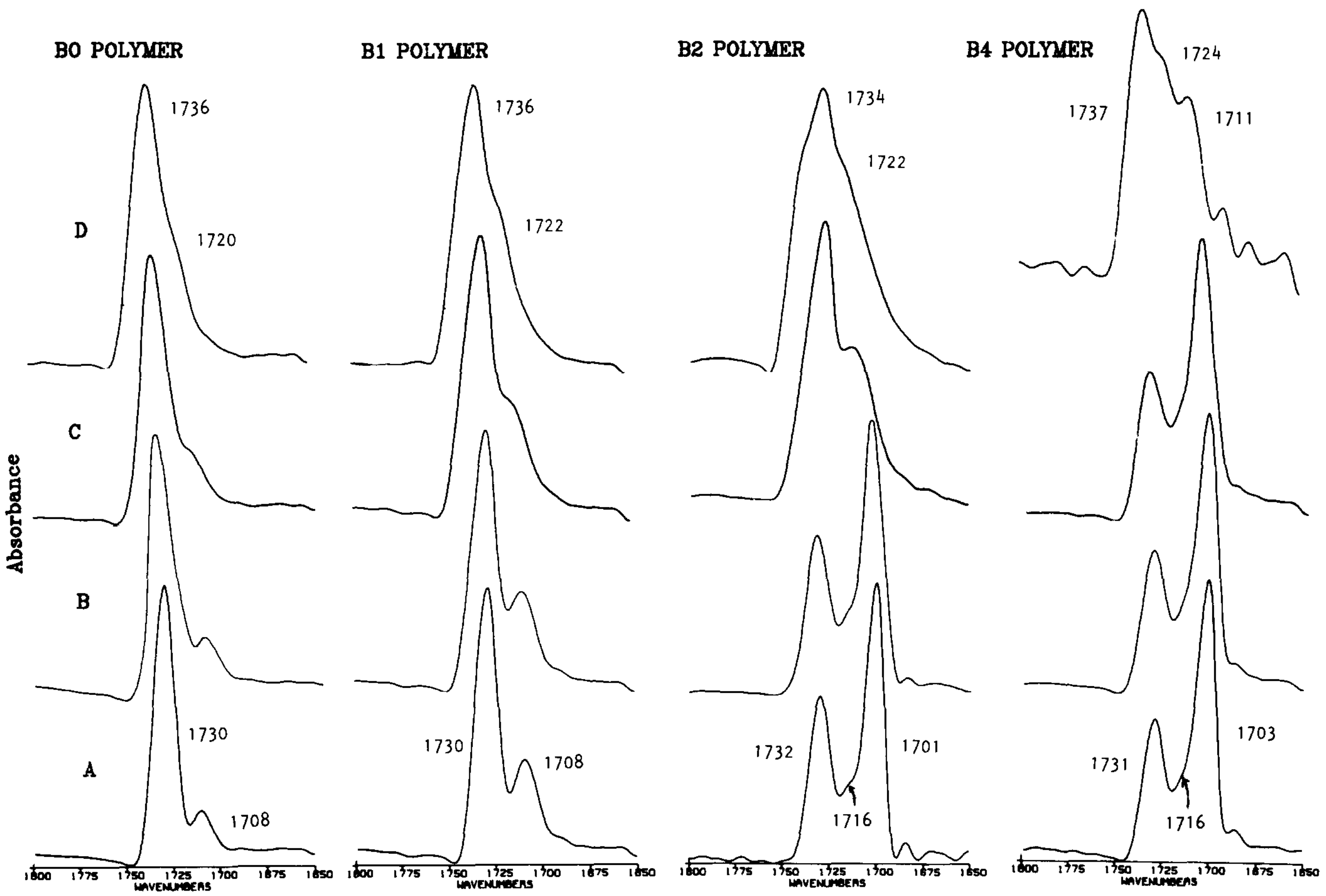


Figure 5 Representative variable temperature Fourier deconvoluted infra-red spectra for the model polyurethanes: (A) 25°C, (B) 50°C, (C) 100°C and (D) 175°C. (4 cm^{-1} resolution, 256 scans, bandwidth = 16.0 cm^{-1}, $K = 1.8$)

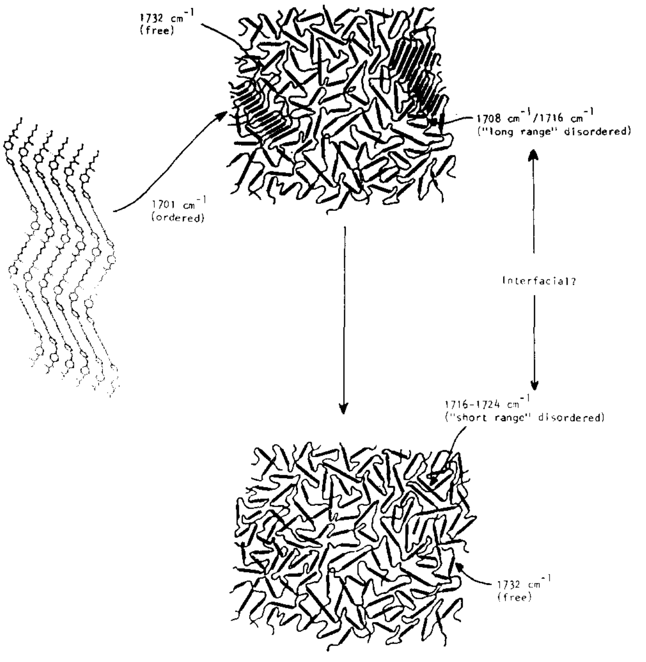


Figure 6 Summary of the model used to interpret the various observed carbonyl stretching vibrations in the model polyurethanes. (Part of the figure has been abstracted from refs. 31 and 32)

at room temperature could be thought of as being associated with an interfacial region. Here, the interface is defined as the region where the hard and soft segments come together. Additionally, the interface would be composed of neither ordered hydrogen bonded materials or free carbonyl groups (i.e. 1708–1724 cm^{-1} absorptions are indicative of disordered and/or interfacial groups). For the well defined model B2 and B4 polymers, little or no absorption between 1701 and 1734 cm^{-1} is observed for the polymers. However, for the B0 and B1 polymers, absorptions around 1708 cm^{-1} occur due to disordered material which would also be similar to interfacial material in the B2 and B4 polymers. Therefore, the appearance of an intermediate absorption (1708–1724 cm^{-1}) in a room temperature spectrum would indicate disordered and/or interfacial hard phase material is present. In the B2 and B4 polymers, due to the well defined chain length, very little interfacial/disordered hard phase material is present. Some absorption is observed at 1716 cm^{-1}. As the temperature is increased the transition from an ordered to disordered state is observed by the disappearance in the 1701 cm^{-1} absorption band. A question which must be specifically addressed is: do the absorption bands in the 1708–1724 cm^{-1} discriminate between disordered *versus* interfacial material?

Ethylene/acid copolymers

Figures 7–9 present the spectra in the carbonyl stretching region (as-recorded and Fourier deconvoluted) for three ethylene/acid copolymers at r.t., 225°C, and upon cooling to r.t. From the as-recorded spectra, it is obvious that the absorption bands are very asymmetric. From the deconvoluted r.t. spectra for the various ethylene/acrylic acid copolymers, one observes that a variety of hydrogen bonded carbonyl structures are present. For the 9.0% acrylic acid copolymer, hydrogen bonded carbonyl absorption frequencies are observed at 1696 and 1710 cm^{-1}. For the 6.5% acrylic acid copolymer, the hydrogen bonded carbonyl absorption frequency occurs at 1706 cm^{-1}. For the 6.5% methacrylic acid copolymer the hydrogen bonded carbonyl absorption occurs at 1696 cm^{-1}.

Upon heating the material to 225°C, the acrylic acid copolymers form two absorption bands associated with free carbonyl groups, 1745 and 1758 cm^{-1}. Upon cooling to r.t. after heating, essentially the same absorption band frequencies are obtained compared to the spectra before heating. However, the relative intensities of some of the hydrogen bonded carbonyl stretching absorptions have changed. *Table 2* summarizes the absorption frequencies.

A weak absorbing band is observed at about 1733 cm^{-1} which is attributed to oxidized polymer. Heating and cooling the sample had no effect on this absorption. Otocka and Kwei have observed bands in the r.t. spectrum of an ethylene/acrylic acid copolymer at 1750, 1735, 1705 and 1690 cm^{-1} using a curve analyser[13]. Their assignment of the 1735 cm^{-1} absorption to an oxidation product agrees with our assignment. However, they did not assign the 1690 cm^{-1} band and the assignment for the 1750 and 1705 cm^{-1} absorptions were free and dimerized hydrogen bonded carbonyl linkages, respectively.

In contrast to the polyurethanes, the ethylene/acid copolymers show essentially all of the carbonyl groups to be hydrogen bonded at room temperature. This is evidenced by the very weak absorptions observed at 1745 and 1758 cm^{-1}. As mentioned, these two absorptions have been assigned to free carbonyl groups. The

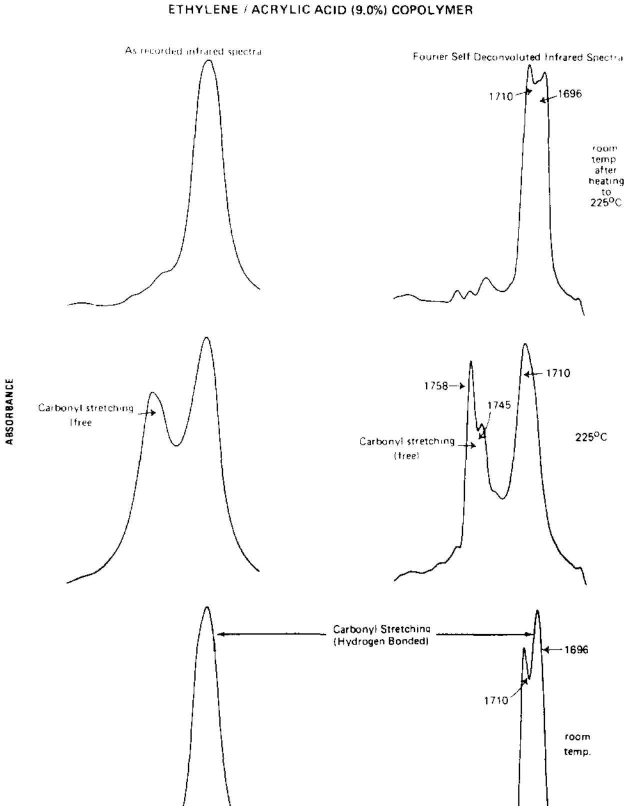


Figure 7 As recorded and Fourier deconvoluted (bandwidth = 12.0 cm^{-1}, $K = 2.0$) spectra for an ethylene/acrylic acid copolymer (9% acid) in the carbonyl stretching region (2 cm^{-1} resolution, 256 scans)

appearance of the two absorption bands for the ethylene/acrylic acid copolymers suggests strongly that some conformational effects, either from the backbone or from a rotational isomer of the carboxyl side group, may be giving rise to the two absorptions. In the case of the ethylene/methacrylic acid copolymer, essentially only one free carbonyl band (1758 cm^{-1}) is observed for the 6.5% acid material. This suggests that the methyl group on the backbone causes predominately one free carbonyl structure to be present in the material upon heating. This additionally supports that a backbone conformational effect is significant in the case of the ethylene/acrylic acid copolymers. The ethylene/acrylic acid copolymer likely has a greater potential for *gauche* compared to *trans* conformations than the methacrylic acid copolymer.

The main question to be addressed and of significance is the assignment of the structures associated with the absorption bands at 1696, 1706 and 1710 cm^{-1}. Previously, essentially all reported work involving acid copolymers has assumed the acid groups to be hydrogen bonded as cyclic dimers[9-11,27]. If local symmetry arguments for a planar cyclic dimer are made, the dimer would have a symmetry of C_{2h} which has symmetry elements of the identity, a C_2 axis of rotation, a centre of inversion (i) and a horizontal plane of symmetry (σ_h). In this case, the symmetric carbonyl stretching vibration of the planar cyclic dimer has a symmetry species of A_g which is not infra-red allowed. The antisymmetric carbonyl stretching vibration of the planar cyclic dimer has a symmetry species of B_u which is infra-red allowed. For the methacrylic acid copolymer, the presence of one

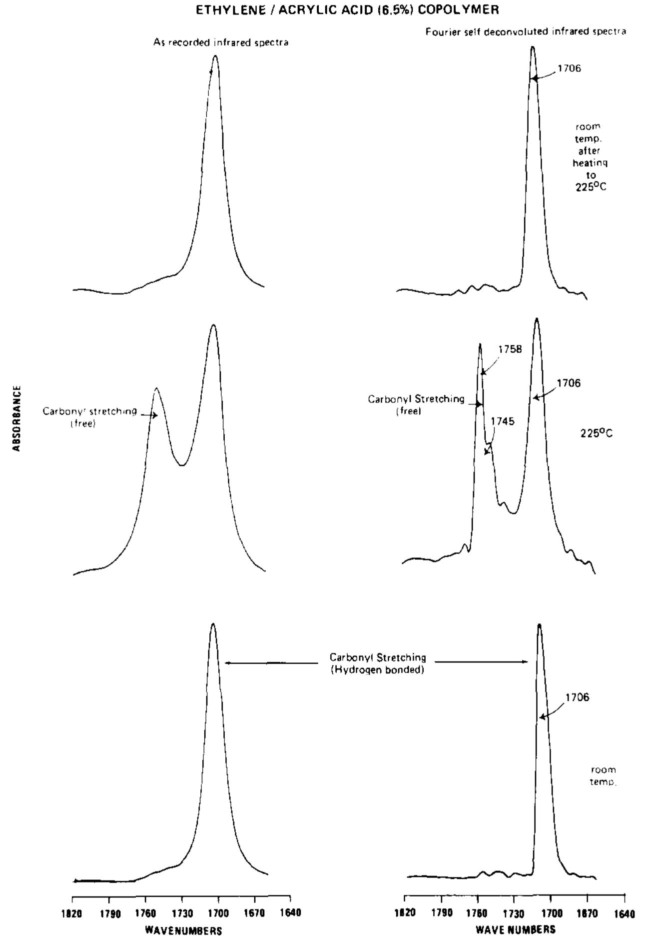


Figure 8 As recorded and Fourier deconvoluted (bandwidth = 12.0 cm^{-1}, $K = 2.0$) infra-red spectra for an ethylene/acrylic acid copolymer (6.5% acid) in the carbonyl stretching region (2 cm^{-1} resolution, 256 scans)

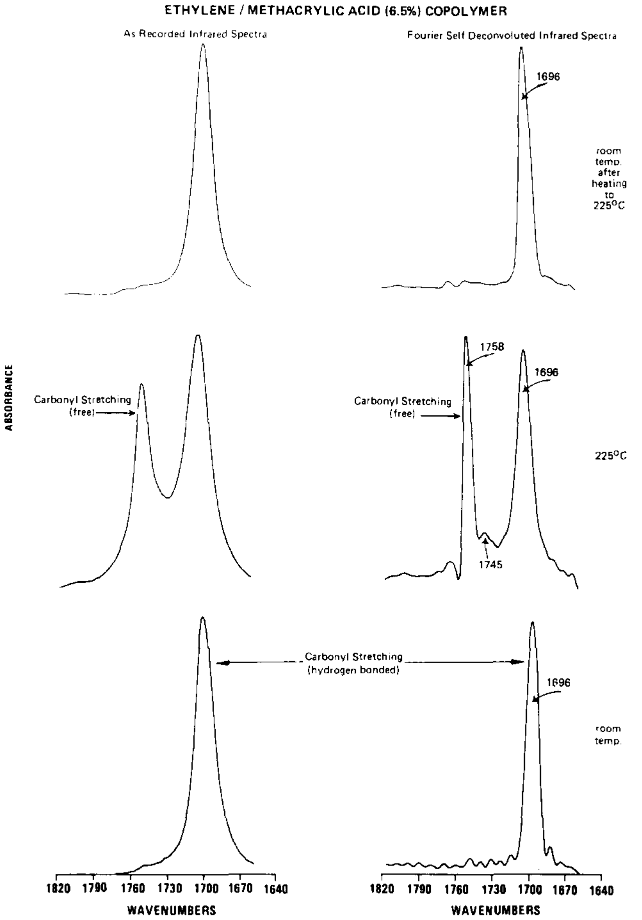


Figure 9 As recorded and Fourier deconvoluted (bandwidth = 12.0 cm^{-1}, $K = 2.0$) infra-red spectra for an ethylene/methacrylic acid copolymer region (2 cm^{-1} resolution, 256 scans)

Table 2 Frequencies and assignment of the carbonyl stretching absorption from Fourier deconvoluted spectra of various ethylene/acrylic and methacrylic acid copolymers

	Hydrogen bonded carbonyl groups			
		Open		
Copolymer	Closed/cyclic dimers	'Long'	'Short'	Free carbonyl groups
Ethylene/methacrylic acid (6.5% acid)	1696			(1745)[a], 1758
Ethylene/acrylic acid (6.5% acid)		1706		1745, 1758
Eetylene/acrylic acid (9.0% acid)	1696		1710	1745, 1758

[a] The 1745 cm^{-1} band is much less intense for the methacrylic than acrylic acid copolymer

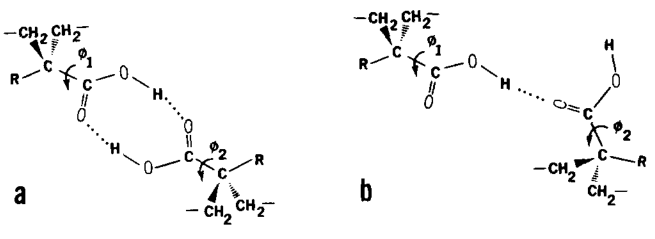


Figure 10 Examples of (A) a closed or cyclic dimer and (B) an open structure of hydrogen bonding between two acid groups ($R = H$ or CH_3)

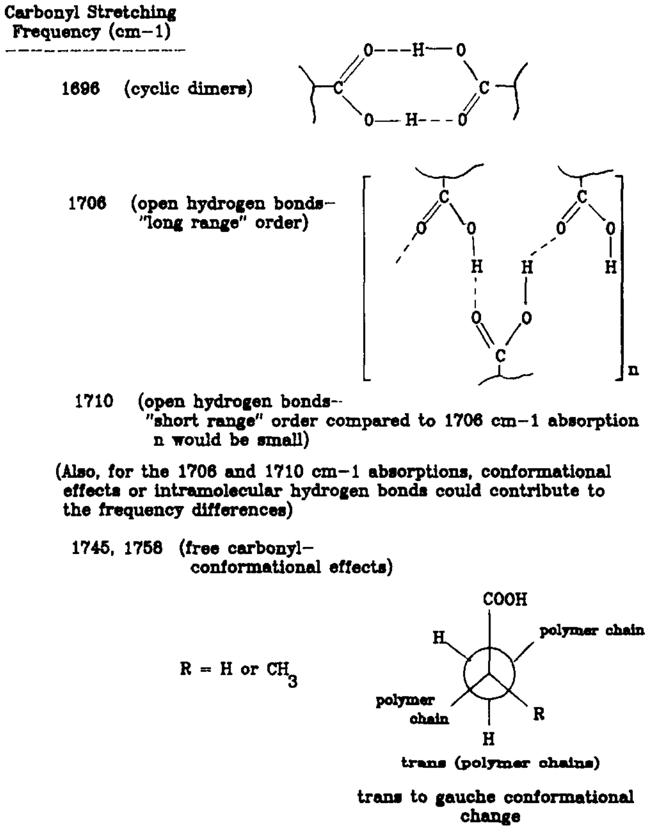


Figure 11 Summary of the model used to interpret the various observed carbonyl stretching vibrations in the ethylene/acid copolymers

absorption band, the antisymmetric carbonyl stretching, suggests that the acid groups form the cyclic dimer. Based on this and previous work[9–11,27] the 1696 cm^{-1} absorption band is assigned to the planar cyclic dimer. A lower frequency for the cyclic (or closed) dimer is expected compared to the open dimer. For example, based on the longer bond length determined for the alpha (open) form that the beta (closed) form of crystalline oxalic acid, it follows that the beta form should have a lower carbonyl stretching absorption frequency[28–30].

Figure 10 shows examples of what is meant by an open and closed structure for two acid groups. In the case of the 9.0% acrylic acid copolymer, the 1696 cm^{-1} band is more thermally sensitive than the 1710 cm^{-1} absorption band (see *Figure 7*), but is reversible upon cooling to room temperature. The greater rigidity of the cyclic or closed dimer apparently results in a less thermally stable hydrogen bonded structure than the open structure or the equilibrium concentration of the open hydrogen bonded species is affected to a lesser extent by temperature.

The band at 1710 cm^{-1} is being assigned to the open dimer structure in a more 'short range' hydrogen bonded structure. The absorption at 1706 cm^{-1} would be an open dimer structure due to 'long range' order of the acid groups. Additional experiments are needed to conclusively assign the origin and significance of these absorption bands. Alternate explanations of the absorption bands could be conformational effects and, less likely, intramolecular hydrogen bonded carbonyls. *Figure 11* summarizes the assignments of the various carbonyl absorptions.

CONCLUSIONS

The research reported here shows how the infra-red spectra of a polymeric material contain detailed information about the hydrogen bonding structure. The use of computer assisted tools to more easily extract this information from the spectra has been shown. Fourier deconvolution and second derivative spectra give better frequency accuracy and provide for effective resolution enhancement. In the case of both polyurethanes and ethylene/acid copolymers, the hydrogen bonding structures present have been shown to be more complex than has generally been observed. Preliminary interpretation of the new data has been done to show the sensitivity of the hydrogen bonding structure in polymers to temperature, order and chain conformation. The implications of a more detailed knowledge of hydrogen bonded structures and/or the associated structures of a polymer can lead to characterization of the phase, domain and/or interfacial structure and adhesion mechanisms/chemistry of a material. The information can then be further used to understand polymer properties from a molecular structure and morphological perspective.

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