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Infrared, Raman, and Near-Infrared Spectroscopic Evidence for the Coexistence of Various Hydrogen-Bond Forms in Poly(acrylic acid)

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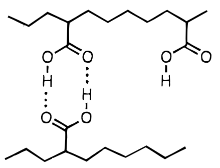
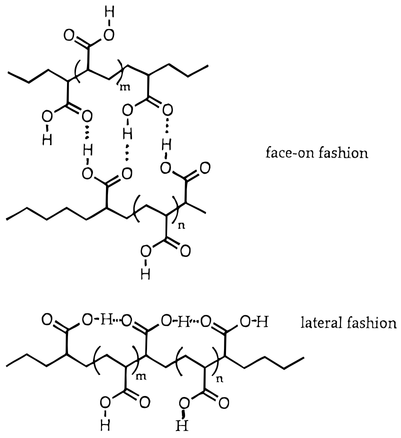
ABSTRACT: Fourier-transform infrared (FT-IR), near-infrared (NIR)-excited FT-Raman, and FT-NIR spectra have been measured for poly(acrylic acid) (PAA) in a cast film over a temperature range of 40−140 °C, to investigate structures of hydrogen bonds and their dissociation. The C═O stretching bands in the FT-IR spectra are unraveled by a prevalent multiple species model for small aliphatic acids with various kinds of associated forms of carboxylic acid groups, namely cyclic dimer, linearly associated oligomers of COOH, and free COOH groups. These different structures of hydrogen bond persist even when the temperature rises well above the glass transition temperature. The FT-Raman spectra confirm the existence of such COOH groups. Temperature-dependent intensity changes in the first overtone of an OH stretching mode of PAA reveal that the COOH groups dissociate significantly at high temperatures. We propose that the coexistence of various possible hydrogen-bond forms analogous to those in small aliphatic acids best interprets the vibrational spectral features of PAA. The oligomeric chains of COOH groups in PAA may explain the previously proposed cooperative hydrogen bond in PAA or polymer blends containing PAA.

Introduction

Poly(acrylic acid) (PAA) and its copolymers have recently received keen interest because they are very useful as thickening agents for latices and adhesives, as well as ingredients in the formulation of pharmaceuticals, cosmetics, coatings, and agricultural chemicals. In order to elucidate the interesting properties that PAA shows, e.g., special viscosity behavior in solutions, many researchers have been extensively studying the conformational changes and hydrogen bonds of the macromolecular chains, that are responsive to changes in pH, ionic strength, temperature, and shear stress.[1−4] Hydrogen bonds in PAA certainly play a major role in exhibiting its properties. Previously, Koenig *et al.*[5] studied the conformational transitions of syndiotactic poly(methacrylic acid) (PMA) in water by using Raman spectroscopy. They found that hydrogen bonds between carboxylic groups persisted in aqueous solutions, but no attention was paid to possible forms of the hydrogen bond. Recently, a Raman spectroscopic study of PAA and its monomer analogues indicated that dissociation of COOH groups into free species is more unfavorable for PAA than that for model compounds of PAA repeating units.[4] In order to account for this distinction, the researchers proposed that some cooperative hydrogen bonds may exist in PAA aqueous solutions.



A: Cyclic dimer and free monomer of COOH



B: Inner and terminal COOH in linear oligomeric forms

Figure 1. Four possible forms of carboxylic acid groups in the condensed phase: cyclic dimer, free monomer, and inner and terminal COOH groups in oligomeric forms.

The hydrogen bonds between carboxylic groups of organic acids have long been investigated, and it is well-known that cyclic dimers mainly exist in the pure liquid or solid states.[6,7] An alternative structure of organic acids in the condensed states is a long polymeric chain of hydrogen-bonded carboxylic groups (Figure 1). In concentrated solutions, pure liquid, or crystalline states, the existence of several associated species of acetic acid and formic acid, namely cyclic dimers and linear open chain oligomers[8] including open dimers, was revealed by infrared (IR), Raman spectroscopy, X-ray scattering, and other techniques.[9−12] For highly concentrated solutions of acetic, propionic, and *n*-butyric acids, the monomeric and polymeric forms of carboxylic groups have been demonstrated by factor analysis and band resolution of a Raman peak due to the C═O stretching mode.[13,14] According to these studies, an additional component in the resolved C═O stretching band other than dimeric and monomeric species was attributed to the existence of a face-on bonded structure of COOH

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groups in an oligomeric chain form (Figure 1B). On the other hand, laterally hydrogen-bonded acid oligomers were also proposed for several kinds of long-chain fatty acids in monolayer films on solid surfaces, based on FT-IR spectroscopic studies (Figure 1B).[15,16]

In contrast to the studies of low molecular weight aliphatic acids, there has been no report which suggests the existence of linearly associated hydrogen-bonding structures for polymers (see Figure 1). As pointed out by Coleman *et al.*,[17] however, the functional group of a polymer can form hydrogen bonds according to its intrinsic proclivities. As long as the chain is flexible, the association of its repeating units is very similar to that of a "small" molecule of equal molar volume.

The intermolecular interactions for the formation of supramolecular hydrogen-bonding structures of the carboxylic group can be explored not only by IR and Raman spectroscopies but also by near-IR (NIR) spectroscopy. In the NIR region, there appear overtones and combination bands of O−H and N−H stretching modes, for which shifts due to the hydrogen bonding are much larger in the NIR spectra, compared with the IR region.[18,19]

Here, we report vibrational spectroscopic studies of possible forms of hydrogen bonds of PAA in a solid state. The existence of the linearly associated hydrogen bonds of carboxylic groups is proposed for the first time for the polymer. It is well established that upon heating, PAA does not become thermoplastic but cross-links, chars, and decomposes. Therefore, we have investigated the interactions at relatively low temperatures. By using complementary techniques, IR, NIR, and Raman spectroscopies, we find that although PAA is usually regarded as strongly self-associated, it is actually a complex hydrogen-bonding mixture with a considerable amount of dissociated species.

Experimental Section

Poly(acrylic acid) (PAA) (molecular weight 450 000, with a nominal T_g 105 °C) was supplied by Aldrich Chemical Co. and used as received. Films of PAA were cast onto Teflon plates or glass plates from 1% aqueous solutions. After evaporation of the majority of water under an infrared lamp, the samples were placed in a vacuum oven at 50 °C for at least 3 days to remove residual water and stored under vacuum before spectral measurements.

IR spectra were collected at a 4 cm^{-1} resolution on a Nicolet Magna 550 FT-IR spectrometer equipped with a cooled MCT detector. A minimum of 200 scans were coadded. FT-Raman spectra were measured with a JEOL JRS-FT 6500N FT-Raman spectrometer equipped with an InGaAs detector. An excitation wavelength at 1064 nm was provided by a continuous wave (cw) Nd:YAG laser (Spectron SL 301 1355), and the laser power at the sample position was about 500 mW. All the Raman data were collected at a spectral resolution of 4 cm^{-1}, and 500 scans were accumulated. NIR spectra were obtained at a 8 cm^{-1} resolution with the same spectrometer as that used for the Raman measurements. A TGS detector was employed instead of the InGaAs detector for the NIR measurements, and 200 scans were coadded.

In order to investigate temperature-dependent spectral changes, a copper block device with a ceramic heater inside was used. The polymer film was inserted into a sample holder in the block, and temperature was controlled by using an Omron E5T program thermocontroller, which has a temperature stability of better than ±0.1 deg. The calculation of second derivative of the spectra and curve-fitting analysis were performed by Grams/386 (Galactic Industries Co.). Principal component analysis was carried out by employing cross-validation, using the PLSplus/IQ software for Grams/386. The peak resolution was achieved by using nonlinear least-squares analysis using widely accepted modified Marquardt method. During the curve-fitting, a simple Gaussian function was found to be adequate to resolve the bands, though Gauss−Lorentz hybrid functions were also attempted.

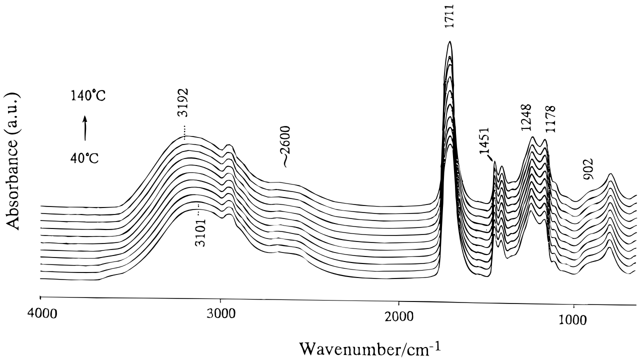

Figure 2. FT-IR spectra of PAA recorded over a temperature range of 40−140 °C (10 deg interval with a rising rate of 1 °C/min).

Table 1. Observed Frequencies and Assignments of Infrared and Raman Bands of PAA in a Cast Film

IR (ν/cm^{-1})	Raman ($\Delta\nu$/cm^{-1})	assignments[3,20,21]
3101, broad		O−H stretching
2947	2927, 2877	CH_2 or CH stretching
2700−2500		overtones and combinations of bands near 1413 and 1248 cm^{-1} enhanced by Fermi resonance with the broad OHstretching peak
1711 strong	1698	C═O stretching
1451	1457	CH_2 deformation
1413		C−O stretching coupled with O−H in-plane bending
	1333	CH_2 twisting
1248		C−O stretching coupled with O−H in-plane bending
1178	1191	C−O stretching coupled with O−H in-plane bending
1112	1105	C−CH_2 stretching
	1026	CH_2 rocking
902 broad		O−H out-of-plane bending
	846	C−COOH stretching
804		CH_2 twisting and C−COOH stretching

Results and Discussion

Figure 2 shows IR spectra of PAA in a cast film recorded over a temperature range of 40−140 °C. In common with other strongly self-associated polymers, such as poly(vinyl alcohol) and polyamide, the IR spectrum of PAA is characterized by relatively broad and conformationally sensitive backbone modes and hydrogen-bonded −COOH modes.[3,20,21] The assignments for major IR bands are shown in Table 1.

Previous IR studies of PAA revealed that syndiotactic PAA shows a characteristic absorption at 1240 cm^{-1} whereas atactic PAA gives a strong band at 1250 cm^{-1} with a weak shoulder at 1300 cm^{-1}.[22,23] The spectra in Figure 2 elucidate that the PAA sample is nearly atactic. The facile solubility of our PAA sample in water and dioxane also supports the atacticity, in accordance with the work by Monjol *et al.*[22] This circumvents the possible complexity of crystalline bands or bands arising from vibrational modes of groups in the crystalline region. Indeed, no significant feature shows such undesirable modes in the IR spectra as will be shown below. It is known from differential scanning calorimetry and thermal gravimetric analysis of PAA that the formation of anhydride cross-links is very slow and can

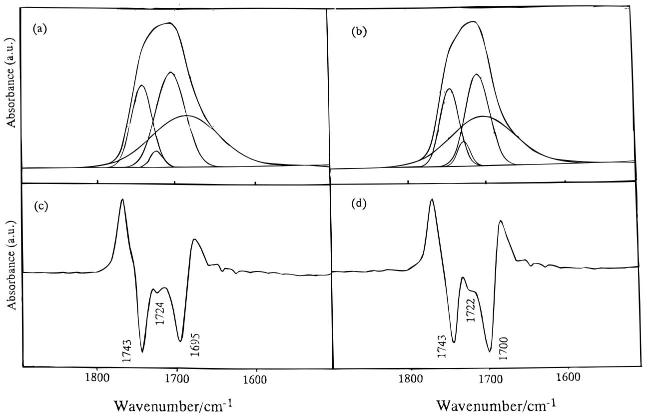

Figure 3. FT-IR spectra of PAA in the C=O stretching region: (a) recorded at 40 °C; (b) recorded at 140 °C; (c) second derivative plot of spectrum (a); (d) second derivative plot of spectrum (b). The results of curve-fitting are also shown in the spectra (a) and (b).

be neglected below 150 °C.[23] IR studies of poly(styrene-*co*-acrylic acid) copolymers also revealed that the dehydration through two acid groups starts at 150 °C.[24,25] We found that bands due to the anhydride groups appeared near 1803 and 1030 cm^{-1} very weakly at 150 °C. Therefore, in the present study the temperature was controlled below 140 °C.

In Figure 2, the peak maximum of the OH stretching band gradually shifts from 3101 to 3192 cm^{-1} as the temperature is raised from 40 to 140 °C. The broadness of the O−H peak reflects the existence of OH groups engaging in hydrogen bonds of varying strengths. With increasing temperature, the average strength of the hydrogen bonds decreases, as is indicated by the shift of the O−H stretching band to a higher wavenumber side. Consistent results for the changes in the strength of hydrogen bonds were obtained upon cooling and heating the sample again. This region does not indicate the existence of a band due to an O−H stretching mode from free (non-hydrogen-bonded) carboxylic groups. However, the broad satellite band in the 2700−2500 cm^{-1} region, assignable to combination bands of lower-frequency vibrations involving the COOH group, enhanced by Fermi resonance with the OH fundamental,[21,26,27] decreases monotonically in intensity with temperature, also implying the weakening of hydrogen bonds.

Parts a and b of Figure 3 display an enlargement of the C=O stretching band region recorded at 40 and 140 °C, respectively. As the temperature is raised, the absolute absorbance appears to increase. The asymmetric nature of the C=O stretching band (FWHM ca. 75 cm^{-1}) prompts us to use second derivative analysis for it. As shown in Figure 3c,d, second derivative plots plainly reveal three bands for the sample recorded at 40 °C, appearing at 1743, 1724, and 1695 cm^{-1}, and three bands for that at 140 °C, appearing at 1743, 1722, and 1700 cm^{-1}. Similar results were obtained from second derivative plots for other temperatures. We would expect that the C=O band is contributed by at least three possible species of carboxylic groups.

The number of the spectral band components contributing to the band envelope can be obtained by principal component analysis (PCA),[28,29] which has been widely utilized to determine the correct number of components (species, or factors) from IR, Raman, and NIR spectral data of complex systems, like polymer blends and copolymers.[30] In PCA, the determination of the number of factors (NF) is based on standard theorems of algebra rather than on any assumed band shape. Often several functions are used as criteria to evaluate the NF so as to separate the experimental random noise from the primary factors. The real error (RE), which describes the difference between the built error-free data and the actual experimental results, is calculated from the PCA eigenvalues λ_j by

Table 2. Principal Component Analysis of PAA in the C=O Stretching Region of 1900−1550 cm^{-1}

NF	eigenvalue × 10^8	RE × 10^8	IE × 10^8	IND × 10^8
1	763137	0	0	0
2	3111	15472	0	0
3	218	5420	65420	316
4	71	3787	28164	150
5	56	3072	22625	151
6	16	2037	20609	192
7	7	1606	14971	226
8	7	0	0	0

$$\mathrm{RE} = \left[\frac{\sum_{j=i+1}^{n_s} \lambda_j}{n_v(n_s - i)} \right]^{1/2}$$

where n_s is the number of spectra, n_v is the number of data points per spectrum, and i is the number of pure components. The imbedded error (IE), a function of the eigenvectors also associated with the experimental error, can be estimated by[28]

$$\mathrm{IE}_i = \mathrm{RE}_i(i/n_s)^{1/2}$$

RE or IE will show a leveling once the optimum number of primary factors has been reached. Malinowski's indicator function (IND) can be calculated from the equation

$$\mathrm{IND}_i = \mathrm{RE}_i/(n_s - i)^2$$

This indicator function attains its minimum value when the correct number of factors or that of nonzero eigenvalues has been selected.

The results of the calculations are given in Table 2. The difference between the RE values when NF = 4 and NF = 3 or 5 suggests a 4-dimensional factor space. IE values level off after NF = 4. There is not much difference when NF = 4 or 5. A minimum is clearly observed in the IND when NF is 4. Therefore, the number of components is decided to be 4.

In order to analyze the C=O stretching band region, we have also carried out curve-fitting analysis. The results from the curve-fitting suggest the presence of four Gaussian bands in this region, instead of just three spectral components judged by the second derivative spectra. During the curve-fitting, a linear baseline was assumed from 1900 to 1500 cm^{-1}. Neither the frequency nor the width of the bands was fixed. The results, as indicated by reduced χ^2 values and standard deviation from the least-squares program, exceeded our expectation.

For all the spectra recorded from 40 to 140 °C, we always obtain four bands that best fit the CO envelope while a three band fit always leaves some discrepancy. Typical resolved spectra are shown in Figure 3a,b, which display four component bands at 1686, 1705, 1723, and 1742 cm^{-1} for the sample at 40 °C and 1699, 1706, 1725, and 1743 cm^{-1} for that at 140 °C, respectively. The

Table 3. Results for Curve-Fitting of the IR C═O Stretching Band

T/°C	frequency[a]	$W_{1/2}$[b]	A[c]	frequency	$W_{1/2}$	A	frequency	$W_{1/2}$	A	frequency	$W_{1/2}$	A
40	1742.1	31.6	21.3	1723.4	18.8	2.5	1705.2	43.0	33.5	1686.0	101.6	42.7
50	1742.5	31.4	21.2	1723.7	19.0	2.7	1705.3	42.9	33.4	1687.0	102.0	42.8
60	1742.8	31.1	21.0	1724.0	19.4	2.9	1705.4	42.7	33.3	1688.2	102.1	42.8
70	1742.9	31.0	21.3	1724.1	19.6	3.2	1705.4	41.7	32.7	1689.8	101.3	42.9
80	1742.9	30.9	21.6	1724.1	19.6	3.5	1705.4	40.2	31.9	1691.6	100.1	43.0
90	1742.7	30.9	22.1	1724.0	19.7	3.9	1705.3	38.7	30.9	1693.4	98.6	43.2
100	1742.5	31.0	22.3	1723.9	19.5	3.9	1705.4	37.5	30.6	1694.7	97.5	43.2
110	1742.5	30.9	22.1	1724.0	19.6	4.0	1705.7	37.1	30.8	1695.8	97.5	43.2
120	1742.7	30.7	21.8	1724.3	19.8	4.2	1705.7	37.0	30.5	1696.7	98.2	43.5
130	1743.1	30.7	21.7	1724.2	19.9	4.2	1705.2	37.7	29.6	1697.2	99.9	44.5
140	1743.3	30.3	21.0	1724.8	20.2	4.5	1705.7	37.1	30.1	1698.7	100.7	44.4

[a] Band frequency in cm^{-1}. [b] Band width in cm^{-1}. [c] Relative band area in %.

components at 1705 and 1742 cm^{-1} may be assigned to C═O stretching modes of the cyclic hydrogen-bonded COOH group in dimeric form and free (non-hydrogen-bonded) COOH group, respectively (illustrated in Figure 1A).[13,14,21,27] The temperature-dependent variations in the frequencies of the resolved bands are shown in Table 3. The position of the free CO band near 1742 cm^{-1} changes little with temperature and is very close to those previously found for free COOH groups in various systems.[15,16,19,24,25,31−33] For example, the carbonyl band of free COOH groups in poly(ethylene-*co*-methacrylic acid) or fatty acids appears weakly near 1740 cm^{-1} at room and elevated temperatures.[19,32] IR studies of styrene−acrylic acid copolymers (PS−PAA) showed that monomer species of the acid group exhibit a band near 1742 cm^{-1} in the copolymers which can be viewed as PAA "diluted" in polystyrene.[24,25]

The frequency of the C═O asymmetric stretching in the cyclic dimer remains almost constant with temperature, owing to its fixed configuration. The C═O band of cyclic dimers has been studied in detail for various carboxylic acids.[21,24,27,34] The present results for the frequency and temperature dependence of the C═O band of the cyclic dimer are in good agreement with the previous ones. For example, in PS−PAA copolymers, a band due to the cyclic dimer form was observed at 1705 cm^{-1}, and its intensity decreased with increasing temperature.[24]

It is very interesting to note that the appearance of a C═O band component near 1685 cm^{-1} in Figure 3 corroborates the previous IR observations of PS−PAA copolymers with AA contents higher than 59%.[24] The position of this band moves to the higher wavenumber side with increasing temperature. Its presence reminds us of the possible contribution from additional forms of hydrogen bonds. Several researchers have resolved the structure of the self-associated acetic acid by various techniques.[9−12] Ng and Shurvell,[13] for example, carried out a quantitative analysis of the Raman spectra of acetic acid in aqueous solutions by factor analysis and band contour resolution techniques. Their results confirmed the prevalent notion that monomeric, dimeric, and polymeric species coexist in the pure liquid state and in highly concentrated solutions. They also observed that the band position of the inner hydrogen-bonded carbonyl group of the linear dimer/polymer moves to higher frequencies on dilution of the acid. This observation suggested that the polymeric species are broken down into smaller units, until eventually only the linear dimer is present in the solution. Various hydrogen-bonded species present in acetic, propionic, and *n*-butyric acids were also identified by Tanaka *et al.*[14] If we follow the interpretation by the above researchers, that is, the C═O band component near 1686 cm^{-1} in Figure 3 is attributed to the inner hydrogen groups of the oligomeric COOH groups, while the residual band near 1725 cm^{-1} is due to the terminal group in the oligomeric COOH chains, then it is not surprising to see the band shift of the 1686 cm^{-1} component, since on heating, the oligomeric COOH chains are broken down into shorter chains, until eventually only the open dimer is present in the sample. The C═O band widths of the inner hydrogen-bonded groups are much broader than those of other species, reflecting a broad distribution of the oligomer chains of variable lengths. The less restricted motion of the linear dimeric/oligomeric COOH as compared to the cyclic dimer can account for the slightly lower frequency observed for the linear dimer/oligomers. Moreover, the C═O groups in the oligomeric chains may couple with two adjacent C═O groups in contrast to the C═O group in the cyclic dimer in which only two C═O groups couple with each other. This may also explain the appearance of the C═O stretching band of the oligomers at the lower wavenumber side than that of the cyclic dimer species. In fact, a tail of the C═O stretching band was observed at the lower wavenumber side in previously published IR spectra of PAA.[3,20,23,24] However, no explanation was given in these studies.

The structure of PAA should be more unfavorable than that of small carboxylic acids for the dimerization because many more COOH are neighboring a chain. Tanaka *et al.*[4] compared the dissociation of PAA with that of its monomer analogues in aqueous solutions and found that dissociation of COOH groups into free species is more unfavorable for PAA than that for glutaric acid (model compound for the dimer of the PAA repeating unit) and 1,3,5-pentanetricarboxylic acid (model compound for the trimer of the PAA repeating unit). To reconcile this fact, they suggested that some sort of cooperative or nonadditive hydrogen bond may be formed in PAA solution which makes the dissociation more unfavorable than in monomer analogues. We propose that the oligomerization of COOH groups in 2- or 3-dimensional arrays of the group linkage may account for such cooperative hydrogen bonds.

Table 3 also shows temperature-dependent changes in the integrated band areas for the four C═O stretching bands. It can be seen that the integrated band area of the cyclic dimer decreases with temperature while those of the linear chain and terminal species increase continuously, implying the breakage of the most stable cyclic dimer rings and the formation of metastable open chain species at higher temperatures.

The complicated profile of the C═O stretching band associated with the COOH group might originate from several other possibilities. One possibility arises from transition dipole−dipole interactions that exist among

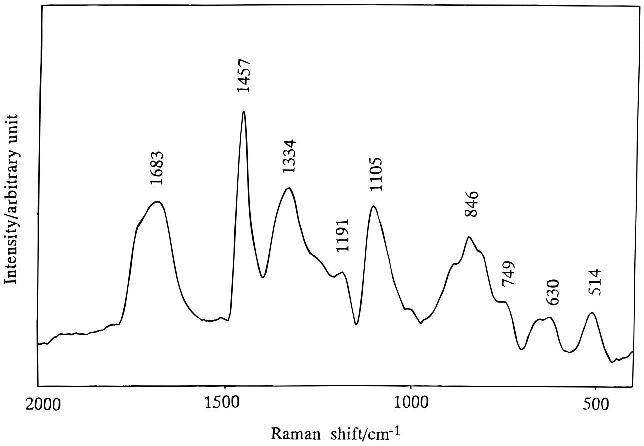

Figure 4. FT-Raman spectrum of PAA measured at 64 °C.

the PAA carbonyls. With increasing temperature, such interactions should be weakened, resulting in the reduction of the intensity of the absorption band. Unexpectedly, only the increase in the absolute intensity was observed, allowing one to suppose that the dipole interaction mechanism does not have an appreciable contribution to the origin of the 1686 cm^{-1} band. Another explanation may be presented if it is assumed that wide variations in the molecular conformation induce changes in the profile of the C═O band. The temperature effect could then be argued from changes in the populations of trans and gauche bonds. With increasing temperature, low-energy conformational states will be gradually converted to high-energy states. We have examined in detail how the conformational changes influence the IR C═O stretching band of PAA and performed the analysis of conformer populations to derive the conformational energies.[35]

In the IR region below 1500 cm^{-1} (Figure 2), one can find the intensity changes of the bands associated with the COOH groups. By taking the 1451 cm^{-1} band as an internal standard, we see that the 1178 cm^{-1} band shows a continuous increase in intensity. More interestingly, the 902 cm^{-1} band, originated from the OH out-of-plane bending of the cyclic dimer,[21,25,27] decreases with temperature. This corroborates the results from the peak resolution of the C═O stretching region.

An FT-Raman spectrum of PAA is shown in Figure 4, and its major bands are listed in Table 1. In contrast to the corresponding IR spectrum, the Raman spectrum shows a strong broad band at 846 cm^{-1}, implying the presence of a wide distribution of backbone internal rotational angles, including some helical structure and a planar zigzag conformation over very short segments.[3,5,36] In the Raman spectrum, an asymmetric band due to C═O stretching modes centers near 1690 cm^{-1} and spans from 1800 to 1550 cm^{-1}, as shown in Figure 5a on an expanded scale. A second derivative of the spectrum in Figure 5b shows at least three bands existing in the C═O stretching region, which are located at 1741, 1715, and 1671 cm^{-1}, respectively. The curve-fitting easily indicates four bands in this band envelope, located at 1742, 1715, 1680, and 1660 cm^{-1}, respectively. The 1680 cm^{-1} band may be assigned to an in-phase C═O stretching vibration of the cyclic dimer form,[3,5,13,14,21,34] while the other bands at 1742, 1715, and 1660 cm^{-1} correspond to C═O stretching modes of free COOH, and terminal and inner COOH in the oligomeric forms, respectively.[13,14] Note that the frequency of the dimer species in the Raman spectrum does not coincide with its counterpart in the IR spectrum.

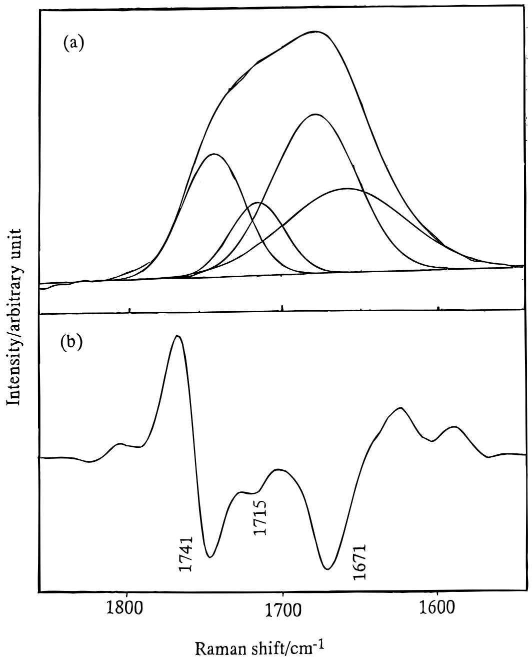

Figure 5. Scale-expanded Raman spectrum of PAA showing the components contributing to the C═O stretching band: (a) a curve-fitting result; (b) second derivative plot.

This observation seems reasonable since the Raman band arises from a normal mode involving the in-phase $(CO)_2$ stretching while the IR band results from the out-of-phase $(CO)_2$ stretching in the dimer.[21,25,34]

When the temperature is raised, the C═O stretching band in the Raman spectrum remains broad and asymmetric, and four peaks can be resolved in a manner similar to that shown in Figure 5. This seems to exclude the possibility that the complex CO band profile in the IR spectra might have contributions from the dispersive effect,[37] since the consistent Raman bands are associated with inelastic scattering free from the disturbances due to the variations of the refractive indices which sometimes make the IR bands arising from optical artifacts. Thus, the results of Raman spectra also support the existence of the linear oligomers in PAA. One may doubt if the hydrogen bonds in polymers would take the same forms as those in small molecules, since the COOH groups are arranged in a regular manner alongside a covalent backbone chain. Coleman *et al.*[17] discussed various possible kinds of hydrogen-bonding species in polymers and adopted Flory's lattice filling methodology to describe two sets of chains, one covalent, the other hydrogen-bonded, both of which share the same segments. One interesting feature is that the association of the repeating units is independent on the covalent chain length and can be treated as a "small" molecule (one containing a single functional group) of equal molar volume. We postulate that the hydrogen bond structure in the oligomeric forms may take a face-on fashion[13,14] proposed for acetic acid, propionic acid, and *n*-butyric acid or a lateral fashion[15,16] proposed for fatty acids adsorbed on a solid surface (Figure 1B). In a very recent report, lateral hydrogen-bonded structures were also proposed for polymaleamic derivatives bearing a carboxylic acid group near the main chain.[38] Since it is difficult to distinguish these two fashions from IR and Raman measurements at present, we cannot conclude which fashion of COOH chains is favored in PAA.[39] Note that the formation of oligomeric COOH groups does not require the hydrogen bonding between the adjacent

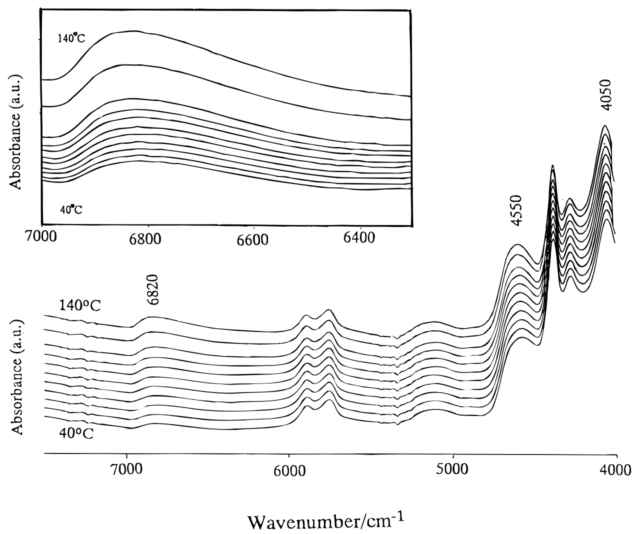

Figure 6. FT-NIR spectra of PAA recorded over a temperature range of 40−140 °C (10 deg interval with a rising rate of 1 °C/min). Inset: scale-expanded NIR spectra showing the first overtone of an OH stretching mode.

repeating units in the same hydrocarbon chain since both oligomers and dimers can be formed between COOH located on different parts of the chains, as shown in Figure 1B. It may be worthwhile noting that the coexistence of various possible hydrogen-bond forms of carboxylic acid groups, including linear associated structures, has been a common notion for biological polymers.[40]

The species due to monomeric COOH groups is not well resolved in the IR OH stretching region and CO stretching region in the IR and Raman spectra. We resort to NIR spectroscopy to clarify this point. Figure 6 shows FT-NIR transmission spectra of PAA measured over a temperature range of 40−140 °C. A broad band around 6820 cm^{-1} is due to the first overtone of the OH stretching mode of the free carboxylic group.[18,19] The long tail in the lower wavenumber side of this band can be attributed to the terminal free carboxylic groups in the oligomeric forms with different chain lengths. The intensity of the tail increases with temperature, as can be easily verified from difference spectra of this region. In the NIR region, bands due to hydrogen-bonded OH groups are extremely weak while that due to the free OH group is relatively strong. The large displacement of the light proton in the free OH group allows it to be in the “free” state, relative to the case of hydrogen-bonded OH groups, resulting in a greater breakdown of the harmonic oscillator approximation and hence the selection rules that in principle do not permit the appearance of overtones and combinations of bonded species.[41,42]

As can be seen from the enlargement of the 7000−6300 cm^{-1} region (the inset in Figure 6), the intensity of the 6820 cm^{-1} band gradually increases with temperature. Broad bands in the 4600−4500 and 4060−4030 cm^{-1} regions, both associated with COOH combination vibrations, also increase with temperature, whereas the intensities of other bands irrelevant to the COOH group vibrations are temperature independent. In the inset in Figure 6, the band area of the free COOH species increases significantly above 100 °C. It is quite reasonable that above the T_g of PAA, the segmental motion accelerates the considerable gain of the free COOH groups as the macromolecular chains disentangle at the expenses of the hydrogen-bonded forms. In the IR region, neither the OH stretching band due to free COOH (near 3500 cm^{-1}) nor the intensity change of the free COOH group (the 1742 cm^{-1} band in Table 3) is obviously detectable. However, this is not a problem in the NIR region.

Conclusions

In the present work, IR, Raman, and NIR measurements were undertaken to illustrate the hydrogen-bond forms in PAA at elevated temperatures. Apart from the presence of the monomer and cyclic dimer form of COOH, additional spectral features are interpreted in terms of the presence of oligomer species. The dissociation of the COOH groups at high temperatures is verified by FT-NIR spectra. These various hydrogen-bond species of COOH groups in PAA are analogous to those found in aliphatic acids. Thus, hydrogen bonds in the cyclic dimer and linear oligomers yield a supramolecular structure superimposed on the PAA backbone chains, which may explain the previously proposed cooperative hydrogen bond in PAA or polymer blends containing PAA. The coexistence of such hydrogen-bonded species of the COOH groups in PAA may provide new insight into the thickening mechanism of the polymer.

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Supporting Information Available: Figures of (a) the temperature dependence of the frequency of a C═O stretching band of oligomeric chain and (b) the temperature dependence of band intensity of the first overtone of an OH stretching mode near 6820 cm^{-1} (2 pages). Ordering information is given on any current masthead page.

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