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Analysis on Structural Changes of Poly(vinyl acetate) by Two-Dimensional Correlation Infrared Spectroscopy

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Poly(vinyl acetate) (PVAc) was investigated using generalized two-dimensional infrared (2D IR) correlation spectroscopy and moving-window two-dimensional spectroscopy (MW2D) with temperature raising from 10 to 200 ºC. The glass transition of poly(vinyl acetate) determined by MW2D measurement is 52 ºC. Four types of C=O stretching modes in different phase were clearly detected by asynchronous spectrum as poly(vinyl acetate) transfers from solid phase to liquid phase. The bands at 1762 cm^{-1} arise from free bonded C=O groups in liquid phase and 1753 cm^{-1} attributes to the free or non-interaction C=O groups in solid phase. The bands at 1733 and 1724 cm^{-1} attribute to the C=O groups involved in the C=O and OH interactions in liquid phase and solid phase, respectively. The sequential order of bands changes is also discussed. In addition, seven bands are identified at 3020, 2990, 2980, 2972, 2957, 2903 and 2851 cm^{-1} by 2D correlation spectra. The bands at 2990, 2980 and 2972 cm^{-1} are assigned to CH_2 groups. The bands at 2957, 2851 cm^{-1} and 2903 cm^{-1} attribute to O-CH_3 (ester group) asymmetric stretching, symmetric stretching and CH asymmetric stretching vibrations, respectively. With the temperature increasing, CH_3 or CH group responds firstly and then CH_2 group, after that HC=CH group follows, which denotes the side chain takes place prior to major chain.

Keywords: Poly(vinyl acetate), Moving-window two-dimensional correlation infrared spectroscopy, 2D IR correlation spectroscopy.

INTRODUCTION

After more than two decades, polymer blends have been widely studied because the structural and some physical properties of the modified polymers can be over the constituent polymer. However, most polymer blends are immiscible due to the absence of specific interaction and entropy of mixing of two polymers is negligibly small. As a result, many investigations have been carried out with emphasis on hydrogen bonds as miscibility enhancers[1-14]. In order to investigate and elucidate the hydrogen bonds in polymer blends, the blends of poly(vinyl acetate) as the typical proton-acceptor material and other proton-donor polymers are often discussed[1-5]. The miscibility of poly(vinyl acetate) with polycaprolactone (PCL) was studied using DSC and a single transition temperature was observed for the complete range[4]. The miscibility of poly(vinyl acetate) and atactic poly(epichlorohydrin) was also investigated by fourier transform infrared spectroscopy (FT-IR) and suggests that the carbonyl groups of poly(vinyl acetate) may not involve in a hydrogen-bonding interaction with α-hydrogen of atactic poly(epichlorohydrin)[1]. Because of the formation of hydrogen bonding between hydroxyl groups of phenolic resin and carbonyl groups of poly(vinyl acetate), the blend of phenolic resin and poly (vinly acetate) is miscible in the amorphous over entire composition[3].

Poly(vinyl acetate) is also used for the preparing solid polymer electrolytes[15,16]. By the results of the peak shift in the IR region of C-O-C and C=O in poly(vinyl acetate), it confirms that both C-O-C and C=O groups have an important interaction to the lithium cations and ClO_4^- anions[15].

By the FTIR spectra of pure poly(vinyl acetate) (PVAc) and PVAc/SiO_2 composites, it is believed that the hydrogen bonds between the silanol groups of the silica particles and the hydroxyl groups (not the carbonyl groups) of poly(vinyl acetate) played a dominating role in the formation of stable PVAc/SiO_2 colloid[17].

However, little attention has been paid to chemical structure and structure changes of poly(vinyl acetate). In order to further elucidate the transformation process of hydrogen bonding of phenolic resin and poly(vinyl acetate) blend as temperature rises, our groups tried to use temperature-dependent infrared spectra analysis to study. However, the information that we got from poly(vinyl acetate) with the temperature increasing by moving-window 2D (MW2D) and 2D correlation spectroscopy (2D IR) is more complex than our expected. It is well known that the chemical structure of polymer will affect

the miscibility, phase behaviour and some physical properties in polymer blends. So it is necessary to get more details on the chemical structure and structure changes of poly(vinyl acetate) with temperature increasing.

Fourier transform infrared spectroscopy (FT-IR) has been proved to be an excellent tool of studying the hydrogen bond and structure in different polymers. However, the obtained IR spectra are complicated because they contain many overlapping bands involved with the different species of hydrogen bonding. The application of generalized two-dimensional correlation infrared spectroscopy analysis[18,19] has been proved extremely useful in revealing these subtle responses that are hidden in the complex dynamic infrared data. Asynchronous 2D spectra are very powerful in differentiating highly overlapped bands that vary out of phase under the external perturbation[20]. The signs of synchronous and asynchronous cross peaks indicate the sequential order of the events taking place under the applied perturbation[21,22].

Moving-window 2D (MW2D) correlation spectroscopy, which was proposed first by Thomas and Richardson in 2000[23], is a powerful method to visualize spectral correlation variation along both spectral variable and perturbation variable axes. Our groups have successfully applied the MW2D correlation analysis to investigate some complex molecular chain movements and transitions of SEBS[24].

By the analysis of IR spectra in the C=O stretching band region, the crystallization and melting behaviour of crystalline polymer have been successfully studied. It has demonstrated that C=O groups in crystalline polymers will spilt into two or three even more bands[25-29]. However, few studies have pay attention to the types of C=O in amorphous polymer as temperature increases. Poly(vinyl acetate) is typical amorphous polymer, which is also often chosen as a model low-molecular polymer for structural relaxation studies. The experimental methods for these studies are based on differential scanning calorimetry measurements (DSC), mercury dilatometry[30-38]. However, most of these ways to study structural relaxation are concerned with some macroscopic property (volume, enthalpy and refraction index) departing during continuing cooling.

In the present study, the aim is to elucidate the structure and structural changes of poly(vinyl acetate) by two-dimensional correlation infrared spectroscopy. Temperature-depended IR of poly(vinyl acetate), a type amorphous polymer, has never been analyzed in detail. Therefore, result of the present study is not only important for the study of amorphous polymers but also for the further study of blends of poly(vinyl acetate).

EXPERIMENTAL

Poly(vinyl acetate) used in this study was obtained from Sinopharm Chemical Reagent Co., Ltd. Poly(vinyl acetate) was directly used in experiment without further purification.

A film of poly(vinyl acetate) sample was prepared by spreading on one side of a KBr disk *via* solvent casting. The solution was fully dissolved in THF solution. The KBr disk together with poly(vinyl acetate) was dried in a vacuum-dried oven at 80 ºC for 8 h. The sample was then placed into a programmed temperature control instrument including heating cell. The temperature-dependent absorbance IR spectra were measured with Tensor 27 spectrometer, which was equipped with a deuterated l-α-alanine doped triglycine sulfate (DLaTGS) detector. In order to avoid the oxidation of the poly(vinyl acetate) film sample, the sample was protected by dried high-purity nitrogen gas during measurement. Ninety-five IR spectra were collected from 10 to 200 ºC at about 2 ºC increments and the temperature increasing rate was 5 ºC/min.

Before performing the 2D and MW2D correlation analysis, baseline correction and mean normalized (each IR spectrum was divided its intensity mean value) was applied. The software of 2D and MW2D was developed in our laboratory, were applied to processed and calculated. The theory of 2D and MW2D correlation spectroscopy has been described elsewhere[18-21,24,39].

RESULTS AND DISCUSSION

As shown in Fig. 1, complicated spectral variations are observed in the temperature-dependent IR spectra of poly(vinyl acetate) (not all displayed here). The prominent IR bands O-H stretching modes (3500-3400 cm^{-1}), C-H stretching vibration region (3100-2800 cm^{-1}) and C=O stretching bands (1800-1650 cm^{-1}) are of interest to our study.

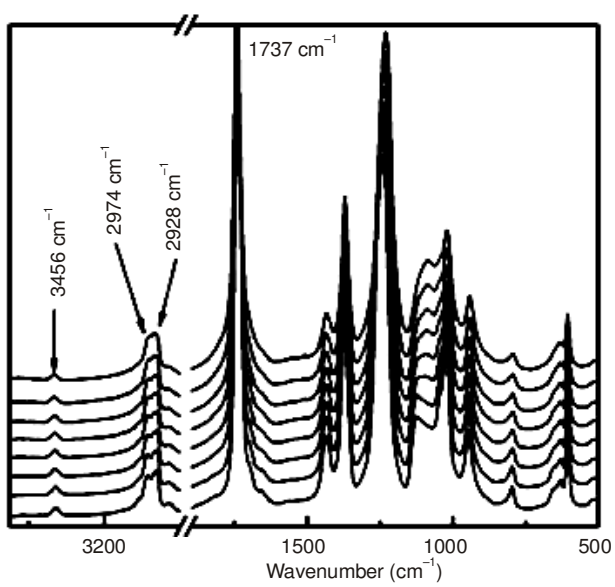

Fig. 1. Temperature-dependent IR spectra (not all displayed here) of poly(vinyl acetate) (10-200 ºC)

O-H stretching region (3500-3400 cm^{-1}): Fig. 2a shows the 1D IR spectra of OH stretch bands in the region 3500-3400 cm^{-1} from 10 to 200 ºC. The obtained 1D IR spectra show only one small (it is really narrow) band at 3456 cm^{-1}. This indicates poly(vinyl acetate) has only one kind of hydroxyl group. We can get more useful information from two-dimensional correlation infrared spectroscopy and moving-window two-dimensional correlation infrared spectroscopy. It is found that two correlation peaks shifting along the perturbation direction are clearly observed in the MW2D correlation map (Fig. 2b). Obviously, the bands at 3456 cm^{-1} is splitting into two bands. One is 3443 cm^{-1} and the other is 3475 cm^{-1}, corresponding to the hydrogen-bonded hydroxyl groups and the free hydroxyl groups, respectively. It is well known that peak shift

in the frequency range of the X -H vibration is often used as a simplest and powerful spectroscopic criterion for the existence of H-hydrogen bond[13,14]. This formation of hydrogen bond may be attributed to the interaction between the hydroxyl groups and the carbonyl groups of the poly(vinyl acetate). At 52 ºC, two positive correlation intensity peaks are obviously observed. It is obviously a consequence of the poly(vinyl acetate) glass transition. The glass transition of poly(vinyl acetate) by DSC measurement is 46 ºC and this value is close to the result.

Fig. 2c, d shows synchronous and asynchronous 2D correlation spectra in the 3500-3400 cm^{-1} region calculated from the IR spectra in the temperature rang from 10 to 200 ºC. In this paper, blue and red areas in the 2D contour maps mark positive and negative correlation intensities, respectively. The synchronous spectra in Fig. 2c is dominated by two auto-peaks at about 3475, 3443 cm^{-1}, respectively. This result is consistent with the result of MW2D correlation analysis, which also shows two peaks along the perturbation direction (Fig. 2b). The negative cross-peaks at (3475, 3443) cm^{-1} reveal that the direction of the bond intensity changes at 3475 cm^{-1} is opposite to that of the intensity changes at 3443 cm^{-1} with temperature increasing. It can well draw a conclusion that the intensity of hydrogen-bonded hydroxyl groups decreases and that of the free hydroxyl groups increase with temperature increasing.

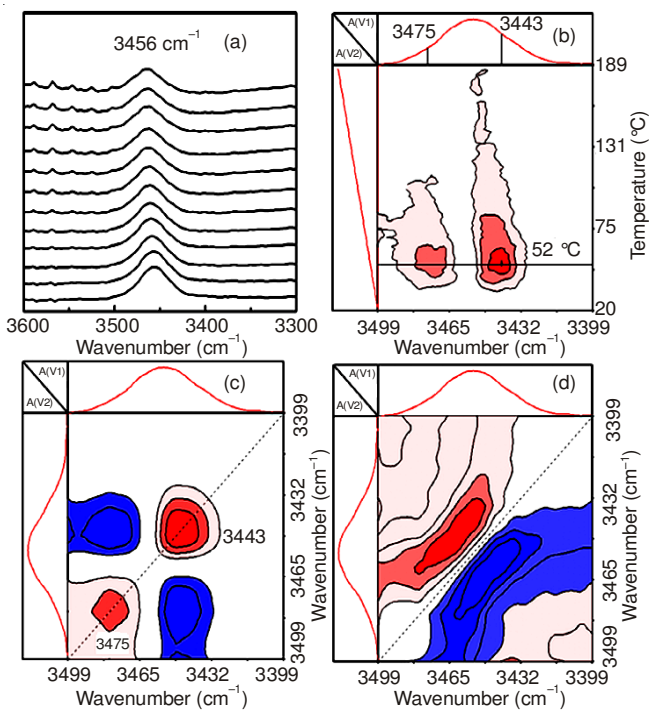

Fig. 2. Temperature- dependent IR spectra (not all displayed) (a), MW2D correlation spectrum (b), synchronous (c) and asynchronous 2D correlation spectrum (d) in the 3500-3400 cm^{-1} region of poly(vinyl acetate) (10-200 ºC)

C=O stretching region (1800-1650 cm^{-1}): Fig. 3a shows the temperature-dependent IR spectral of poly(vinyl acetate) in the C=O stretching bands region. From the 1D IR, it is also difficult to get more information. Fig. 3b shows the MW2D correlation spectrum based on autocorrelation calculations in the 1800-1650 cm^{-1} region. At 52 ºC, two positive correlation intensity peaks are obviously observed. Two correlation peaks shift along the perturbation direction is clearly found in the MW2D correlation map, which denotes the existence of H-hydrogen bond by the interaction between C=O and OH in poly(vinyl acetate)[13,14].

Fig. 3c-d shows synchronous and asynchronous 2D correlation spectra in the 1800-1650 cm^{-1} region constructed from the IR spectra in the temperature range from 10 to 200 ºC. The synchronous spectra in Fig. 3c is dominated by two auto-peaks at about 1756, 1730 cm^{-1}, respectively. This result is consistent with the result of MW2D correlation analysis, which also shows two peaks along spectral variable (Fig. 3b). From Fig. 3b, c, it can be well inferred here in poly(vinyl acetate) has at least two types of C=O. The negative cross-peaks at (1756, 1730) cm^{-1} reveal that the direction of the bond intensity changes at 1756 cm^{-1} is opposite to that of the intensity changes at 1730 cm^{-1} with temperature increasing.

However, the corresponding asynchronous 2D correlation spectrum in Fig. 3d provides four deconvoluted bands at 1760, 1752, 1733, 1723 cm^{-1}. Moreover, be similar to Zhang *et al.*'s[40] study, there is a so-called "butterfly pattern" in the C=O stretching region in the asynchronous correlation spectra. Usually, the appearance of this pattern is attributed to a peak shift combined with the intensity changes or bands splitting[41-44].

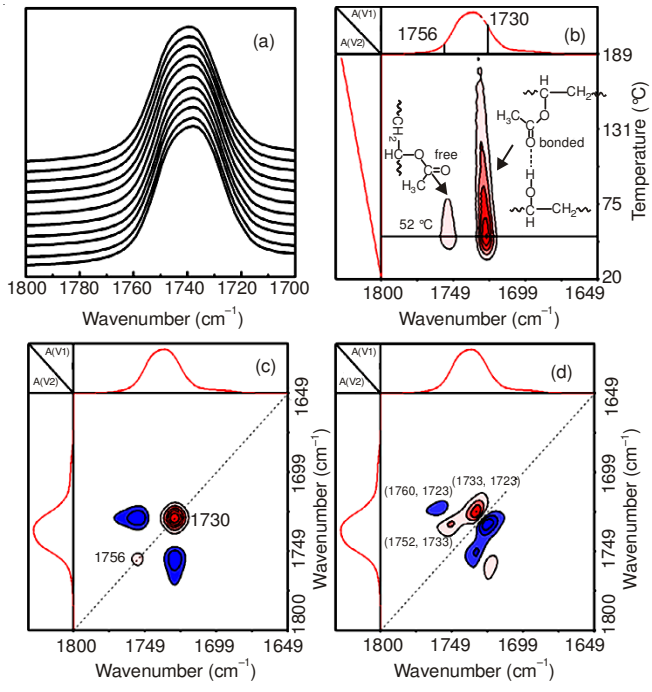

Fig. 3. Temperature-dependent IR spectra (not all displayed) (a), MW2D correlation spectrum (b), synchronous (c) and asynchronous 2D correlation spectrum (d) in the 1800-1650 cm^{-1} region calculated from temperature-dependent spectral variations of poly(vinyl acetate) between 10 and 200 ºC

These results demonstrate that the asynchronous spectrum is more powerful in the bonds deconvultion in comparison with synchronous spectrum. From above analysis, there have at least four types of C=O in poly(vinyl acetate). Many previous studies have demonstrated that C=O groups in crystalline polymers will spilt into two or three even more bands which

contributes to the amorphous structure, or the highly ordered crystalline component, or the less ordered crystalline structure[25-29]. However, it is well known that poly(vinyl acetate) is an amorphous polymer. Why the amorphous poly(vinyl acetate) have four types of C=O? There maybe the reason of hydrogen bond by the formation C=O---H-O. But it should have only two types of C=O that one is free, the other is hydrogen bonded.

Galbiati *et al.*[45] measured the IR and Raman spectra of several aliphatic esters, namely of the series of CH_3-COO-$(CH_2)_n CH_3$ (n = 0 to 11) in gas, liquid and solid phases. It was revealed that the observed frequencies of the C=O stretching vibrations ($\nu_{C=O}$) of the compounds can be grouped into three wave number regions for the three phases: (1) $\nu_{C=O}$ > 1760 cm^{-1} for the gas phase, (2) 1750 cm^{-1} > $\nu_{C=O}$ > 1740 cm^{-1} for the liquid phase and (3) 1730 cm^{-1} > $\nu_{C=O}$ > 1720 cm^{-1} for the solid phase. Because the poly(vinyl acetate) glass temperature in our system is only about 52 ºC, we can safely inferred that the amorphous poly(vinyl acetate) probably transfers from solid phase to liquid phase by raising temperature from 10 to 200 ºC. May be the C=O in different phase were clearly detected by asynchronous spectrum. In order to demonstrate the deduction, MW2D and 2D correlation spectra in the 1800-1650 cm^{-1} region are calculated from the IR spectra from 10 to 60 ºC and from 60 to 200 ºC, respectively. From Fig. 4a,b and 5a,b, the corresponding MW2D and 2D synchronous correlation spectrum also show two major deconvoluted bands, which similar to Fig. 3a,b, although there is some difference at the values of peak wave numbers. But the asynchronous 2D correlation spectra in the 1800-1650 cm^{-1} region from 10 to 60 ºC are much difference to that from 60 to 200 ºC.

Fig. 4c shows asynchronous 2D correlation spectra in the 1800-1650 cm^{-1} region in the temperature range from 10 to 60 ºC, which shows only one asynchronous cross peaks at (1752, 1728) cm^{-1}. According to the general rules proposed by Noda[18-21], it reveals that 1752 cm^{-1} changes at first and then 1728 cm^{-1} with temperature increasing. Because the temperature is below 60 ºC, poly(vinyl acetate) is of solid phase. It can make a conclusion that 1752 cm^{-1} attributes to free C=O stretching mode and 1728 cm^{-1} is due to hydrogen bonded C=O structure in solid phase.

Fig. 5b,c shows synchronous and asynchronous 2D correlation spectra in the 1800-1650 cm^{-1} region constructed from the IR spectra in the temperature rang from 60 to 190 ºC. The synchronous spectra in Fig. 5b is dominated by two auto-peaks at about 1756, 1730 cm^{-1}, respectively. The corresponding asynchronous 2D correlation spectrum in Fig. 5c provides four deconvoluted bands at 1762, 1753, 1733, 1724 cm^{-1}. From above analysis, some poly(vinyl acetate) changes to liquid phase as temperature raises, so it can safely conclude that the band at 1762 cm^{-1} attribute to free bonded C=O groups in liquid phase and 1753 cm^{-1} due to the free C=O groups in solid phase, 1733 and 1724 cm^{-1} arise from the C=O groups involved in the C=O and OH interactions in liquid phase and solid phase, respectively. By Noda rules, it can also reveal that 1762 cm^{-1} (free bonded C=O groups in liquid phase) takes place in prior to 1724 cm^{-1} (hydrogen bonded C=O in solid phase) and 1753 cm^{-1} (non-interaction C=O groups in solid phase), 1733 cm^{-1} (hydrogen bonded C=O in liquid phase) take place in prior to 1753 and 1724 cm^{-1} (hydrogen bonded C=O in solid phase) with temperature increasing.

Temperature-dependent changes in the C-H stretching vibration region (3100-2800 cm^{-1}): The temperature-dependent changes in the IR spectra of poly(vinyl acetate) in the 3100-2800 cm^{-1} region are shown in Fig. 6a. For the C-H stretching vibration region, bands at 2932 and 2862 cm^{-1} are ascribed to O-CH_3 (ester group) asymmetric stretching and symmetric stretching vibrations, respectively. That appeared around 2970 cm^{-1} is attributed to the CH_2 antisymmetric stretching vibration. The vibrational bands observed at 3020 cm^{-1} is due to C=CH antisymmetric stretching vibration. Fig. 6b,c illustrate the synchronous and asynchronous 2D correlation spectra in the 3020-2800 cm^{-1} region constructed from the temperature-dependent IR spectra. Five autopeaks are clearly observed at 3020, 2990, 2957, 2903 and 2851 cm^{-1} in the synchronous map. The bands at 2990, 2957 cm^{-1} are assigned to CH_2 and CH_3 asymmetric stretching modes, respectively, although the frequency of them in synchronous correlation spectra has a difference to that in the 1D IR spectra of poly(vinyl acetate). A new band at 2903 cm^{-1} is due to CH asymmetric stretching. The strong auto-peaks at 2990 and 2957 cm^{-1} indicate the significant temperature-dependent intensity variation of the

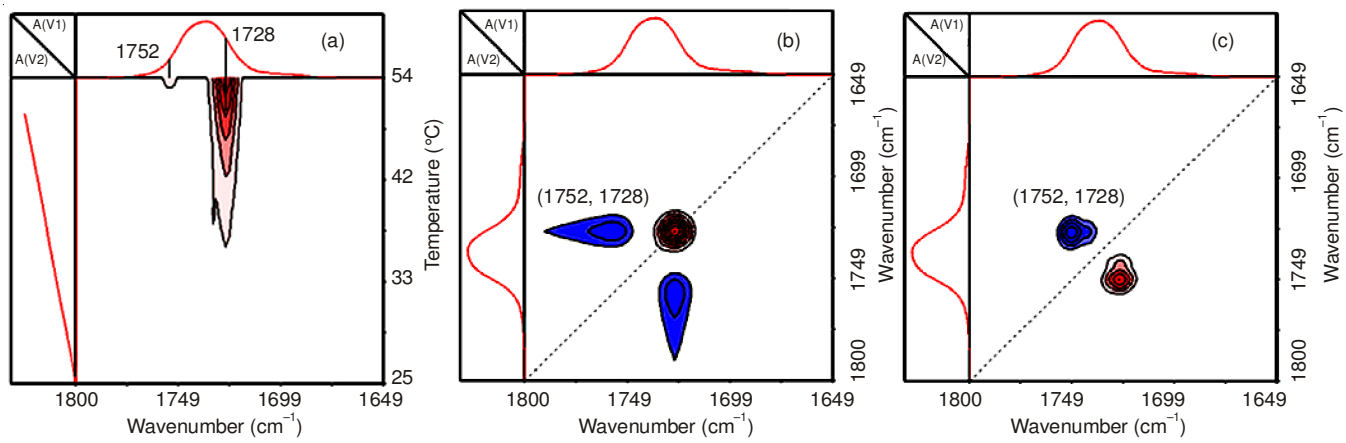

Fig. 4. MW2D correlation spectrum (a), synchronous (b) and asynchronous 2D correlation spectrum (c) in the 1800-1650 cm^{-1} region calculated from temperature-dependent spectral variations of poly(vinyl acetate) between 10 and 60 ºC

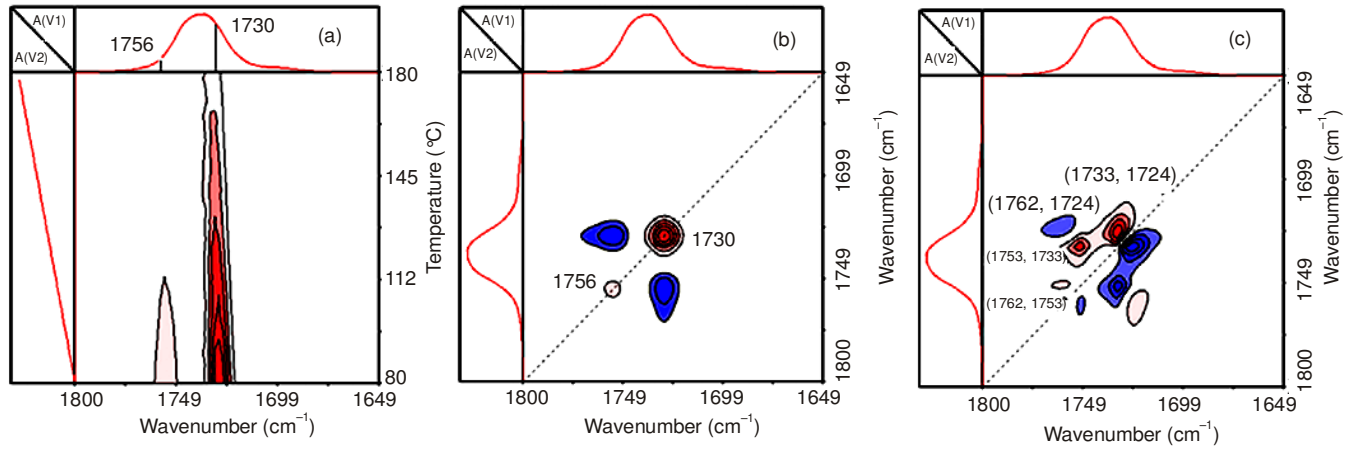

Fig. 5. MW2D correlation spectrum (a), synchronous (b) and asynchronous 2D correlation spectrum (c) in the 1800-1650 cm^{-1} region calculated from temperature-dependent spectral variations of poly(vinyl acetate) between 60 ℃ and 190 ℃

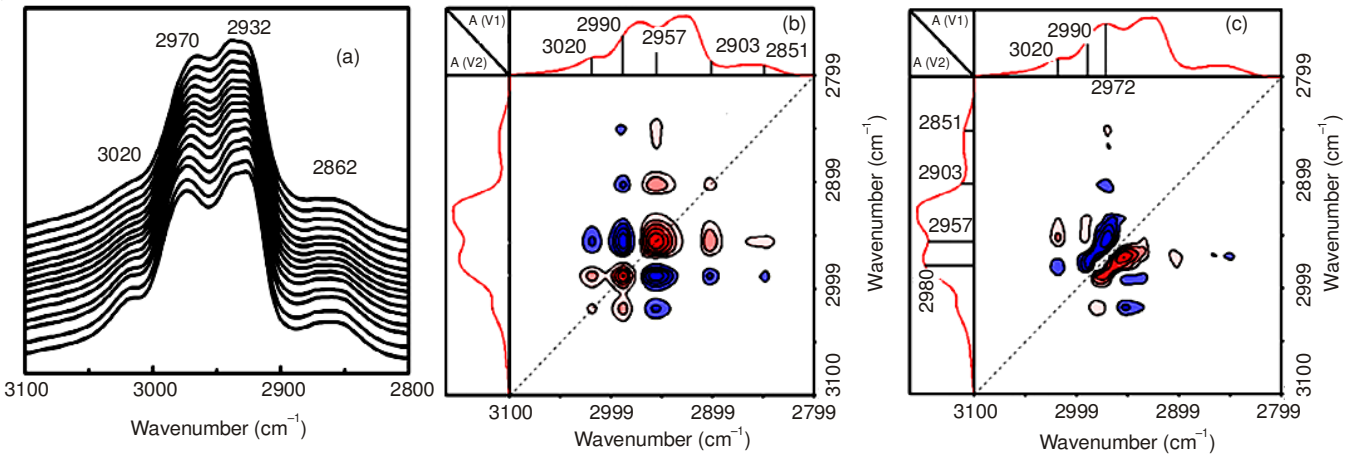

Fig. 6. Temperature- dependent IR spectra (not all displayed) (a), synchronous (b) and asynchronous 2D correlation spectrum (c) in the 3100-2800 cm^{-1} region calculated from temperature-dependent spectral variations of poly(vinyl acetate) between 10 and 200 ℃

hydrocarbon chains. Three positive cross-peaks are observed at (3020 *versus* 2990), (2957 *versus* 2851 and 2903) cm^{-1} and four negative cross-peaks are detected at (3020, 2957), (2990 *versus* 2957, 2903 and 2851) cm^{-1} on the left up side of the synchronous correlation spectra. According to Node's rule, it is suggested that HC=CH and CH_2, CH_3 and CH have the same orientation behaviors, but HC=CH, CH_2 and CH_3, CH show different orientation behaviors as temperature increase from 10 and 200 ℃. Fig. 7 gives the frequency changes of two vibrational modes as a function of temperature, these two bands can be assigned to the stretching modes of the CH_2 and CH_3, respectively. Obviously, with temperature increasing, the CH_2 stretching mode shift to lower frequency. However, the CH_3 stretching mode shifts to higher vibration frequency. The result confirms that CH_2 and CH_3 have different orientation behaviors as temperature increases.

The asynchronous correlation spectra have excellent deconvolution ability. It should be noticed that two new bands at 2972 and 2980 cm^{-1} are identified. As the group of HC=CH exists in the main chain of poly(vinyl acetate), there is more than one types of CH_2 in poly(vinyl acetate). The bands at 2972 and 2980 cm^{-1} are also assigned to CH_2 asymmetric stretching modes. Accord to the rules proposed by Noda, the sequential order of bands changes is: 2957 > 2990, 2972 > 3020 and 2903 > 2990, 2972 > 3020 cm^{-1}. This sequence means

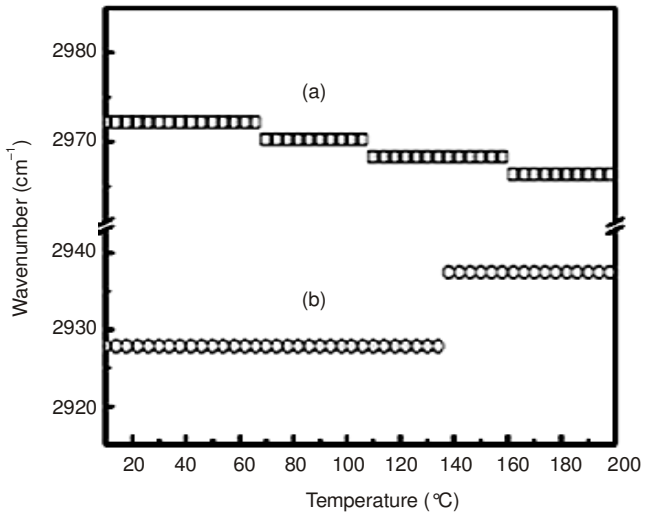

Fig. 7. Temperature dependences of the frequency of CH_2 (a) and CH_3 (b) of stretching modes in poly(vinyl acetate)

CH_3 or CH group changed its movement first and then CH_2 group and HC=CH group following. Thus, we can conclude that, along with the temperature increasing in 10-200 ℃ regions, the side chain takes place prior to major chain. The sketch of chemical structure and the sequence of groups' movements are shown in Fig. 8. The results of 2D correlation

spectra of poly(vinyl acetate) in the 3100-2800 cm^{-1} region from 60 and 200 ºC are similar to Fig. 6, but the relative intensity of autopeaks has slightly difference.

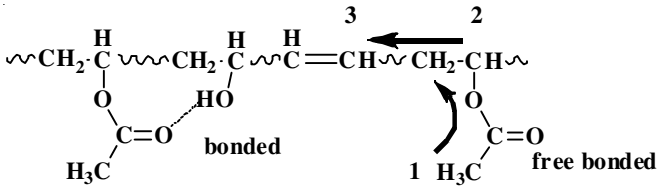

Fig. 8. Sketch of chemical structure and the sequence of groups' movements of poly(vinyl acetate)

Conclusion

The chemical structure and structure changes of poly(vinyl acetate) were investigated using MW2D and 2D IR correlation spectroscopy. The glass transition of poly(vinyl acetate) by MW2D correlation spectroscopy is determined at 52 ºC, which is close to the value measured by DSC measurement. In the 3500-3400 and 1800-1650 cm^{-1} region, two correlation peaks are clearly observed in MW2D and synchronous 2D correlation map. Furthermore, they shift along the perturbation direction in the MW2D correlation map. The results denote the existence of H-hydrogen bond with the interaction between C=O and OH in poly(vinyl acetate).

The C=O in different phase were clearly detected by asynchronous spectrum as poly(vinyl acetate) transfers from solid phase to liquid phase by raising temperature from 10 to 200 °C. Four deconvoluted bands at 1762, 1753, 1733, 1724 cm^{-1} were detected by the asynchronous 2D correlation spectrum. The bands at 1762 cm^{-1} arise from free bonded C=O groups in liquid phase and 1753 cm^{-1} due to the free or non-interaction C=O groups in solid phase. 1733 and 1724 cm^{-1} attribute to the C=O groups involved in the C=O and OH interactions in liquid phase and solid phase. It can also be revealed that the sequential order of bands changes is: 1762 cm^{-1} (free bonded C=O groups in liquid phase) > 1724 cm^{-1} (hydrogen bonded C=O in solid phase), 1753 cm^{-1} (non-interaction C=O groups in solid phase) and 1733 cm-1 (hydrogen bonded C=O in liquid phase) > 1753, 1724 cm^{-1}.

In the 3100-2800 cm^{-1} region, seven bands are identified at 3020, 2990, 2980, 2972, 2957, 2903 and 2851 cm^{-1} by 2D correlation spectrum. The bands at 2990, 2980 and 2972 cm^{-1} are ascribed to CH_2 in different structure environments as the group of HC=CH (3020 cm^{-1}) exists in the main chain of poly(vinyl acetate). The bands at 2957 and 2851 cm^{-1} attribute to O-CH_3 (ester group) asymmetric stretching and symmetric stretching vibrations, respectively. The band at 2903 cm^{-1} is due to CH asymmetric stretching. The intensity of bands changes in the following sequence with temperature: 2957 > 2990, 2972 > 3020 and 2903 > 2990, 2972 > 3020 cm^{-1}, which denotes that the side chain takes place prior to major chains.

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